THE INSTITUTE OF APPLIED PHYSICS

With manuscript title U.D.C: 546.72-32:548.5(043.2) 546.650-32:548.5(043.2)

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CRYSTAL ENGINEERING OF HOMOMETALLIC Fe^{III} AND HETEROMETALLIC Fe^{III}/4f CARBOXYLATE CLUSTERS AND COORDINATION POLYMERS: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

144.07 - SOLID STATE CHEMISTRY

Doctoral thesis in chemical sciences

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CHISINAU, 2019

INSTITUTUL DE FIZICĂ APLICATĂ

Cu titlu de manuscris

C.Z.U: 546.72-32:548.5(043.2)

546.650-32:548.5(043.2)

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INGINERIA CRISTALELOR CLUSTERILOR DE CARBOXILAT ȘI POLIMERILOR COORDINATIVI HOMOMETALICI Fe^{III} ȘI HETEROMETALICI Fe^{III}/4f: SINTEZA, CARACTERIZAREA ȘI STUDIUL PROPRIETĂȚILOR

144.07 - CHIMIA CORPULUI SOLID

Teză de doctor în științe chimice

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CHIŞINĂU, 2019 2 © Botezat Olga, 2019

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ADNOTARE

Botezat Olga, "Ingineria cristalelor clusterilor de carboxilat și polimerilor coordinativi homometalici Fe^{III} și heterometalici Fe^{III}/4f: sinteza, caracterizarea și studiul proprietăților", teză de doctor în științe chimice, specialitatea 144.07 - chimia corpului solid. Chișinău, 2019. Teza este alcătuită din introducere, 4 capitole, concluzii generale și recomandări, bibliografie din 259 titluri, 113 pagini text de bază, 8 tabele, 50 figuri, 4 anexe. Rezultatele obținute sunt publicate în 21 lucrări științifice: 7 articole, 14 teze la conferințe.

Cuvinte cheie: ingineria cristalelor, fier, lantanide, carboxilați, clusteri, polimeri coordinativi, magnetism.

Domeniul de studiu: științe ale naturii.

Scopul și obiectivele tezei: obținerea clusterilor noi de carboxilat homometalici Fe^{III} și heterometalici $Fe^{III}/4f$ și a polimerilor coordinativi în baza lor, antrenândnd principiile ingineriei cristalului. Pentru realizarea scopului s-au stabilit următoarele **obiective**: *elaborarea* abordărilor pentru obținerea clusterilor homo- și heterometalici $Fe^{III}/4f$ și a polimerilor coordinativi cu nuclearitate și topologie variabilă, inclusiv a polimerilor coordinativi în baza clusterilor; *sinteza* compușilor nou proiectați; *determinarea* structurii cristaline a acestora cu ajutorul difracției razelor X pe monocristal; *caracterizarea* proprietăților fizico-chimice ale compușilor obținuți; *investigarea* proprietăților magnetice în bază susceptibilității magnetice funcție de temperatuiră.

Noutatea și originalitatea științifică constă în elaborarea metodelor și condițiilor de sinteză, inclusiv sinteze hidro(solvo)termale, cu microunde și ultrasonice, ce au rezultat cu obținerea a 42 compuși noi de $\text{Fe}^{III}/\text{Fe}^{III}$ -4f. Pentru prima dată au fost obținuți compuși inelari heterometalici cu nuclearitatea { $\text{Fe}_{18}\text{Ln}_6$ }. În baza rezultatelor a fost analizată influența naturii metalelor și liganzilor asupra compoziției, structurii și proprietăților magnetice ale compușilor Fe/Fe-Ln.

Problema științifică soluționată. Au fost stabilite condițiile de sinteză optimale pentru obținerea clusterilor coordinativi Fe^{III}/Fe^{III} -4f cu proprietăți magnetice îmbunătățite și a polimerilor coordinativi ai Fe^{III} (0D, 1D și 3D) cu porozitate notabilă, folosind precursori de carboxilat ai Fe^{III} și liganzi cu atomi *N*,*O*-donori. Au fost obținuți clusteri heterometalici de tip { Fe_4Dy_2 }, { Fe_6Dy_3 }, { Fe_6Dy_4 }, { Fe_7Dy_4 }, { $Fe_{18}Dy_6$ } și { $Fe_{18}Tb_6$ } ce au arătat comportament magnetic.

Semnificația teoretică. Teza contribuie la elaborarea unor strategii eficiente pentru obținerea unor materiale noi cu proprietăți magnetice în baza compușilor coordinativi ai metalelor Fe^{III} și Ln^{III}. Rezultatele experimentale ale măsurărilor structurale, spectroscopice și magnetice lărgesc cunoștințele despre această clasă de compuși și oferă informație pentru înțelegerea aprofundată a principiilor care reglează comportamentul magnetic al clusterilor discreți și al structurilor în baza lor. Valoarea aplicativă a lucrării constă în faptul că compușii noi sintetizați d/d-f pot fi folosiți ca materiale potențiale pentru elaborarea senzorilor magnetici și a dispozitivelor de memorie.

Implementarea rezultatelor științifice. Datele structurale și magnetice referitor la clusterii polinucleari obținuți au fost utilizate pentru dezvoltarea programului *wxJFinder* care calculează constantele de cuplaj Heisenberg *J* pentru sistemele $Fe^{III}(\mu_{2+n}-O)Fe^{III}$.

ANNOTATION

Botezat Olga, «Crystal engineering of homometallic Fe^{III} and heterometallic $Fe^{III}/4f$ carboxylate clusters and coordination polymers: synthesis, characterization, and properties», PhD thesis in chemistry, speciality 144.07 – solid state chemistry. Chisinau, 2019. The thesis consists of introduction, 4 chapters, general conclusions and recommendations, bibliography of 259 titles, 113 pages of the basic text, 8 tables, 50 figures, 4 annexes. The obtained results were published in 21 scientific papers: 7 articles and 14 theses at conferences.

Keywords: crystal engineering, iron, lanthanides, carboxylates, clusters, coordination polymers, magnetism.

Field of study: natural sciences.

The goal and objectives of the thesis: the construction of new homo- and heterometallic Fe^{III}/Fe^{III}-4f carboxylate magnetic clusters and coordination polymers based on them using crystal engineering principles. To achieve this goal the following **objectives** were set: *development* of synthetic approaches for the preparation of Fe^{III}/Fe^{III}-4f coordination clusters with variable nuclearity and topology and cluster-based coordination polymers; *synthesis* of new crystalline designed compounds; *determination* of their structures using a single crystal X-ray diffraction analysis; *characterization* of their physico-chemical properties; *investigation* of their magnetic properties by variable temperature susceptibility measurements.

Scientific novelty and originality: consists in the elaboration of methods and conditions of syntheses, including hydro(solvo)thermal, microwave and ultrasonic treatment, that resulted in 42 new Fe^{III}/Fe^{III}-4f compounds. For the first time, a series of the largest wheel-shaped heterometallic $\{Fe_{18}Ln_6\}$ -type clusters has been obtained. The influence of the nature of metals and ligands on the composition, structure, and magnetic properties of Fe/Fe-Ln compounds has been determined.

Scientific problem solved. The optimal synthetic conditions for the obtaining of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}-4\text{f}$ carboxylate clusters with enhanced magnetic properties and coordination polymers of Fe^{III} (0D, 1D and 3D) with notable porosity, using Fe^{III} oxo-carboxylate precursors and *N*,*O*-donor ligands have been established. The prepared heterometallic {Fe₄Dy₂}, {Fe₆Dy₃}, {Fe₆Dy₄}, {Fe₆Tb₄}, {Fe₇Dy₄}, {Fe₁₈Dy₆}, and {Fe₁₈Tb₆}-type clusters showed a magnet-like behavior.

The theoretical significance. The thesis contributes to the elaboration of effective strategies for obtaining new materials based on coordination compounds of Fe^{III} and Ln^{III} metals with magnetic properties. Experimental results of structural, spectroscopic, and magnetic measurements extended the knowledge of this class of compounds and provided novel insights in the fundamental understanding of the principles that govern magnetic behavior in the discrete clusters and cluster-based structures. **The applied value** of the work consists in the fact that new synthesized d/d-f compounds can be used as prospective materials for developing of magnetic sensors and memory devices.

Implementation of scientific results. The structural and magnetic data of the obtained polynuclear clusters have been used for the development of the *wxJFinder* program to calculate the Heisenberg coupling constants J in Fe^{III}(μ_{2+n} -O)Fe^{III} systems.

АННОТАЦИЯ

Ботезат Ольга, «Инженерия кристаллов гомометаллических Fe^{III} и гетерометаллических Fe^{III}/4f карбоксилатных кластеров и координационных полимеров: синтез, характеристика и изучение свойств», Диссертация доктора химических наук, специальность 144.07 – химия твердого тела. Кишинэу, 2019. Диссертация состоит из введения, 4 глав, общих выводов и рекомендаций, библиографии из 259 наименований, 113 страниц основного текста, 8 таблиц, 50 фигур и 4 приложений. Полученные результаты были опубликованы в 21 научных работах: 7 статьях и 14 докладах на научных конференциях.

Ключевые слова: инженерия кристаллов, железо, лантаноиды, карбоксилаты, кластеры, координационные полимеры, магнетизм.

Область исследования: естественные науки.

Цель и задачи диссертации: получение новых гомометаллических Fe^{III} и гетерометаллических Fe^{III}-4f карбоксилатных кластеров и координационных полимеров на их основе с использованием принципов инженерии кристаллов. Для достижения этих целей были поставлены следующие задачи: *разработка* синтетических подходов для подготовки Fe^{III}/Fe^{III}-4f координационных кластеров различной ядерностью и топологией, и координационных полимеров на основе кластеров; *синтез* новых разработанных соединений; *определение* их кристаллических структур, используя метод рентгеновской дифракции; *характеристика* их физико-химических свойств; *исследование* их магнитных свойств при изменении температуры в широком интервале.

Научная новизна и оригинальность работы состоит в разработке методов и условий синтеза, в том числе сольво(гидро)термальный, микроволновой и ультразвуковой синтезы, что привело к получению 42 новых Fe^{III}/Fe^{III}-4f соединений. Впервые была получена серия самых больших колец с конфигурацией {Fe₁₈Ln₆}. Определенно влияние природы металлов и лигандов на состав, структуру и магнитные свойства Fe^{III}/Fe^{III}-4f соединений.

Решенная научная проблема. Были установлены оптимальные условия синтеза для получения Fe^{III}/Fe^{III} -4f карбоксилатных кластеров с улучшенными магнитными свойствами, и координационных полимеров железа (0D, 1D and 3D) с заметной пористостью, используя оксо-карбоксилатные прекурсоры железа и *N*,*O*-лиганды. Полученные гетерометаллические кластеры типа {Fe₄Dy₂}, {Fe₆Dy₃}, {Fe₆Dy₄}, {Fe₆Tb₄}, {Fe₇Dy₄}, {Fe₁₈Dy₆} and {Fe₁₈Tb₆} показали поведение магнита.

Теоретическая значимость. Диссертация вносит вклад в разработку эффективных стратегий получения новых материалов на основе координационных соединений металлов Ln^{III} и Fe^{III} с магнитными свойствами. Экспериментальные результаты структурных, спектроскопических, магнитных измерений расширили знания об этом классе соединений и предоставили новые представления в фундаментальном понимании принципов, регулирующие магнитное поведение в дискретных кластерах и структурах на основе кластеров. **Прикладная ценность** работы состоит в том, что новые синтезированные d/d-f соединения могут быть использованы в качестве потенциальных материалов для разработки магнитных датчиков и запоминающих устройств.

Внедрение научных результатов. Структурные и магнитные данные полученных полиядерных кластеров были использованы для разработки программы *wxJFinder* для расчета констант Гейзенберговского обмена *J* для систем Fe^{III}(µ_{2+n}-O)Fe^{III}.

Abbreviations

| ∂D | zero – dimensional | MOFs | metal organic frameworks |
|--------------|---|---------------------|---------------------------------|
| 1D | one – dimensional | naH | nicotinate |
| 2D | two – dimensional | $pdmH_2$ | 2,6-pyridinedimethanol |
| 3D | three – dimensional | phen | 1,10-phenanthroline |
| 4,4'-bpy | 4,4-bipyridine | pivH | pivalic acid |
| ac | alternating-current | praoH | pyrrole-2-carboxaldehydeoxime |
| | | | ligand |
| AcH | acetic acid | ру | pyridine |
| $bdeaH_2$ | N-butyldiethanolamine | pyEt | 1,2-bis(4-pyridyl)ethane |
| $bdcH_2$ | 1,4-benzenedicaboxylic acid | S | strong |
| bpm | 2,2'-bipyrimidine | salen | salicylaldehyde-Ethylenediamine |
| dppo | 1,3-di(2-pyridyl)-1,3- | SBB | supermolecular building block |
| | propanedione | | |
| brd | broad | SBU | secondary building units. |
| СР | coordination polymer | sca | sodium dicyanamide |
| CSD | cambridge structural database | sh | shoulder |
| dc | direct-current | SMM | single molecule magnet |
| dca | 1,5-dicyanamide | str | s-triazine |
| diox | 1,4-dioxane | tcaH | trichloroacetic acid |
| dmf | dimethylformamide | teaH ₃ | triethanolamine |
| dpa | 2,2'-dipyridylamine | $tedaH_4$ | N,N,N,N-tetrakis(2- |
| | | | hydroxyethyl)ethylenediamine |
| Et_2O | diethyl ether | thdH ₃ | trihydroxy Schiff-base ligand |
| $heenH_2$ | <i>N</i> , <i>N</i> '-bis(2-hydroxyethyl) | thmeH ₃ | 1,1,1-tris(hydroxymethyl)ethane |
| | ethylenediamine) | | |
| HFEPR | high-frequency electron | $tegH_2$ | triethyleneglicol |
| | paramagnetic | | |
| hmpH | 2-(hydroxymethyl)pyridine | tpt | 2,4,6-tripyridyl-s-triazine |
| IR | infrared spectroscopy | vanoxH ₂ | o-vanillinoxime |
| isH | isobutyric acid | VS | very strong |
| М | magnetisation | vw | very weak |
| т | medium | W | weak |
| | | | |

| MBBs | molecular building blocks | χ | magnetic susceptibility |
|-----------|---------------------------|---|-------------------------|
| тссе | 2-carbamoyl-2- | μ | magnetic moment |
| | cyanoethanimidate | | |
| $mdeaH_2$ | N-methyldiethanolamine | | |

INTRODUCTION

Coordination clusters that incorporate multiple iron ions held together by bridging ligands have attracted great attention over the past decades due to their role as model structures for diverse natural processes. Iron is the most abundant transition element in the Earth's crust and the key and essential element in the metabolism of almost all living organisms. The oxidationreduction properties of iron make this metal extremely useful, for instance, in eukaryotes; most of the iron participates in the processes of metabolism or transfer of oxygen. Besides that, ironcontaining proteins act as enzymes and catalyze chemical reactions in complexes that carry electron transfer. Iron binds to proteins, which participate in various metabolic actions [1].

Additionally, high-nuclear iron coordination clusters are also attractive because of their fascinating architectures and their great potentials as "intelligent" multifunctional materials for information storage devices, spintronics, magnetic refrigeration and quantum computation [2]. Paramagnetic metal clusters have become a focus of interest since the discovery that certain 3d-based systems [3-6] could behave as single molecule magnets (SMMs) [7, 8]. To be functional as SMMs molecular clusters require well defined spin ground state (S) as large as possible to be well separated from the first excited state and significant uni-axial anisotropy (which can be a result of a favorable zero-field splitting parameter D) [9]. Mn-containing clusters have been proven to be one of the most fruitful sources of SMMs, starting from the first most known "Mn₁₂-acetate"cluster [10, 11]. In the search of better SMMs the Mn-based complexes have been extended to various other metal ions, including Fe, Ni, Co or Cr-based clusters that exhibit classical blocking magnetic behaviors of SMMs.

More recently, mixed metal clusters based on 3d and 4f metals have attracted much interest in the SMM field as scientists have tried to combine the high spin-states of transition metals and the large predominately anisotropic - magnetic moment of some lanthanide ions to achieve the exceptional SMM properties in heterometallic clusters compare to homometallic ones. The first example of mixed-metal complex that act as a SMM was a binuclear complex with Cu and Tb ions [12]. A huge number of heterometallic 3d-4f complexes have been prepared so far, and mostly studied compounds were Mn-4f, Cu-4f, Co-4f, and Ni-4f species [13-16]. Although several Fe-4f clusters have also been reported displaying SMM behaviour [17-23], the use of magnetic iron clusters as building blocks with 4f ions for the assembly of magnetic coordination aggregates is a field, which has been little explored. Part of the reason for this is in the relative lack of synthetic methodology. Thus, the development of new synthetic strategies towards highnuclearity homo- and heterometallic Fe^{III}/Fe^{III}-4f coordination compounds that might show the better magnetic properties and SMM behavior remains an attractive target. Moreover, note that not all factors influencing the type and energy of magnetic exchange interactions in discrete coordination clusters are well understood, and it often is difficult to predict the magnetic characteristics of such compounds. The corresponding multidimensional systems lack adequate theoretical understanding even more, as in these networks, numerous inter- and intra-cluster interactions determine the resulting magnetism. Thus, further studies in this young field are essential to attain real control and understanding of the way that complex building blocks assemble and interact.

The scope and objectives of the thesis. The main goal of the thesis is the obtaining of new homometallic Fe^{III} and heterometallic Fe^{III}-4f carboxylate clusters and coordination polymers based on them with potential magnetic and SMM properties. Thus, in order to achieve the main goals of the research have been set following objectives:

- Development of crystal engineering strategies towards the synthetic approaches for the preparation of new homo- and heterometallic polynuclear Fe^{III} and Fe^{III}-4f carboxylate clusters and coordination polymeric networks based on them.
- Design and synthesis of new homo- and heterometallic polynuclear coordination clusters and cluster-based polymers employing different carboxylate and/or O-based and N-based ligands.
- Characterization of their physico-chemical characteristics and chemical reactivity by using a range of physical methods including IR spectroscopy and thermogravimetric analysis.
- Structural analysis of obtained complexes using X-ray diffraction analysis (single-crystal and powder X-ray diffraction methods).
- *Examination* of the physical properties of both metal clusters and coordination polymers based on them, looking for unusual magnetic behaviour: dc magnetic susceptibility and magnetization studies for characterizing the intra-cluster and inter-cluster exchange interactions and ac measurements for identification of slow magnetization relaxation (SMM behavior).
- *Revealing* the dependency of coordination polymer's structure on the nature and topology of polynuclear complex, used as "building blocks", as well as the structure and topology of bridging ligands, used for linking of such building blocks.

 Probing the influence of the linking mode of polynuclear structural blocks (including nanosized molecules-magnets) on magnetic properties of the resulting coordination network.

Scientific novelty and originality of the results:

- Practical and broadly applicable approaches for the synthesis of homometallic Fe^{III} and heterometallic Fe^{III}-4f carboxylate clusters and cluster-based coordination polymers were developed. This includes the use of conventional solution chemistry and novel synthetic procedures such as hydro(solvo)thermal synthesis and ultrasonic irradiations.
- A range of appropriate bridging ligands that include multiple donor atoms to connect metal ions and bulky groups to separate molecules from each other has been used to construct polynuclear Fe^{III}/Fe^{III}-4f coordination clusters.
- By employing the different synthetic strategies an extensive series of both homo- and heterometallic Fe^{III} and Fe^{III}-4f compounds with different nuclearity ranging from di-, tritetra-, hexa-, hepta-, octa-, nona-, undeca-, doicosa- up to tetraicosanuclear cores, metal ratio and coordination topology have been obtained.
- The potential of structure-directed semiflexible amino alcohols and carboxylate bridging ligands has been successfully applied to design and prepare a new family of the currently largest d/f coordination wheels, namely the tetraicosanuclear [Fe₁₈M₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·n(solvent) (M^{III} = Dy (25, 26), Gd (27), Tb (28), Ho (29), Sm (30), Eu (31), and Y (32)) compounds.
- The use of different *O*,*N*-donor bridging ligands led to the formation of coordination networks of different dimensionality (1D and 3D) by connection the {Fe₃O}- and {Fe₄O₂}-type carboxylate clusters. A novel µ₃-oxo-centered cationic homometallic {[Fe₃O(piv)₆(4,4'-bpy)_{1.5}](OH)·0.75(CH₂Cl₂)·x(H₂O)}_n (19) three-dimensional coordination polymer possessing a 6-fold interpenetrated network with rare (8,3)-c (etc) topology has been synthesized.
- By appropriate choice of bridging ligands, it was possible to gain control over dimensionality of the network and the control of the magnetic interactions among the building polynuclear blocks, which is the fundamental for physical properties.
- Detailed studies of magnetic properties of a large number of new synthesized Fe^{III}/Fe^{III}-4f clusters and cluster-based coordination polymers were performed that allowed to establish the nature of magnetic interactions between metal ions in these compounds.

- Magnetic measurements revealed predominant antiferromagnetic intracluster interactions in homometallic compounds {Fe₄} (4, 5), {Fe₇} (7), {Fe₆} (8), {Fe₁₂} (13, 14), and {Fe₂₂} (15, 16)), oxo-tetranuclear {Fe₄O₂} (18) and oxo-trinuclear {Fe₃O} (19) cluster-based coordination polymers, as well as in heterometallic wheel-shaped ({Fe₆Dy₃} (20), {Fe₆M₄} (M^{III} = Dy (21), Gd (22), Ho (23), Y(24)), {Fe₁₈M₆} (M^{III} = Sm (29), Eu (30), Ho (31), Y(32)), {Fe₄M₂} (M^{III} = Dy (35), Gd (36), Tb (37), Y (38), Er (39), Tm (40)) and {M₄Dy₂}-type (41) (M^{III} = Fe, Mn) compounds. Additionally, ferromagnetic exchange interactions were found in the ring structure {Fe₁₈Ln₆} (Ln^{III} = Dy (26), Gd (27), Tb (28)) and condensed cluster 42.
- In a series of {Fe₈O₃} (9-11) propeller-like clusters magnetic studies revealed the presence of antiferromagnetic exchange interactions dominating along the edges of the propeller, while a moderate ferromagnetic interaction is found along the propeller axis.
- The wheel-shaped charge-neutral {Fe₆Dy₃}-(20), {Fe₆Dy₄}- (21), {Fe₁₈Dy₆}- (26), {Fe₁₈Tb₆}- (28) type coordination clusters and the condensed {Fe₄Dy₂}- (35), {M₄Dy₂}(M^{III} = Fe, Mn) (41) and {Fe₇Dy₄}- (42) type coordination clusters were found to exhibit slow magnetization relaxation.

Solved scientific problem. The optimal and effective synthetic conditions for the preparation of porous coordination polymers of iron (0D, 1D and 3D) that incorporate clusters and Fe^{III}/Fe^{III}-4f carboxylate clusters that showed slow magnetic relaxation have been established. At the same time, the possibility of obtaining compounds with a desired properties through the combination of pre-designed carboxylate precursor with various *N*,*O*-organic ligands was demonstrated.

Theoretical and practical significance of this work consists in the rational use of different multidentate ligands in construction of new coordination species (clusters and clusterbased coordination polymers) providing compounds that possess different structures, and this in its turn allows to manage physical and chemical properties of the compounds, and improve their magnetic properties and behavior. The synthetic methods and approaches that were developed may be used in the preparation of similar polynuclear iron and iron/lanthanide coordination clusters and coordination polymers. The obtained knowledge show the relationship structure-properties of homo- and heterometallic Fe^{III}/Fe^{III}-4f compounds and contribute to a better understanding of the physical and chemical properties of these species as well as the fundamental principles that govern the magnetism of these species, in particular when moving from isolated molecules to nano-dimensional systems and for their possible application in the future. Based on the prepared Fe-oxo coordination clusters a new semiempirical program *wxJFinder* has been developed by the group of Prof. Dr. P. Kögerler, Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany (<u>http://www.ac.rwth-aachen.de/extern/ak-koegerler/wxjfinder.php</u>). The program provides accurate prediction the exchange energies in the Fe^{III}(μ_{2+n} -O)Fe^{III} systems.

Dissemination and publication of the research findings. The most important achievements of this research were presented at international and national scientific meetings. Fourteen abstracts have been published at the following conferences: The 9th International Conference on Materials Science and Condensed Matter Physics is dedicated to the 90 anniversary of the prominent Moldovan physicists Academician Sveatoslav Moskalenko and Academician Vsevolod Moskalenko, Chisinau, Republic of Moldova (September 25-28, 2018); the 4th Central and Eastern European Conference on Thermal Analysis and Calorimetry, Chisinau, Republic of Moldova (August 28, **2017**); the 8th International Conference Materials Science and Condensed Matter Physics, Chisinau, Republic of Moldova (September 12-16, 2016); the International Scientific Conference of PhD students "Contemporary trends of development of science: views of young researchers" in the University of Academy of Sciences of Moldova, Chisinau, Republic Moldova (Mai 25, 2016); the XVIII-th Conference "Physical Methods in Coordination and Supramolecular Chemistry", Chisinau, Republic of Moldova (October 8-9, 2015); the International Scientific Conference of PhD students "Contemporary trends of development of science: views of young researchers" in the University of Academy of Sciences of Moldova, Chisinau, Republic of Moldova (March 10, 2015); the International Scientific Conference of PhD students: "Contemporary trends of development of science: views of young researchers" in the University of Academy of Sciences of Moldova. Chisinau, Republic of Moldova (March 10, **2014**); the 7th International Conference on Materials and Science and Condensed Matter Physics, dedicated to the 50th anniversary of the Institute of Applied Physics of the Academy of Sciences of Moldova", Chisinau, Republic of Moldova (September 16-19, 2014); IX COPS 2011, 9th International Symposium on Characterisation of Porous Solids, Dresden, Germany, Conference proceedings (June 5-8, 2011); the 5th Conference on Materials Science and Condensed Matter Physics MSCMP 2010, Chisinau, Republic of Moldova (September 13-17, **2010**). Additionally one oral presentation "Assembly of ultra-large Fe^{III}-Ln^{III} coordination wheels" has been given at the 8th International Conference Materials Science and Condensed Matter Physics, Chisinau, Republic of Moldova, 2016.

The research results described in this thesis have been published in peer-reviewed journals (six papers in journals with impact factor and one without co-authors in journal of A grade):

- Botezat O., van Leusen J., Kögerler P., Baca S. G. Tuning the Condensation Degree of {Fe^{III}_n} Oxo Clusters via Ligand Metathesis, Temperature, and Solvents. In: Inorg. Chem., **2018**, vol. 57 (13), p. 7904–7913. DOI: 10.1021/acs.inorgchem.8b00994 (IF: 4.857).
- Botezat O. Iron-lanthanide single molecule magnet compound. In: Mold. J. Phys. Sc., vol. 16, N 3-4, 2017, p. 191-210.
- Botezat O., van Leusen J., Kravtsov V. Ch., Kögerler P., Baca S. G. Ultralarge 3d/4f coordination wheels: from carboxylate/amino alcohol-supported {Fe₄Ln₂} to {Fe₁₈Ln₆} rings. In: Inorg. Chem., **2017**, vol. 56 (4), p. 1814–1822. Doi: 10.1021/acs.inorgchem.6b02100 (IF: 4.82).
- Botezat O., van Leusen J., Kravtsov V. Ch., Ellern A., Kögerler P., Baca S. G. Iron(III) carboxylate/aminoalcohol coordination clusters with propeller-shaped Fe₈ cores: approaching reasonable exchange energies. In: Dalt. Trans., **2015**, vol. 44, p. 20753-20762. Doi: 10.1039/C5DT03024B (IF: 4.197).
- 5. Botezat O., van Leusen J., Kravtsov V. Ch., Filippova I. G., Hauser J., Speldrich M., Hermann R. P., Krämer K. W., Liu S.-X., Decurtins S., Kögerler P., Baca S. G. Interpenetrated (8,3)-c and (10,3)-b Metal-Organic Frameworks Based on {Fe^{III}₃} and {Fe^{III}₂Co^{II}} Pivalate Spin Clusters. In: Cryst. Growth Des., **2014**, vol. 14(9), p. 4721-4728. Doi: 10.1021/cg5008236 (IF: 4.558).
- Baca S. G., Filippova I. G., Keene T. D., Botezat O., Malaestean I. L., Stoeckli-Evans H., Kravtsov V. Ch., Chumacov I., Liu, S.-X., Decurtins S. Iron(III)-pivalate-based complexes with tetranuclear {Fe₄(μ₃-O)₂}⁸⁺ cores and N-donor ligands: formation of cluster and polymeric architectures. In: Eur. J. Inorg. Chem., **2011**, p. 356–367. DOI: 10.1002/ejic.201000838 (IF: 1.38).
- Baca S. G., Botezat O., Filippova I., Speldrich M., Jeanneau E., Kögerler P. A Heptanuclear Iron(III) Oxo-Carboxylate Cluster. In: Z. Anorg. Allg. Chem., 2011, p. 821–823. DOI: 10.1002/zaac.201100021 (IF: 1.249).

Thesis overview

The thesis consists of introduction, four chapters, conclusions and recommendations, bibliography of 259 sources, four annexes, 113 pages of the basic text, 50 figures and 8 tables. The introduction describes the relevance of the work, identifies goals and objectives of the

thesis, and describes the results of scientific novelty, theoretical and practical importance, dissemination and publication of the research findings and publications on the topic of work.

Chapter 1 – "Current state of research in the field of homo- and heterometallic Fe^{III}-Ln^{III} polynuclear carboxylates" contains four subchapters. The first subchapter gives a brief introduction of a crystal engineering and the next two present an overview of analyzed information about achievements in the field of homo- and heterometallic Fe^{III} and Fe^{III}-4f^{III} carboxylate clusters and polymers. The chapter includes the design of these materials with the prevailing characteristics and properties that depend on the structural features of the compounds; therefore, a special attention was given to the topology of the reported complexes.

Chapter 2 – "Experimental methods of synthesis and investigations" consists of six subchapters describing the preparation of homometallic Fe^{III} and heterometallic Fe^{III}-4f coordination compounds, including homometallic cluster-based coordination polymers. This chapter includes detailed information on the synthetic methods, equipments and instruments (X-Ray crystallography, elemental and TG/DT analysis, IR spectroscopy and magnetic SQUID measurements) used during the experimental research. In total, 42 coordination compounds have been synthesized and characterized.

Chapter 3 – "Homometallic polynuclear Fe^{III} clusters and coordination polymers" is devided into three sections. The first subchapter being addressed to the design and synthesis of homometallic oxo-bridged complexes, whereas the second subchapter describes preparation of 1D and 3D coordination polymers constructed from tri- or tetranuclear clusters. These sections include synthesis schemes, results of single-crystal X-ray diffraction, spectral (IR) and thermogravimetric studies, also structural characterisation, and examination of the magnetochemical properties of the obtained compounds. The chapter ends by the conclusions.

The final **Chapter 4** – "Heterometallic polynuclear Fe^{III} -Ln^{III} carboxylate compounds" chapter is divided into three subchapters and includes a synthetic approach towards the design and preparation of heterometalic Fe^{III} -4f coordination clusters, their structural characteristics, and the results of the spectral (IR) and thermal analyzes. The magnetic dc and ac measurements have been performed to study of the magneto-chemical properties of these compounds. The chapter ends by the conclusions.

1. CURRENT STATE OF RESEARCH IN THE FIELD OF HOMO- AND HETEROMETALLIC Fe^{III}-Ln^{III} POLYNUCLEAR CARBOXYLATES

1.1. Crystal engineering: brief introduction

Crystal engineering is a rapidly growing subject during the last 30 years that has brought together investigators from many disciplines [24] and assumes the rational design of molecular crystalline solids with predictable structure and specific physical and chemical properties through an understanding and manipulation of intermolecular interactions. Engineering strategies are based mostly on coordination bonds or hydrogen bonding, but can also use other interactions, such as halogen bonds, π - π and lipophilic interactions. Crystal engineering has been emerging as a major cross-disciplinary field of basic and applied investigations including organic chemistry, inorganic chemistry, physical chemistry, X-ray crystallography, materials sciences and computational chemistry. The conceptual origins of crystal engineering go back to the beginning of X-ray crystallography when Bragg noted similarities between the crystal structures of naphthalene and anthracene and, correlation between a crystal property and a molecular property [25] as well related with Robertson's work in 1951, where he identified a series of molecules (aromatic hydrocarbon structures), determined their crystal structures and correlated the molecular structure of an organic compound with its crystal structure [26, 27]. The term "crystal engineering" was introduced by Pepinsky [28] in 1955 at a Meeting of an American Physical Society in Mexico in the abstract entitled "Crystal engineering: New Concept in Crystallography" where he postulated that "crystals with advantageous properties can be "engineered". This term has been further implemented and elaborated by Schmidt, who has addressed the problem of crystal structure prediction in the context of organic solid-state photochemical reactions [29]. In his research, Schmidt suggested that by understanding the ways in which molecules interact, it should be possible to design packing motifs in crystals for rational planning of solid-state reactions. Later, his work was followed by other contributions from Israel most especially from the groups of Cohen [30], Herbstein [31], Lahav and Leiserowitz [32, 33]. They described in their works the design of topochemical (2+2) reaction polymerization. Thomas and co-workers published a series of cyclic ketones that showed solid-state reactivity [34]. Wegner showed that polymerization of the crystalline diacetylenes is governed by topochemical rules [35]. This area of research also has been extended by work of Curtin and Paul from the University of Illinois on phase transitions, gas-solid reactions, crystal polarity and polymorphism [36-38]. The above-described work of scientists contributed to the development of organic solidstate chemistry. These studies are very important, as they helped to gain the identity of crystal engineering, and attracted great attention of scientists, chemists and crystallographers. Development of the Crystal engineering continued work by Ermer in the University of Cologne on the crystal structure of adamantane-1,3,5,7-tetracarboxylic acid and reported novel analysis of the complex packing of this molecule in the crystal, in terms of interpenetrated networks, is the forerunner of the topological approach to the description of crystal structures of molecular solids [39]. That was the first systematic analysis of an interpenetrated solid. In the paper reported by Desiraju and Gavezzoti were classified the structures of polynuclear aromatic hydrocarbons and identified the molecule \rightarrow crystal paradigm as a primary concern of crystal engineering [40]. The identification of an organic crystal as a 'supramolecule non par excellence' was performed by Dunitz, in his words a molecular crystal may be viewed as a solid supermolecule [41, 42] and later by Lehn [43, 44]. In 1987, Cram, Lehn and Pedersen were awarded the Nobel Prize in supramolecular chemistry for their work in the field of organic synthesis of molecules that mimic biological processes [45]. Since then, several reviews and books have been published on this fascinating field of supramolecular chemistry.

Desiraju in 1989 gave broader and meaningful definition of the modern crystal engineering as ,,the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties" [46]. The seminal works by Desiraju and Etter afforded the concept of supramolecular synthons [47, 48] and led hydrogen bonds being the most exploited of the noncovalent interactions in the context of crystal engineering of organic solids.

However, the provocative comment by Maddox that it remains impossible to predict crystalline architectures from knowledge of chemical composition illuminates an issue that still represents the challenge of scientific and technological importance [49]. The chemist is restricted to the knowledge of the structures of just the starting molecule and the final crystal. The interest to this topic of research was also motivated by well-known quote of Feynman "What would the properties of materials be if we could really arrange the atoms the way we want them?" [50] and the number of scientists whose interest is directed to crystal engineering in order to study the self-assembly process and molecular recognition is increasing permanently.

The physical and chemical properties of crystals are deriving from their molecular components and the manner in which these components are connected. This statement may be easy illustrated by different properties (melting point, solubility, density etc.) of polymorphs.

At the same time, the need in functional solid-state materials has promoted the search for and development of new synthetic strategies as a means to tune and/or enhance the respective properties. Robson extended Wells work on inorganic network structures [51, 52] into the realm of metal-organic compounds and coordination polymers. He suggested "node and spacer" approach that has been remarkably successful at producing predictable network architectures [53-58].

The metal centers act as "nodes" and the "spacer" ligands as linkers. The first compound Robson made in 1989, $[Cu(C(C_6H_4CN)_4]]$ had a diamond network [59]. That is the starting point of studies of coordination polymers and later the introduction of the term metal-organic frameworks (MOFs). The another successful strategies of crystal engineering are based on a molecular building blocks (MBBs) that offer great potential for the rational design and synthesis of functional materials and nanostructures and represent indeed an evolution of the "node-andspacer" approach [60-66].

This approach simplifies the complex problem of structure prediction into a simple problem of network architecture (like building things from LEGO ® blocks) and has proven to be successful in metal–ligand directed assembly [67]. The bigger size of inorganic MBBs (coordination clusters) vs metal ions has afforded unprecedented advances in terms of scale and possibility to involve predesigned clusters with desirable physical properties into the polymeric networks. The further development of design strategy led to the concept of modular chemistry and secondary building units (SBU). The latter represent molecular complexes and cluster entities in which ligand coordination modes and metal coordination environments can be utilized in the transformation of these fragments into extended networks using polytopic linkers [68]. Supermolecular Building Block (SBB) approach assuming the multimetal clusters which can be externally functionalized for nets where the vertex figures indicate the need for high connectivity has been also suggested [69, 70].

Crystal engineering today is one of the mainline interdisciplinary research activity, dealing with the self-assembly of molecular crystals, metal-organic architectures, nanostructures, and coordination polymers using hydrogen bonding, electrostatic, and van der Waals interactions, and metal coordination bonding. Crystal engineering is an area about making crystals that have specific function and whose many properties are related to the crystal structure. Molecular crystals with particular chemical and physical properties find their application as sensors, devices and in catalysts. For instance, MOFs are often compared with zeolites because they have frameworks with large porosity. These materials are able to adsorb large quantities of gases and adsorb gases selectively, which is very useful in separation and catalysis.

It is important to emphasize few important factors that have contributed to evolution and development of modern crystal engineering. These factors are advances in computer controlled single-crystal diffractometer, methods for structure solutions and visualization, including software for analysis and processing crystallographic data [71, 72], database development and analysis, for example Cambridge Structural Database (CSD) [73]; now contains organometallic and metal-organic compounds.

Although powerful computational models for crystal structures prediction with reasonable accuracy are still absent, the success of the building block approach and the voluminous structural information available in the literature promise the successfull design of new advanced materials using crystal engineering principles and crystal engineering became an integral part of every molecular material design.

1.2. Homometallic Fe^{III} carboxylate clusters and cluster-based coordination polymers

There are numerous reasons that stimulated continuing interest in the synthesis and investigation of polynuclear transition-metal coordination clusters. Among them, there are a remarkable variety of species with fascinating structural architectures, and attractive spectroscopic and physical properties. The large polynuclear iron clusters may possess large spin (*S*) values in their ground states due to a relatively large number of unpaired electrons of high-spin Fe^{III} ions. The exchange interactions between Fe^{III} ions are usually antiferromagnetic, but high enough nuclearities and appropriate topologies of such compounds can result sometimes in large ground-state spin values and spin frustration effects among the various pairs of iron exchange pathways [74], and can even manifest single-molecule magnet (SMM) behaviour [75]. The SMMs are molecules that display slow magnetization relaxation rates below a certain (blocking) temperature and SMMs exhibit magnetic hysteresis of purely molecular origin.

In terms of synthetic strategies, the routes to producing coordination clusters with metal ions were well investigated. Both metal salts and small nuclearity coordination clusters, may serve as a starting material to produce a multitude of coordination clusters via self-assembly routes or by imposing specific binding regimes on the metal ions in a more directed synthesis.

Nuclearity and topology of the polynuclear metal complexes depend strongly on the nature of ligands and the number of possible binding modes shown by them that complete the peripheral coordination of the cluster, acting as bridging or terminal groups. For instance, aminopolyalcohol organic ligands containing mixed-set of donor atoms have been widely employed in the preparation of homo- and heterometallic complexes. The presence of templating units, solvents, molar ratio of the components, the concentrations and the type of counterions also play a decisive role in the formation of polynuclear clusters or coordination polymers. In its turn, the topological structure of compound, number of nuclei and their connectivity affect the properties. In Fe chemistry, the carboxylate groups have been proven to be a useful functional group for obtaining high-nuclear clusters of iron. The transition metal trinuclear carboxylate clusters have been successfully used as precursors for the preparation of highnuclear clusters, where carboxylate group adopted different coordination modes, as shown in Figure 1.1.



Fig. 1.1. The presentation of coordination modes of carboxylate group.

A huge number of polynuclear Fe^{III} carboxylate clusters and polymers have been published and to date it is reported more than 1600 structures, among them about 1400 polynuclear Fe^{III} carboxylate clusters and 235 Fe^{III} carboxylate polymers (CSD version 5.38) [73].

Dinuclear iron complexes are of interest over many years because they represent a unit that exists in non-heme iron protein in haemerythrin. Dinuclear iron sites often facilitate and catalyze the processes of the activation of the oxygenation of the substrates in biology [76-78]. The first oxo-bridged binuclear iron(III) complex, [Fe(salen)]₂O (salen=salicylaldehyde-ethylenediamine), was prepared by Pferiffer et al. in 1933 [79]. Since then a number of diiron μ -oxo or μ -hydroxo bridged carboxylate complexes have been reported by Ghattas, Jarenmark, Mimmi et al. [80-86]. These compounds possess a nearly linear structure, where L= mono- or multidentate organic ligand; RCO₂ = carboxylic groups (chloroacetic, pivalic, benzoic acid) (Figure 1.2) by Adams [87], Ookubo [88], Yamashita [89], Lippard [90] and Mikuriya [91].



Fig. 1.2. Schematic representation of linear dinuclear Fe(III) clusters.

A great number of trinuclear carboxylate complexes have also been prepared and studied. The majority of trinuclear carboxylates of trivalent iron metals have structures derived from the triangular cluster [Fe₃(μ_3 -O)(RCO₂)₆L₃]⁺ [92-104]. This type of μ_3 -oxo trinuclear iron(III) [105-108] and mixed valence iron(II/III) [109, 110] complexes has been also intensively studied by Moldavian school of chemistry. In such clusters, an oxygen atom is located at the center of an equilateral triangle of iron atoms. Two carboxylate groups bridge each pair of iron atoms, while monodentate ligand is coordinated to each iron center in *trans*-position to μ_3 -O central oxygen atom, giving octahedral surrounding of metal ion. Many triangular clusters that have been magnetically characterized showed that three high-spin iron(III) atoms are antiferromagnetically coupled. Some of such trinuclear Fe^{III} complexes have shown relevance to bioinorganic systems [111] and recent studies have dealt with their relevance to quantum computing [112]. Powell and co-authors reported the synthesis and catalytic properties of a series of ionic liquids which contain seven-charged $[Fe^{III}_{3}O(RCOO)_{6}L_{3}]^{7+}$ cations [100]. Some of them revealed high catalytic activity. There are other analogous triangular clusters containing $\{Fe_3(\mu_3-O)\}^{7+}$ core, where iron ions are bridged by both μ_2 -carboxylates and polydentate ligands [113, 114]. To our knowledge, the first report where ac susceptibility measurements have been used to study the magnetic relaxation of the trinuclear cluster with a $S=\frac{1}{2}$ ground state has been made by Georgopoulou et al. [115]. The μ_3 -oxo centered triangular carboxylate cluster showed out-of-phase signals (up to~5 K) in the presence of external magnetic fields.

Among trinuclear species, ferric complexes with unusual structures and novel core topologies have been found [116]. Isostructural compounds with different Schiff base ligands each possess a $\{Fe^{III}_{3}(\mu_{2}-O)_{3}\}^{3+}$ core and general formulae $[Fe_{3}(O_{2}CMe)_{3}(L)_{3}]$ (L - Schiff base ligand) with three Fe atoms located at the vertexes of an inequilateral triangle (Figure 1.3 a). Each pair of Fe centers is bridged by an ethoxotype O atom of organic ligand and in addition is

bridged by a μ_2 -MeCO₂⁻ ligand. Magnetization studies revealed the ground state of this molecule to be *S*= 5/2, displaying antiferromagnetic exchange interactions within compound.

In literature triiron(III) acetate and pivalate clusters with an uncommon and rare T-shaped topology are also described [117, 118]. The trinuclear Fe^{III} acetate [Fe₃O(MeO)₂(MeCOO)₂ (phen)₂Cl₃] (phen = 1,10-phenanthroline) is illustrated in the Figure 1.3 (b). The core of these complexes is an isosceles triangle bridged by a μ_3 -O ion forming T-shaped geometry. These clusters possess *S*=5/2 ground state displaying antiferromagnetic interactions between iron ions.



Fig. 1.3. Structure of [Fe₃(MeCOO)₃(L)₃] (a) and [Fe₃O(MeO)₂(MeCOO)₂(phen)₂Cl₃] (b). Color definition: Fe – green spheres, O – red, N – blue, C – grey, Cl – violet balls. Hydrogen atoms are omitted.

The Cambridge Structural Database (CSD version 5.38) [73] contains structural data of many Fe^{III} oxo-bridged carboxylate complexes comprising the tetranuclear $\{Fe_4(\mu_3-O)_2\}^{8+}$ butterfly-like core. This core consists of two central so-called "body" Fe atoms doubly bridged by two μ_3 -oxo atoms and two peripheral "wings" Fe atoms. There are "bent" [119-130], "planar" [131-133] and "chair-like" [134-136] core configurations in such clusters (Figure 1.4) with antiferromagnetic exchange interactions between metals.

Other tetranuclear examples of tetranuclear ferric clusters belong to the rectangular type of metal mutual arrangement [121, 137-140]. Note, the tetranuclear iron(III) acetate complex, $[Fe_4(\mu-O)(\mu-OH)(\mu-OAc)_4(L)_2](ClO_4)_3$ (HL = 1,3-bis[(2-aminoethyl)amino]-2-propanol), showed catalase-like activity in water, tris(hydroxymethyl)aminomethane buffer and acetonitrile [139]. Dissimilar to the previous structures, a tetranuclear [Fe_4OCl(O_2CMe)_3(O_3PC_6H_9)_3(py)_5] (where py = pyridine) cluster consisting of a tetrahedral acetate cage with an additional 1-cyclohexen-1-ylphosphonate co-ligand has been reported by Zheng L.-M. and co-workers [141].

The {Fe₄} cluster demonstarates dominant antifferomagnetic interactions between iron(III) centers.



Fig. 1.4. Three types of butterfly-like configurations.

Different types of structures for pentanuclear iron(III) carboxylate clusters are known [116, 142-144]. Isostructural pentanuclear $[Fe_5O(OH)(O_2CC_6H_4-p-NO_2)_4(L1)_4]$, $[Fe_5O(OH)(O_2CMe)_4(L2)_4]$ and $[Fe_5O(OH)(O_2CPh)_4(L3)_4]$ complexes reported by Boscovic et al. were prepared with employing Schiff base co-ligands (L1, L2 and L3) [116]. These complexes contain oxo-, hydroxo-, alkoxo-, and carboxylato- bridging units. Antiferromagnetic exchange interactions propagated through these iron-oxygen cores have afforded spin ground states of 5/2. Magnetic studies revealed slow relaxation of the magnetization associated with an anisotropy-induced energy barrier of molecular origin for all compounds.

Kizas et al. reported a series of pentanuclear ferric clusters with unusual topology, formed from the reaction of trinuclear Fe^{III} clusters with the different aliphatic amino-alcohol ligands [143]. Complexes $[Fe_5(\mu_3-O)_2(L)_4(O_2CR)_7]$ (HL = 3-amino-1-propanol (Hap) or 2-(hydroxymethyl)piperidine, R = Ph; CMe₃) possess a quasi-planar $[Fe_5(\mu_3-O)_2]^{11+}$ core consisting of two vertex-sharing $[Fe_3(\mu_3-O)]^{7+}$ units. Other pentanuclear complex with aliphatic amino-alcohol ligand, $[Fe_5(\mu_4-O)(\mu_3-O)(O_2CCMe_3)_8(ap)_2Cl(HO_2CCMe_3)]$, possesses the $[Fe_5(\mu_4-O)(\mu_3-O)]^{11+}$ core, in which the five Fe^{III} ions adopt a monocapped trigonal pyramidal topology. This cluster with ground state of 5/2 showed out-of-phase signals in the presence of external magnetic fields.

A series of hexanuclear Fe^{III} carboxylate species with acetic, pivalic, and benzoic acids has been reported [145-160]. Their structures comprise six iron(III) ions that can be described as two triangular [Fe₃(μ_3 -O)] units joined together via two bridging hydroxide [145-151], two bridging carboxylate groups [152-153], or μ_2 -oxo ions [144, 154-160]. The {Fe₆} clusters basically show antiferromagnetic exchange interactions between iron(III) centers. Pentanuclear [Fe₅O₂(O₂CPh)₇(teda)(H₂O)] and hexanuclear [Fe₆O₂(piv)₈(tedaH)₂] (tedaH₄ = N,N,N,N-tetrakis(2-hydroxyethyl)ethylenediamine) carboxylate clusters reported by Bagai and co-workers showed in-phase signals and out-of-phase (χ_{M}'') ac susceptibility peaks above 1.8 K. [144]. Pentairon(III) benzoate and hexairon(III) pivalate complexes have been prepared from the reaction between trinuclear carboxylates with general formula of [Fe₃O(O₂CR)₆(H₂O)₃]⁺¹ and aminopolyalcohol ligand (tedaH₄). The pentanuclear complex is build up from butterfly-like subunit on the top of which is situated an iron atom attached by teda^{4–} ligands, whereas the structure of the hexanuclear cluster consists of two triangular [Fe₃(µ₃-O)]⁷⁺ units held together by four alkoxide teda^{4–} O atoms. The peripheral ligation of the latter is provided by six $\eta^1:\eta^1:\mu$ -bridging pivalate groups and two monodentate pivalates.

Trettenhahn reported a hexanuclear cluster $[Fe_6O_3(OH)(p-NO_2C_6H_4CO_2)_{11}(dmf)_4]$ which comprises of $[Fe_6O_3(OH)]^{11+}$ core, where the six Fe atoms are distributed within triangular $[Fe_3(\mu_3-O)]$ units bridged by nitro-benzoate and acetate groups [161]. The complex showed a remarkable catalytic activity in the oxidation of cyclohexane. Another Fe₆(acetate) complex based on 3,4,5-trimethoxybenzoate reported by Milunovic adopts a recliner conformation $[Fe_6(\mu_4-O_2)(\mu_3-O)_2]^{12+}$ [162]. The complex acts as a catalyst precursor for the oxidation of cyclohexane with aqueous H₂O₂, in the presence of pyrazinecarboxylic acid and exhibits high activity in an exceptionally short reaction time (45 min), being unprecedented for any metal catalyzed alkane oxidations by H₂O₂.

A number of the reported heptanuclear {Fe₇} and octanuclear {Fe₈} carboxylates display a three-blade propeller topology, with the central Fe atoms representing the axle of the propeller [163-170]. The core of octanuclear acetate, propionate and benzoate complexes with aminopolyalcohol ligands closely resembles a core of heptanuclear propeller clusters, but contains the two axial iron atoms located in the center of the propeller [163, 167-170]. The investigation of magnetic properties of these species display antiferromagnetic coupling between iron(III) centers. Moreover, the heptanuclear propeller-like cluster derived from the reaction of methyldiethanolamine (mdeaH₂) with μ_3 -oxo trinuclear pivalate, [Fe₇O₃(piv)₉(mdea)₃(H₂O)₃], has spin ground state S = 5/2 [166]. The performed high-frequency electron paramagnetic (HFEPR) measurements revealed that the cluster is a SMM having a negative uniaxial zero-field-splitting parameter D = -0.36 cm⁻¹ resonance.

Interestingly, the heptanuclear benzoate-based $[Fe_7O_2(O_2CPh)_9(O_3PC_6H_9)_4(py)_6]$ and acetate-based $[Fe_7O_2(O_2CMe)_9(O_3PPh)_4(py)_6]$ (py = pyridine) clusters reported by Yao [141], Tolis [171] and Khanra [172] display different structural topology. The core of these complexes

can be described as two equivalent trinuclear oxo-centered $\{Fe_3(\mu_3-O)\}^{7+}$ units connected via a single iron atom through four phosphonate ligands. The magnetic exchange interactions in these cages are all antiferromagnetic [141, 172].

Several octanuclear iron(III) carboxylates mentioned in [173-175] have a core that can be described as two distorted {Fe₄O₂} butterfly units linked end-to-end by alkoxide arms and the central μ_4 -oxide ligands. Further, the reported benzoate and pivalate ferric [Fe₈(O₂CR)₁₂(thme)₄] (R = Ph, CMe₃; thme =1,1,1-tris(hydroxymethyl)ethane) clusters display a ring-like structures [176-178].

A range of nonanuclear {Fe₉} carboxylate clusters have been synthesized and magnetically characterized: pivalate clusters with thmeH₃ ligand [178], phosphonate groups [179] and cyclopentylphosphonic acid [180], and campyl phosphonic acid [172, 181, 182]. Among nonanuclear iron(III) species, to our knowledge, only two clusters showed SMM behavior. Nonanuclear [Fe₉(μ_3 -O)₄(O₃PPh)₃(piv)₁₃] pivalate complex is made via the reaction of trinuclear iron(III) pivalate with PhPO₃H₂ in MeCN and Et₂O [183]. Authors describe the structure of the cluster as tridiminished icosahedron. The compound consists of four {Fe- μ_3 -O} triangles out of which three triangles are formed by six iron centers and joined into {Fe₆O₃} unit. Remaining discrete triangle is bound to the {Fe₆O₃} unit by three phenylphosphonate and three pivalate ligands (Figure 1.5 a). Magnetic dc measurements showed strong antiferromagnetic coupling with S = 1/2 ground state for the molecule. Single crystal micro-SQUID measurements show the existence of temperature and sweep rate dependent hysteresis loops at low temperature, suggesting [Fe₉(μ_3 -O)₄(O₃PPh)₃(piv)₁₃] to be a SMM.

A SMM nonametallic benzoate cluster $[Fe_9O_4(OH)_4(O_2CPh)_{13}(heenH)_2]$ (Ph = C₆H₅; heenH₂= N,N'-bis(2-hydroxyethyl)ethylenediamine) described in the literature (Figure 1.5 b) [184]. In preparation of this cluster the combination of carboxylate and *N*,*N*'-bis(2hydroxyethyl)ethylenediamine (heenH₂) ligands have been used. The structure of the cluster (Figure 1.5 b) revealed the aggregate of nine Fe^{III} centers linked by four μ_3 -OH⁻, four μ_3 -O²⁻ ions and nine $\eta^1:\eta^1:\mu$ -bridging carboxylate ligands, and tridentate heenH⁻ ligand. Fitting of the low temperature magnetisation data was consistent with *S* = 7/2 ground state, *D* = -0.85(1) cm⁻¹ and *g* = 2.0. Magnetic measurements of the {Fe₉} cluster indicated predominantly antiferromagnetic interactions in complex and hysteresis loops confirming the SMM behaviour.

A range of decanuclear {Fe₁₀} carboxylate wheels with general formula $[Fe(OMe)_2(O_2CR)]_{10}$ have been obtained from the reaction of μ_3 -oxo trinuclear iron(III) carboxylates [185, 190] or iron(III) salt [186, 189, 191], or both starting materials [187, 188] in

methanol solution. The ring structures have been obtained with different carboxylate anions: chloroacetate, acetate, 3-(4-methylbenzoyl)propionate, benzoate and diphenylacetate. Their structures consist of ten ferric ions in a circular array, which are held together by twenty μ_2 -OMe ligands and ten bridging carboxylate ligands. The {Fe₁₀} wheels reported by Taft [188], Jiang [189] and Stamatatos [190] demonstrated the antiferromagnetic interactions between neighbouring iron centers.



Fig. 1.5. Structure of [Fe₉(µ₃-O)₄(O₃PPh)₃(piv₁₃] (a) and [Fe₉O₄(OH)₄(O₂CPh)₁₃(heenH)₂]
(b). Color definition: Fe – green spheres, O – red, N – blue, P –yellow and C – grey balls. Hydrogen atoms are omitted.

There are also examples of the larger cyclic polymetallic iron(III) carboxylate clusters: dodecanuclear {Fe₁₂} benzilate [192] and benzoate [193], hexadecanuclear {Fe₁₆} benzoate [175, 176] and octadecanuclear {Fe₁₈} [194] acetate. Complexes {Fe₁₆} with S = 0 and {Fe₁₈} with S = 5/2 show antiferromagnetic interactions between the iron(III) centers. Hexadecanuclear benzoate-based cluster additionally bridged by polytopic thme^{2–} ligands and EtO[–] groups, whereas octadecanuclear acetate-based cluster bridged by the dianion of m-xylylenediamine bis(Kemp's triacid imide) ligand [194].

The anionic $\{Fe_{28}\}$ acetate wheel is the largest cyclic ferric carboxylate cluster yet reported [195]. This cluster was obtained by the interaction of iron(III) nitrate with chiral tartrate ligand. The structure of the wheel can also be viewed as four $\{Fe_7\}$ fragments connected by four tartrate linkers.

Koumousi et al. reported deca- and dodecanuclear clusters, namely $[Fe_{10}O_4(OH)_4(piv)_{14}(praoH)_4] \cdot 2.2 MeCN \cdot 1.6 H_2O$ and $[Fe_{12}O_8Cl_2(piv)_{12}(praoH)_6(H_2O)_2]$ ·MeCN · 0.7 H₂O, that have been obtained from the reaction of oxo-centered pivalate trinuclear

complex with N-containing pyrrole-2-carboxaldehydeoxime ligand (praoH) [196]. The clusters showed the in-phase (χ_M') ac temperature-dependent signals in the 4–15 K region.

The family of undecanuclear {Fe₁₁} complexes is small, despite this, among them there are compounds that showed interesting properties. Some of them possess SMM features due to their capacity to retain magnetization after removal of a magnetic field. For instance, undecanuclear benzoate (NEt₄)[Fe₁₁O₄(O₂CPh)₁₀(thme)₄(dmhp)₂Cl₄] cluster with tripodal polyalchol ligand 1,1,1-tris(hydroxymethyl)ethane (thmeH₂) reported by Jones et al. [178]. The metallic core of the complex (Figure 1.6 a) contains four butterfly-like [Fe₄O₂]⁸⁺ subunits where two peripheral tetranuclear subunits are connected to two central subunits (Figure 1.6 a). These subunits additionally bridged by ten benzoates and four thme^{2–} ligands. The {Fe₁₁} cluster exhibits a spin ground state of S = 11/2 displaying Fe^{III}...Fe^{III} antiferromagnetic exchange interactions. Low temperature magnetization studies revealed the presence of hysteresis loops below 1.2 K, demonstrating that the cluster is a SMM.



Fig. 1.6. Structure of [Fe₁₁O₄(O₂CPh)₁₀(thme)₄(dmhp)₂Cl₄] anion (a) and [Fe₁₁O₇(mdea)₃(piv)₁₂] (b). Color definition: Fe –green spheres, O – red, Cl – violet, N – blue, C – grey balls. Hydrogen atoms are omitted.

Other undecanuclear $[Fe^{III}_{11}(\mu_4-O)_3(\mu_3-O)_4(mdea)_3(piv)_{12}]Cl\cdot5MeCN$ (mdeaH₂ = methyldiethanolamine) cluster was reported by Ako et al. [197]. The reaction of the Fe^{III} salt with polytopic mdeaH₂ leads to the formation of the SMM complex. The structure of the [Fe₁₁] cluster (Figure 1.6 b) consists of an $[Fe_{11}(O)_7]^{19+}$ core, where eleven iron(III) centers held together by three μ_4 -O²⁻ and four μ_3 -O²⁻ bridges. Peripheral ligation is provided by twelve bridging pivalates and three tridentate chelating mdea²⁻ ligands. The magnetic susceptibility studies indicated strong antiferromagnetic interactions between the Fe^{III} ions. The undecanuclear

cluster has a S = 13/2 ground state with D = -0.025 cm⁻¹. The frequency dependence of the ac susceptibility under an applied dc field appears around 10 Hz and above 1500 Hz. Hysteresis loops were observed at low temperature (0.7-0.04 K), confirming that the cluster is a SMM.

The undecanuclear 3,4,5-trimethoxybenzoate-based cluster with an unprecedented topology of a $[Fe^{III}_{11}Cl(\mu_4-O^{2-})_3(\mu_3-O^{2-})_5]^{16+}$ core consisting of nine six-coordinate and two five-coordinate ferric ions has been reported by Pombeiro A. J. L. et al. [162]. The {Fe₁₁} complex act as a catalyst precursor for the oxidation of cyclohexane to cyclohexanol and cyclohexanone with aqueous H₂O₂ in the presence of pyrazinecarboxylic acid.

Reaction between Fe(ClO₄)₂, NaO₂CPh, NaN₃, and 1,3-di(2-pyridyl)-1,3-propanedione (dppo) results in the formation of the [Fe₁₂O₄(OH)₁₂(C₇H₅O₂)₈(C₁₃H₉N₂O₂)₄](ClO₄)₄ ·*x*MeCN·*y*H₂O complex (Figure 1.7 a) [198]. The core of the dodecanuclear cluster can be described as a [Fe₄(OH)₄] cubane connected to eight peripheral iron(III) ions through μ_3 -O²⁻, μ_2 -OH⁻, and $\eta^1:\eta^1:\mu_2$ -O₂CPh⁻ bridges, respectively. The ligand dppo⁻ coordinates to iron(III) ions in a $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$ bridging mode. Magnetic susceptibility data demonstrated ferromagnetically coupled the peripheral iron (III) ions and the [Fe₄(OH)₄] core, while antiferromagnetic exchanges are present between the [Fe₄(OH)₄] core and the peripheral iron(III) ions (*S* = 5/2 and *g* = 2). Ac susceptibility studies show the frequency-dependent behavior and out-of phase signals.

Among the high nuclear iron(III) large clusters can be distinguished species with the outstanding and unusual topologies [178, 199-202]. Successful obtaining of high-nuclearity complexes was reached by the using of the trinuclear iron(III) complexes as starting building blocks. The use of new N/O-chelate ligands has led to a series of polynuclear $\{Fe_9\}$, $\{Fe_{14}\}$, Fe_{16} { Fe_{18} } and { Fe_{22} } clusters: $Fe_9O_4(OH)_2(O_2CMe)_{10}(pdm)(pdmH)_4$](NO₃) (pdmH₂ = 2,6pyridinedimethanol) [199], $[Fe_{14}O_4(OH)_4(H_2L)_2(HL)_4(piv)_{20}]$ (H₃L = 2-amino-2-(hydroxymethyl)propane-1,3-diol) [200], [Fe₁₆(EtO)₄(O₂CPh)₁₆(Hthme)₁₂](NO₃)₄ (thmeH₂ = 1,1,1-tris(hydroxymethyl)ethane) [178], $[Fe_{16}O_8(OH)_8(DMP)_{12}(OAc)_{12}(dmso)_4]$ $\cdot 2(\text{dmso}) \cdot 1.5(\text{H}_2\text{O})$ (DMP = dimethyl phosphate) [201], [Fe₁₈O₈(OH)₂(piv)₂₈(heen)₄] $\cdot 4(C_5H_{12}) \cdot 4(CH_2Cl_2)$ (heen $H_2 = N_1N_2$ -bis(2-hydroxyethyl)ethylenediamine) [202]. and $[Fe_{22}O_{14}(OH)_3(O_2CMe)_{21}(mdea)_6](ClO_4)_2 \cdot 4(H_2O) \cdot 4(EtOH) \cdot 4(Et_2O)$ N- $(mdeaH_2)$ = methyldiethanolamine) [203] compounds. Odd-numbered {Fe₉} acetate cluster has been obtained from the reaction of precursor with still poorly explored in Fe^{III} chemistry pyridylalcohol 2,6-pyridinedimethanol [199]. The complex has unprecedented structure and antiferromagnetic exchange interactions between metal ions with S = 5/2 ground state spin.

Two reported pivalate complexes such as {Fe₁₄} with 2-amino-2-(hydroxymethyl)propane-1,3-diol (hmpdH₃) [200] and {Fe₁₈} with N,N'-bis(2-hydroxyethyl)ethylenediamine [202] possess a chain-like topology structure. Structure of {Fe₁₄} can be described as a chain-like complex where four triangular {Fe₃O} units are linked by pivalate, hydroxide, hmpd²⁻ and hmpdH₂⁻ with two additional Fe^{III} centres linked by the remaining two hydroxides. Magnetization measurements were fitted for {Fe₁₄} to give a spin ground state of *S* = 5 with *g* = 1.96 and *D* = -0.19 cm⁻¹ [200]. The centrosymmetric structure of {Fe₁₈} can be described as the linkage by heen²⁻ alkoxide arms of two central [Fe₄(μ_3 -O)₂]⁸⁺ butterfly units, and then connected to additional [Fe₄(μ_3 -O)₂]⁸⁺ butterfly units at each end via intermediate Fe atoms [202]. Magnetic measurements for the complex revealed the central Fe₄ butterfly units are known to exhibit spin frustration effects with the *S* = 0 ground state and antiferromagnetic interactions between separate butterfly units.

The exciting result was obtained as a result of incorporation of mixed-ligands (phenol and biphenol) in the reaction with the trinuclear iron(III) smaller precursor in dichlormethane solution. The $\{Fe_{16}\}$ cluster possesses intriguing structure with a general formula $[Fe_{16}(OH)_8(OPh-PhO)_4(OPh)_8(piv)_{24}]$ [204]. The complex can be regarded as two $\{Fe_8\}$ wheels linked by four bithenoxides, giving hexadecametallic ,, barrel" (Figure 1.7 b). Magnetic studies revealed exchange interactions within the ring and no interactions between the rings.



Fig. 1.7. Structure of [Fe₁₂O₄(OH)₁₂(C₇H₅O₂)₈(C₁₃H₉N₂O₂)₄]⁴⁺ cation and [Fe₁₆(OH)₈(OPh-PhO)₄(OPh)₈(piv)₂₄] (b). Color definition: Fe – green spheres, O – red, N – blue, C – grey balls. Hydrogen atoms are omitted.

The oxo-, hydroxo-pivalate types of iron(III) clusters can be synthesized using solvothermal method. Thus, polynuclear $[Fe_{11}O_6(OH)_6(piv)_{15}]$, $[Fe_{11}O_6(EtO)_9(piv)_{12}]$

 \cdot 5(CH₂Cl₂)·MeCN, hexadecanuclear [Fe₁₆O₁₃(EtO)₆(piv)₁₆]·0.25thf [206], and tetradecanuclear [Fe₁₄O₁₀(OH)₄(piv)₁₈] [205] pivalate aggregates have been reported. The {Fe₁₁} and {Fe₁₆} clusters were obtained from the solvothermal heating of μ -oxo Fe^{III} trinuclear pivalate, whereas the {Fe₁₄} complex was synthesized from the solvothermal reaction of a hexanuclear Fe^{III} pivalate precursor. The latter comprises a unique {Fe₁₄O₁₄} core fragment. Magnetic susceptibility measurements indicated strong antiferromagnetic exchange interactions in these complexes.

Heptadecanuclear benzoate complex $[Fe_{17}(OH)_7O_{11}(O_2CPh)_{20}(N_3)_2] \cdot 4(H_2O) \cdot 10(MeCN)$ comprises $[Fe_{17}O_{11}(OH)_7]$ metal core bridged by twenty benzoate and two azide groups [207]. Magnetization data collected in the ranges 1.8–10 K were fitted for S = 35/2 and D = -0.11 cm⁻¹. The ac susceptibility measurements of the complex showed no evidence of paramagnetic interactions.

Liu et al. reported the largest Fe^{III} polynuclear compound $\{Fe_{64}\}$, $\{[Fe_8O_3(tea)(teaH)_3(HCOO)_6]_8(HCOO)_{12}\}(ClO_4)_{12} \cdot 3(MeOH) \cdot 36(H_2O)$ (teaH₃= triethanolamine) [208]. Magnetic data revealed strong antiferromagnetic interactions between iron centers in $\{Fe_{64}\}$.

Chemically stable porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), which are resistant to reactive species, are of critical importance to a variety of applications, including gas storage, carbon capture, separations and catalysis [209-217]. One of the most successful strategies for constructing PCPs with desired structures/topologies is to use rigid metal carboxylate clusters with well-defined geometries as a building blocks to reduce structural uncertainty during self-assembly and crystallization. Trinuclear clusters that have labile terminal ligands on the metal sites (for instance aqua, or other groups) can be replaced by other organic ligands during the reaction.

To date, several approaches to design coordination polymers have been explored. One of the most frequently used is a "one-pot" reaction based on the mixing of the simple metal salt with different organic ligands in the solvent mixture and under different synthetic conditions, such as room temperature, microwave heating and hydro(solvo)thermal reaction. Another approach is based on the assembly of molecular building blocks or pre-synthesized polynuclear transition metals carboxylate building units with multitopic organic ligands into extended coordination networks.

Only a few examples of iron(III) coordination polymers built from polynuclear cluster blocks have been reported in the literature. They include: 1D chain coordination polymer

[Fe₃O(piv)₆(H₂O)(dca)]n, in which [Fe₃O(piv)₆] units are linked by 1,5-dicyanamide (dca) ligands [218], two 1D coordination polymers based on hexanuclear iron(III) pivalate [Fe₆O₂(O₂CH₂)(piv)₁₂] building blocks linked by 1,4-dioxane (diox) or 4,4'-bipyridine (4,4'-bpy) bridging ligands [219], a 2D coordination polymer [Fe₁₀O₄(OMe)₁₄Cl₄(mcce)] (mcce = 2-carbamoyl-2-cyanoethanimidate) composed of antiferromagnetically coupled {Fe₁₀} clusters [220], and a 3D coordination polymer [{Fe₃O(bdc)₃}₄{Fe(na)₄(H₂O)}₃]X·guest (bdcH₂=1,4-benzenedicaboxylic acid; naH = nicotinate) [221].

1.3. Heterometallic Fe^{III}-Ln^{III} carboxylate clusters

The preparation of high nuclear homometallic iron compounds has been well established, while the area of heterometallic Fe-Ln compounds is less developed. During last few decades more than four hundreds of complexes based on Fe-Ln metallic core have been documented, whereas less than hundred Fe-Ln carboxylate-based compounds are known. The most attractive and valuable compounds are those that show interesting magnetic properties such as SMM behavior. However, among a number of reported polymetallic clusters, a small number of compounds showed the desired property. Besides, the preparation of complexes incorporating Fe and Ln ions in one system is hard to control due to the complicated heterometallic reaction systems and will usually result in structures with one type of metal centers. However, to date, several approaches and an effective strategy towards the preparation of mixed-metal complexes have been introduced, this is so-called "serendipitous self-assembly" approach. The term "serendipitous self-assembly" in the chemistry literature was first introduced by Winpenny in his work "Serendipitous assembly of polynuclear cage compounds" [222]. Thus, design and preparation of Fe-Ln complexes remain a great challenge.

Christou's group was the first who synthesized first Fe-4f SMM complexes in 2006. Clusters $[Fe_2Ho_2(OH)_2(O_2CPh)_4(teaH)_2(NO_3)_3]$ and $[Fe_2Dy_2(OH)_2(O_2CPh)_4(tea)_2(N_3)_2]$ were derived from the trinuclear benzoate iron(III) core with the tetrapodal triethanolamine ligand (teaH₃) [223]. Clusters have the similar structures possessing the incomplete double cuban metallic core, and differ only by the terminal chelating NO_3^- groups in {Fe_2Ho_2} and chelating benzoate one in {Fe_2Dy_2} (Figure. 1.8 a). Magnetic studies show predominantly antiferromagnetic exchange interactions within two complexes. The out-of-phase ac measurements displayed the well-defined hysteresis loop for {Fe_2Dy_2} and with a very small coercivity for {Fe_2Ho_2} at 0.3 K that assumes their SMM properties. The related benzoate {Fe_2Dy_2} complex has been reported later [224]. Magnetic studies of the complex presented no hysteresis loop but showed out-of-phase signals as expected for SMM. Another related benzoate $\{Fe_2Dy_2\}$ complex was derived from trinuclear iron(III) benzoate with thmeH₂ ligand. The investigation of magnetic properties revealed that the compound is not a SMM [225].

Tetranuclear pivalate-based $[Fe_2Ln_2(OH)_2(piv)_4(teg)_2(N_3)_2]$ and $[Fe_2Ln_2(MeO)_2(piv)_4(teg)_2(NO_3)_2]$ (Ln = Dy, Ho) [226] and benzoate-based [Fe₂Dy₂(OH)₂(O₂CPh)₄(teg)₂(N₃)₂] [227] complexes having a similar core motif to above reported coordination clusters have been documented. Pivalate {Fe₂Ln₂} clusters have been prepared by the interaction of simple iron(III) and lanthanide(III) salts with benzoic acid and triethyleneglycol (tegH₂) [226]. The central core of benzoate $\{Fe_2Dy_2\}$ compound represents a coplanar butterfly topology, where Fe^{III} and Dy^{III} ions are bridged by two μ_3 -OH groups (Figure 1.8 b) [227]. Two teg²⁻ anionic ligands coordinate to Dy^{III} centers in a tetradentate coordinate mode and bridge two Fe^{III} centers via two deprotonated alkoxide arms. Antiferromagnetically coupled compound showed frequency dependence χ'' signals, but there is no maxima above 1.8 K.



 $\label{eq:Fig. 1.8. Structure of [Fe_2Ho_2(OH)_2(O_2CPh)_4(teaH)_2(NO_3)_3] (a) and \\ [Fe_2Dy_2(OH)_2(O_2CPh)_4(tea)_2(N_3)_2] (b). Color definition: Fe - green spheres, Ln - yellow, N - blue, O - red and C - grey balls. H-atoms are omitted.$

To facilitate the formation of polynuclear species the polytopic chelate-forming aminopolyalcohol ligands have been often employed as alkoxide arms are good metal bridging group on deprotonation. Furthermore, the hard-donor oxygen tends to bind to lanthanide ions and the soft-donor nitrogen tends to bind to transition-metal ions, thereby leading to the formation of mixed-metal complexes and, in fact, a range of heterometallic polynuclear benzoate [228-231] and pivalate [232-234] complexes with aminopolyalcohol ligands have been reported.

The simplest synthetic route used to synthesize relative benzoate $[Fe_7Ln_3O_2(OH)_2(mdea)_7(O_2CPh)_4(N_3)_6]$ (Ln = Dy and Tb) SMMs [228] is the one-pot approach where simple Fe^{III} and Ln^{III} salts are combined with a bridging N-methyldiethanolamine (mdeaH₂) ligand in the presence of NaN₃. The core of clusters consists of seven Fe^{III} and three Dy^{III} centres holding by two (μ_4 -O)²⁻ and two (μ_3 -OH)⁻ ligands (Figure 1.9 a). Magnetic susceptibility studies revealed dominant antiferromagnetic interactions between Fe^{III} and Dy^{III} ions. Low temperature micro-SQUID measurements gave hysteresis loop for {Fe₇Dy₃} and an effective energy barrier (U_{eff}) of 33.4 K with a relaxation time (τ) of 6.6×10⁻⁸ s. The {Fe₇Tb₃} cluster showed clear out-of-phase signal indicating that cluster exhibits slow relaxation of magnetization.

The reaction of trinuclear iron benzoate with Dy^{III} salt and N-butyldiethanolamine (bdeaH₂) ligand resulted in [Fe₄Dy₂(OH)₂(bdea)₄(O₂CPh)₈] SMM [230]. The cluster consists of two dimeric [Fe₂(bdea)₂]²⁺ units, which are further bridged to a dimeric [Dy₂(μ_3 -OH)₂]⁴⁺ central unit, forming a hexanuclear core (Figure 1.9 b) and revealed the antifferomagnetical coupling with the estimated anisotropy barriers of U_{eff} = 21.4 K and the pre-exponentional relaxation time, τ_0 , of 2.7×10⁻⁸ s.



Fig. 1.9. Structure of $[Fe_7Ln_3O_2(OH)_2(mdea)_7(O_2CPh)_4(N_3)_6]$ (a) and $[Fe_4Dy_2(OH)_2(bdea)_4(O_2CPh)_8]$ (b). Color definition: Fe –green, Ln – yellow spheres, N – blue, O – red and C – grey balls. H-atoms are omitted.

Chen et al. have prepared a hexanuclear $[Fe_4Dy_2(OH)_2(O_2CPh)_8(mdea)_4]$ benzoate complex by the reaction of trinuclear iron benzoate, Dy(III) nitrate and N-methyldiethanolamine (mdeaH₂) [231]. Cluster consists of {Fe₄Dy₂} core, comprising a butterfly-shaped central {Fe₂Dy₂(µ₃-O)₂} unit linked with two perihedral Fe^{III} ions via the oxygens of mdea²⁻ ligand and bridging benzoate (Figure 1.10 a). The microwave heating of solution of {Fe₄Dy₂} clusters

resulted in nonanuclear benzoate [Fe₆Dy₃O₄(O₂CPh)₉(mdea)₅] complex (Figure 1.10 b) [231]. Temperature dependent magnetic measurements for complexes indicated that Fe^{III}-Fe^{III} interactions are antiferromagnetic and Dy^{III}-Dy^{III} interactions are weakly antiferromagnetic. Fitting the frequency dependence ac susceptibility data of complexes with Arrhenius law gave the characteristic SMM effective energy barrier for {Fe₄Dy₂} of $U_{eff} = 7.1$ K, with a relaxation time $\tau = 6.4 \cdot 10^{-6}$ s and for {Fe₆Dy₃} of 17.1 K and relaxation time of $7.4 \cdot 10^{-8}$ s.



Fig. 1.10. Structure of [Fe₄Dy₂(OH)₂(O₂CPh)₈(mdea)₄] (a) and
[Fe₆Dy₃O₄(O₂CPh)₉(mdea)₅] (b). Color definition: Fe – bright green, Ln–yellow spheres, N – blue, O – red and C – grey balls. H-atoms are omitted.

Hexanuclear pivalate $[Fe_4Dy_2O_2(piv)_6(teda)_2(NO_3)_2] \cdot xMeCN \cdot yCH_2Cl_2$ (Ln = Dy, Gd) complexes with $\{Fe^{III}_4Ln_2(\mu_4-O)_2\}^{14+}$ core were obtained from the reaction of FeCl_3·4H_2O, Ln(NO_3)_3·H_2O, pivalic acid, N,N,N,N-tetrakis(2-hydroxyethyl)ethylenediamine (tedaH_4) and phenol in a mixture of acetonitrile and dichloromethane [232] (Figure 1.11 a). The tedaH³⁻ ligand is triply coordinated and chelating to iron center via its two nitrogen and three μ -alkoxo oxygen atoms, and bridges two iron and one dysprosium metals. The $\{Fe_4Dy_2(\mu_4-O)_2\}$ core is characterized by both ferro- and antiferromagnetic interactions. Ac magnetic susceptibility studies of $\{Fe_4Dy_2\}$ showed the temperature dependence of ac susceptibility below 6 K. The estimated energy barrier of U_{eff} = 30.85 K with a relaxation time τ = 3.7×10⁻⁸ s.

Reaction of trinuclear iron(III) pivalate and $Ln(NO_3)_3 \cdot xH_2O$ with N-butyldiethanolamine (bdeaH₂) in the presence of NaOAc $\cdot 3H_2O$ gave a family of heterometallic clusters of general formula [bdeaH₃][Fe₅Ln₈(OH)₁₂(piv)₁₂(bdea)₄(NO₃)₄(OAc)₄] $\cdot x$ (solvent) (Ln = Pr, Nd, Gd) [233]. The complexes consist of a tridecanuclear [Fe₅Ln₈] anionic cluster and a cationic [bdeaH₃]⁺ species for charge balance. Clusters {Fe₅Pr₈} and {Fe₅Nd₈} have revealed predominant
antiferromagnetic interactions, whereas $\{Fe_5Gd_8\}$ complex has revealed both anti- and ferromagnetic interactions between spin carriers.

An undecanuclear pivalate cluster $[Fe_7Dy_4O_4(OH)_3(piv)_7(tea)_2(Htea)_3(NO_3)_2(H_2O)_2]$ (NO₃)·3MeCN has been obtained from trinuclear iron(III) pivalate, Dy(III) nitrate and triethanolamine (teaH₃) [234]. In the structure the central Fe₇ ions linked by two oxo⁻ ligands in a two "butterfly" {Fe₄O₂} motifs, sharing a common Fe center. Two oxo ligands further coordinate to Dy^{III} ions forming {Fe₇Dy₄} core. Magnetic properties of cluster showed both ferri- and antiferromagnetic exchange interactions between metal centers.

Employing an alcohol-containing 2-(hydroxymethyl)pyridine (hmpH) ligand in the reaction with trinuclear iron(III) benzoate resulted in a $[Fe_4Dy_2O_2(hmp)_8(O_2CPh)_6]$ complex (Figure 1.11 b) [235], which comprises $[Fe_4Dy_2(\mu_3-O)_2]$ metallic core of chair conformation and possesses SMM properties. The arrangement of four iron(III) atoms in a central rectangular suggests S = 0 ground state for the {Fe₄} unit that is antiferromagnetically coupled. Fe…Ln interactions are too weak and the presence of an out-of-phase ac signal indicates that this compound exhibits slow relaxation of the magnetization and therefore behaves as an SMM.



Fig. 1.11. Structure of [Fe₄Dy₂O₂(piv)₆(teda)₂(NO₃)₂] (a) and [Fe₄Dy₂O₂(hmp)₈(O₂CPh)₆]
(b). Color definition: Fe –green, Ln–yellow spheres, N – blue, O – red and C – grey balls. H-atoms are omitted.

Reaction of thdH₃ ligand with Ln(NO₃)₃·H₂O and [Fe₃O(piv)₆(H₂O)₃]piv·2(piv) affords the complex [Fe₄Ln₂(thdH₂)₂(thdH)₂(thd)₂(MeOH)₂(piv)₂(NO₃)₂][Ln(NO₃)₄(thdH₃)(MeOH)] NO₃·H₂O (thdH₃ = trihydroxy Schiff-base ligand, Ln = Nd, Gd, Tb, Dy, and Ho) [236]. The hexanuclear clusters are built up from {Fe₄Ln₂}²⁺ cation and mononuclear {Ln}⁻ anion. The metal atoms in the core adopt an "S" topology and coordinated by the μ -pivalato ligands and μ - phenoxide and μ -alkoxide groups of the Schiff-based ligand. Ln^{III} ions are located at the terminal positions and Fe^{III} ions occupy central position of the core. Magnetic studies revealed the presence of both strong antiferromagnetic and weak ferromagnetic interactions among the Fe^{III} ions. Cluster {Fe₄Dy₃} showed a frequency-dependent out-of-phase signal, suggesting that complex indeed behaves as a SMM at low temperatures.

There are examples of heterometallic SMM complexes based on monocarboxylate ligands. For instance, SMM [Fe₃TbO₂(tca)₈(H₂O)(thf)₃] derived from the reaction of iron-barium [Fe₂BaO(tca)₆(thf)₆] (tcaH = trichloroacetic acid) with Tb(NO₃)₃·6H₂O [237]. Compound comprises tetranuclear "butterfly" type metallic core with two triangles sharing the Tb...Fe edge. Compound exhibits strong intramolecular antiferromagnetic exchange between Fe ions. Performed ac measurements showed a weak out-of-phase signal, only the tail of a maximum lying at a temperature below 1.8 K.

The first Fe-Sm compound with SMM properties was reported by Sanudo E. et al. [238]. The hexadecanuclear [Fe₁₂Sm₄O₁₀(OH)₄(O₂CPh)₂₄] cluster was obtained from the solvothermal reaction of trinuclear iron(III) benzoate with Sm(NO₃)₃·9H₂O. The structure consists of two [Fe₄O₂(OH)₂] cuban sub-units, where four Fe^{III} ions bridged by two μ_3 -OH⁻ and two μ -O²⁻ ligands. These two cuban sub-units sandwich four Fe^{III} centers via four μ_3 -O²⁻ bridges. Four Sm^{III} ions are linked with two [Fe₄O₂(OH)₂] cuban sub-units through six μ_4 -O²⁻ bridges giving {Fe₁₂Sm₄} core (Figure 1.12 a). Dc susceptibility data indicated antiferromagnetic coupling between Sm^{III} and Fe^{III} ions. Ac susceptibility of cluster displayed hysteresis loop, observed at 0.5 K. The high nuclearity complex has an energy barrier of $U_{eff} = 16$ K with relaxation time of $\tau = 2 \times 10^{-8}$ s.

Polizou al. reported hexanuclear SMM compound, et a $[Fe_2Dy_4O_2(OH)_{2.36}(OMe)_{1.64}(cyan)_{10}(MeOH)_5(H_2O)] \cdot 3(MeOH) \cdot 0.36(H_2O)$ (cyanH = HO₂CCH₂CN) [239]. The $\{Fe_2Dy_4\}$ complex was derived from the reaction of trinuclear $[Fe_3O(cyan)_6(H_2O)_3](NO_3)\cdot 5(H_2O), Dy(NO_3)_3\cdot xH_2O$ in the presence of (\pm) -3-diisopropylamino-1,2-propanediol, that does not involve in the complex. The structure consists of four Dy^{III} and two Fe^{III} ions linked via two μ_4 -O²⁻ and μ_3 -OH⁻ ligands and that can be described as squashed octahedral with the iron ions at the axial positions (Figure 1.12 b). Eight cyanoacetate groups coordinate to the metallic core in syn, syn- η^1 : η^1 : μ_2 -bridging mode and two groups in η^1 : μ bridging mode. Magnetic studies displayed that antifferomagnetic coupling in squashed octahedral topology core is dominant. The anisotropy barrier was estimated at 34 K (τ_0 = 2.0×10^{-11} s).



[Fe₂Dy₄O₂(OH)_{2.36}(OMe)_{1.64}(cyan)₁₀(MeOH)₅(H₂O)] (b). Color definition: Fe – green, Ln – yellow spheres, N – blue, O – red and C – grey balls. H-atoms are omitted.

Han et al. have recently reported two octanuclear SMM clusters $[Fe_6Ln_2(\mu_3-O)_2(btpH_4)_2(Piv)_{12}]\cdot 0.5(dmf)\cdot (EtOH)\cdot 2.5(H_2O)$ (Ln = Dy and Tb). Complexes were formed from the solvothermal reaction of trinuclear $[Fe_3O(piv)_6(H_2O)_3](piv)$, $Ln(NO_3)_3\cdot xH_2O$, bis-tris propane (btpH₆) and Li(OH)·H₂O in a mixture of EtOH and dmf solvents [240]. The isostructural clusters comprise six Fe^{III} and two Dy^{III} or Tb^{III} ions that are oxo-, hydroxo-linked by two btpH₄^{2–} ligands and twelve pivalates. Magnetic measurements indicated that complexes exhibit ferrimagnetic behaviour. Ac measurements suggest that these compounds exhibit slow magnetic relaxation.

Cyclic Fe-Ln coordination systems are aesthetically attractive and often show interesting physical properties because of their "closed finite chain" nature and may be considered as 0D polymers. Thus, recently have been reported cyclic mixed-metal pivalate [241], acetate [242] and benzoate [243] complexes with triethanolamine ligand. Cyclic complexes have been derived from trinuclear iron(III) carboxylate precursors and lanthanide(III) nitrate.

Two isostructural hexanuclear pivalate ferric-lanthanide $[Fe_4Ln_2(piv)_6(teaH)_4(N_3)_4]$ (Ln = Er and Lu) complexes have been prepared by the reaction of trinuclear Fe^{III} pivalate, Fe(NO₃)₃·6H₂O, Ln(NO₃)₃·6H₂O and NaN₃ with triethanolamine in MeCN/EtOH [241]. Their cores comprise two subunits {Fe₂Ln} forming ring-type structure. Magnetic studies revealed that {Fe₄Er₂} is ferromagnetically coupled, whereas {Fe₄Lu₂} has both anti- and ferromagnetic interactions.

A series of heterometallic $[Fe_{16}Ln_4(tea)_8(teaH)_{12}(O_2CMe)_8](NO_3)_4 \cdot 16H_2O \cdot xMeCN$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho) acetate complexes have been structurally and magnetically investigated [242]. The structure comprises two {Fe₆Ln₂} subunits that are interconnected through four central iron(III) centers, resulting in {Fe₁₆Ln₄} ring. All metal centers in complex are chelated by three and two deprotonated triethanolamine ligands. None of these antiferromagnetically-coupled compounds showed out-of phase signals, except complex with dysprosium that showed negligible out-of phase signals.

A number of iron-ytterbium cyclic benzoate clusters with triethanolamine (teaH₃), 1-[N,N-bis-(2-hydroxyethyl)amino]-2-propanol (Me-teaH₃) ligands $[Fe_5Yb_3(OH)(teaH)_7(O_2CPh)_8]$ (CF₃SO₃)·10(MeCN), $[Fe_4Yb_2(OH)(OMe)_2(Me-teaH)_4(O_2CPh)_7]\cdot3(MeCN)$, $[Fe_3Yb_2(OH)(Me-teaH)_4(O_2CPh)_6]\cdotMeCN$, $[Fe_4Yb_2(Me-tea)_4(Me-teaH)_2(OTs)_2]\cdotMeCN\cdot3(MeOH)$, and $[Fe_{10}Yb_{10}(Me-tea)_{10}(Me-teaH)_{10}(NO_3)_{10}]\cdot21(MeCN)$ possessing intriguing and different topology structures have been published [243]. However, magnetic studies have not been reported for these complexes.

A family of rare examples of odd-numbered cyclic mixed metal benzoate coordination clusters with o-vanillinoxime (vanox) ligand has been reported [244]. The planar cyclic coordination cluster cores are built up from three [Fe₂Ln] subunits, forming nonanuclear wheel [Fe₆Ln₃(OMe)₉(vanox)₆(O₂CPh)₆] (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Gd). The magnetic studies of {Fe₆Ln₃}, including{Fe₆Y₃} indicated the presence of antiferromagnetic interactions between the Gd^{III...}Fe^{III} and weaker antiferromagnetic ones between Fe^{III...}Fe^{III}. The ac measurements revealed out-of-phase maxima in a range from 2.3 to 3.5 K for {Fe₆Dy₃} with the calculated energy barrier of $U_{eff} = 12.4$ K and $\tau_0 = 8.0 \cdot 10^{-5}$ s.

1.4. Conclusions to the Chapter 1

Analysis of the literature on homo- and heterometallic Fe^{III}/Fe^{III}-Ln^{III} carboxylate-based coordination clusters and polymers highlight the latest achievements and identify current problems in this area.

In view of the fact that the polynuclear iron compounds possessing high-spin ground state are of high interest, the scientific task is to find the optimal conditions for obtaining of new multinuclear homo- and heterometal clusters with the desired nuclearity, topology and properties.

Despite the complexity of incorporating transition metals and lanthanides in one molecule, a number of synthetic approaches have been successfully used to obtain the targeted product.

To date, only several Fe-containing cluster-based coordination polymers have been synthesized and there are difficulties related to obtaining such polymers in the crystalline state, in order to get a structure information.

Crystal engineering strategies that take into account the physico-chemical and coordination capabilities of the binding ligands help design new compounds with pre-determined properties, involving in the reaction the pre-designed metal-organic clusters as a starting building block or simple metal salts, multipodal chelate-bridging organic ligands, and employing various synthesis methods and conditions.

In view of the foregoing, the *proposed scientific problem* consists in establishing the optimal and effective synthetic conditions for the preparation of $Fe^{III}/Fe^{III}-4f$ carboxylate clusters, that might show slow magnetic relaxation and cluster-based coordination polymers, having pores and cavities, by the combination of polynuclear Fe^{III} carboxylate precursor with N_{γ}/O - donor organic ligands.

In order to achieve the purpose of this research, the following scientific objectives were set:

- The selection of a starting material, namely polynuclear carboxylate clusters that will be used as a building units for the construction of coordination clusters and polymers.
- The choice of O-based and N-based organic ligands that are capable to bind to metal ions in various ways.
- Incorporation of Ln and Fe ions in one system to obtain the required magnetic properties.
- The optimization and implementation of syntheses to obtain homo- and heterometallic Fe^{III}/Fe^{III}-4f clusters and coordination polymers.
- Characterisation of obtained compounds using different physico-chemical methods of investigations.
- Identification of some useful and desirable properties of the synthesized compounds.

2. EXPERIMENTAL METHODS OF SYNTHESIS AND INVESTIGATIONS

2.1. Materials, general methods of investigation and synthetic strategies

All reagents were purchased from commercial supplies and used without further purification. All synthetic procedures have been performed under aerobic conditions using commercial grade solvents.

New compounds were characterized by a range of methods according to their nature: elemental analyses and infrared spectroscopy, single-crystal X-ray crystallography and TGA, and powder diffraction for the polymeric samples; their magnetic properties were also studied.

IR-spectra (4000–400 cm⁻¹) for **1-32**, **34-42** compounds were performed on Fourier transform, on a Nicolet Avatar-360 FT-IR spectrometer with KBr pellets.

TGA/DTA measurements were carried out with a Mettler Toledo TGA/SDTA 851 in dry N_2 (60 mL min⁻¹) at a heating rate of 5 K min⁻¹ in a different temperature range. Thus, TGA for 1, 4, 5, 7, 9, 18 and 19 clusters were carried out from 25°C to 600°C; in the range between 25°C and 800°C for 2, 3, 6, 8, 10, 11, 13, 14, 20-24, 35-41 compounds; from 25°C to 1000°C for 15, 25-32 complexes.

Elemental analyses for C, H and N were carried out on an Elementar Vario El analyzer for all compouds.

Single-Crystal X-Ray Crystallographic Study. X-ray crystallography is the only method of unambiguously characterizing the polynuclear structures. Different techniques were used for crystal growth: saturation and diffusion methods. Diffraction datasets for all compounds were collected on different diffractometers equipped with graphite-monochromatized Mo-K α radiation. Diffraction datasets for **1**, **2**, **6**, **8**, **9**, **11** - **16**, **20** - **41** were collected on a Bruker APEX II diffractometer equipped with graphite-monochromatized Mo-K α radiation. X-ray data collection were performed with a Nonius Kappa CCD diffractometer using Mo- $K\alpha$ radiation at 150 K (for **4** and **7**), at 190 K (for **5** and **18**) and at 253(2) K (for **3**). Diffraction datasets for **10**, **17** and **19** compounds were collected on an X-Calibur E and SuperNova CCD area-detector diffractometers equipped with graphite and mirror monochromated Mo K α radiation. The structures were solved by direct methods and refined by full-matrix least squares on the weighted F^2 values for all reflections using the SHELX suite of programs [71]. Badly disordered solvent molecules and/or counteranions in **8**, **12-16**, **23**, **34** were removed by the SQUEEZE routine. The number of water molecules and other solvents were confirmed by elemental analyses and

thermogravimetric analyses. The crystallographic data and parameters of compounds 1-35, 37-41 are summarized in Tables 2.1. – 2.7. Crystal data for 36: a = 17.051(1), b = 26.711(3), c = 35.257(1) Å, $\alpha = \beta = \gamma = 90^{\circ}$. Figures were prepared using DIAMOND [245] and Mercury [72] programs and cif files available in CSD for cited compounds 1, 4, 5, 7, 8-11, 13-16, 18, 19, 25-32.

Magnetic measurement. Magnetic Susceptibility/Specific Heat Measurements. Studies of the magnetism of clusters and coordination polymers based on them by variable temperature susceptibility measurements, as well as complementing high-field specific heat capacity measurements have been done. Magnetic susceptibility studies are essential for characterizing the number of unpaired electrons and the exchange interactions between the paramagnetic metal ions in a polynuclear metal cluster. Crystal structures must be known for this before measurements. Variable-temperature data collected in dc fields are required, followed by least-squares fitting to the appropriate theoretical equations. The ac capability allows measurement of magnetization dynamics for identification of slow magnetization relaxation (single-molecule magnetism behavior). The established theoretical models describing the magnetic properties will also require additional data sets from specific heat capacity measurements, which reflect the spin degeneracies of the populated multiplet states – an important additional set of experimental data that can directly be compared with e.g. simulation results.

Magnetic susceptibility data of 4, 5, 7, 8-11, 18, 19, 13-16 and 25-32 were collected using a Quantum Design MPMS-5XL SQUID magnetometer. Technical equipment. A Bandelin Sonorex RK-100H ultrasonic bath operating at 35 kHz with a maximum power output of 160 W was used for ultrasonic irradiation in the syntheses of 3, 6, 9-11, 15, 21-40. Solvothermal syntheses for 8, 13, 14 and 19 were performed in a Teflon-lined stainless steel, placed in Memmert oven UNE 200.

Synthetic strategies toward Fe^{III} and Fe^{III} -Ln/Y^{III} clusters and polymers. This dissertation describes the design and synthesis of 42 novel Fe^{III} and Fe^{III}/Ln^{III} coordination compounds.

One of the challenges of this research is to obtain single crystals suitable for detailed crystallographyc analysis. The most successful synthetic procedures to polynuclear iron clusters relies on the reaction of trinuclear $[Fe_3O(O_2CR)_6(H_2O)_3](X)$ (where $R = CMe_3$ or $CHMe_2$; X = counteranions) species. The core of the trinuclear iron(III) complex serves as a building block for higher-nuclearity compounds. The preparation of all these compounds involves various types of polytopic organic ligands such as nitrogen-containing aromatic and aminopolyalcohol ligands.

In the preparation of bi- and polynuclear coordination compounds have been used several synthetic methods such as one-pot reactions, diffusion reaction, reflux, ultrasonic treatment, microwave heating and hydro(solvo)thermal reaction. Ultrasonic synthesis is becoming more popular and successfully used in synthesizing clusters and polymers. When very high intensity sound waves ultrasound travel through a liquid, a phenomenon known as cavitation occurs. The travelling sound wave causes highpressure areas (compression) of the liquid, which is followed by low pressure and sudden expansion (rarefaction) and the formation of tiny bubbles, which expand to an unsustainable size and then collapse. The expansion and collapse of the bubbles create very localised hot spots, which reach instantaneous pressures of more than 100 MPa (1000 atm) and temperatures of up to 5000°C. The consequent collisions and fast cooling can cause chemical reactions and decomposition to occur. The use of solvothermal techniques has become very popular among scientists as a method for the preparation of single crystals of solid states compounds, especially polymers. In most cases, the polymers are insoluble and cannot be recrystallized in a case, if polymer was not obtained in a crystalline form from the mother solution. Some additional methods were also used: method of slow evaporation of the mother solution, recrystallization (at room temperature and at freeze) and method of liquid-liquid diffusion.

| 9 | $C_{52}H_{92}Fe_6N_2O_{44}$ | 1784.37 | 100(2) | Monoclinic | $P2_{1/n}$ | 12.4170(9) | 21.1702(15) | 14.9790(11) | 06 | 102.2440(10) | 90 | 3848.0(5) | 2 | 1.540 | 1.199 | 1852 | 41364 | 6822 | 1.053 | 0.0604, 0.1629 | 0.0754, 0.1772 |
|---|--------------------------------|-------------------------|-----------------|----------------|-------------|--------------|-----------------------|--------------|------------|----------------|-----------------|-------------|---|------------------------|----------------------------|--------|--------------------------|----------------------------|-------|----------------------------|--------------------|
| S | $C_{54}H_{87}Fe_4N_7O_{18}$ | 1345.71 | 170(2) | Triclinic | <i>P</i> -1 | 13.8170(15) | 22.544(2) | 25.581(2) | 65.674(11) | 83.638(12) | 74.618(12) | 7000.7(11) | 7 | 1.277 | 0.877 | 2832 | 79563 | 17404 | 0.985 | 0.0695, 0.1547 | 0.1750, 0.1899 |
| 4 | $C_{48}H_{78}Fe_4N_4O_{18}$ | 1222.54 | 150(2) | Monoclinic | $P2_{1/n}$ | 11.3471(2) | 23.9570(3) | 22.5758(3) | 06 | 96.641(1) | 90 | 6095.88(15) | 4 | 1.332 | 0.999 | 2568 | 76842 | 12407 | 1.036 | 0.0444,0.1044 | 0.0584, 0.1152 |
| 3 | $C_{48}H_{67}Fe_4N_7O_{19}$ | 1269.46 | 100(2) | Monoclinic | C2/c | 40.1958(10) | 16.8981(2) | 23.6711(5) | 06 | 119.959(3) | 06 | 13929.9(6) | 8 | 1.211 | 0.879 | 5280 | 77509 | 16007 | 0.971 | 0.0623, 0.1793 | 0.1239, 0.2092 |
| 2 | $C_{44}H_{42}Fe_2N_{14}O_{13}$ | 1086.61 | 100(2) | Monoclinic | $P2_{1/n}$ | 12.643(7) | 10.561(6) | 17.346(10) | 06 | 92.551(13) | 90 | 2314.(2) | 2 | 1.560 | 0.710 | 1120 | 25205 | 4283 | 1.013 | 0.0440, 0.0919 | 0.0762, 0.1057 |
| 1 | $C_{28}H_{58}Fe_3N_3O_{21}$ | 940.32 | 100(2) | Triclinic | <i>P</i> -1 | 11.9901(7) | 14.0481(8) | 14.8372(8) | 76.891(10) | 70.477(10) | 71.267(10) | 2210.6(2) | 2 | 1.413 | 1.047 | 986 | 23915 | 7789 | 1.076 | 0.0398, 0.1089 | 0.0430, 0.1109 |
| | Empirical formula | $Mr/g \text{ mol}^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $p(\mathbf{\dot{A}})$ | <i>c</i> (Å) | a (grad) | β (grad) | γ (grad) | $V(x_3)$ | Z | $ ho~({ m Mg~m^{-3}})$ | $\mu \ (\mathrm{mm}^{-1})$ | F(000) | Reflections collected | Independent reflections | GOOF | RI, wR2 [$I>2\sigma(I)$] | RI, wR2 (all data) |

Table 2.1. Crystal data and details of structural determinations for 1-6

| 12 | $C_{80}H_{162}Fe_{12}N_6O_{42}$ | 2550.35 | 100(2) | Triclinic | <i>P</i> -1 | 14.179(8) | 14.717(8) | 15.549(8) | 84.989(9) | 63.426(9) | 71.725(9) | 2750(3) | 1 | 1.540 | 1.614 | 1332 | 29756 | | 9872 | | 1.002 | 0.0566, 0.1219 | 0.0987, 0.1405 |
|----|---|-----------------|-----------------|----------------|--------------|--------------|-----------------|-------------|-----------------|----------------|-----------------|-------------------|---|-----------------------------|----------------------------|--------|-------------|-----------|-------------|-------------|-------|----------------------------|--------------------|
| 11 | C42H84Fe8N12O24 | 1588.01 | 100(2) | Triclinic | <i>P</i> -1 | 13.563(4) | 14.588(4) | 18.696(5) | 97.807(5) | 101.650(5) | 114.870(4) | 3222.8(19) | 2 | 1.636 | 1.829 | 1640 | 24639 | | 7607 | | 1.000 | 0.1457, 0.1060 | 0.0779, 0.1219 |
| 10 | C48H93Fe8N13O27 | 1731.08 | 293(2) | Cubic | Pa-3 | 24.088(1) | 24.088(1) | 24.088(1) | 06 | 06 | 06 | 13976.62(10) | 8 | 1.645 | 1.698 | 7168 | 34700 | | 4344 | | 1.003 | 0.0457, 0.1060 | 0.0779, 0.1219 |
| 6 | C ₆₂ H ₁₂₁ Fe ₈ N ₅ O ₃₅ | 1943.43 | 173(2) | Monoclinic | $P 2_{1/n}$ | 15.843(2) | 20.180(3) | 26.004(3) | 06 | 91.680(2) | 06 | 8310.5(18) | 4 | 1.553 | 1.441 | 4064 | 63708 | | 14174 | | 1.053 | 0.0617, 0.1457 | 0.1116, 0.1784 |
| × | $C_{31}H_{68.50}Cl_6Fe_6$ N _{2.50} O _{17.50} | 1304.18 | 100(2) | Tetragonal | I-42d | 29.277(2) | 29.277(2) | 11.4187(12) | 06 | 06 | 06 | 9787.3(1) | 8 | 1.770 | 2.127 | 5360 | 50636 | | 4125 | | 1.065 | 0.0536, 0.1432 | 0.0715, 0.1588 |
| 7 | $C_{71}H_{115}Fe_{7}N_8O_{29}$ | 1935.66 | 150(2) | Monoclinic | $P2_1/n$ | 24.3303(4) | 17.3655(2) | 26.0350(4) | 06 | 106.553(2) | 06 | 10544.1(3) | 7 | 1.219 | 1.002 | 4009 | 26900 | | 21598 | | 0.956 | 0.0493, 0.1349 | 0.0895, 0.1466 |
| | Empirical formula | $Mr/g mol^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $b(\text{\AA})$ | c (Å) | α (grad) | β (grad) | γ (grad) | $V(\text{\AA}^3)$ | Ζ | $\rho ({ m Mg}{ m m}^{-3})$ | $\mu \ (\mathrm{mm}^{-1})$ | F(000) | Reflections | collected | Independent | reflections | GOOF | R1, wR2 [$I>2\sigma(I)$] | R1, wR2 (all data) |

Table 2.2. Crystal data and details of structural determinations for **7-12**

| 18 | $C_{46}H_{84}Fe_4N_4O_{18}$ | | 1204.57 | 170(2) | Monoclinic | $P2_{1/n}$ | 14.939(3) | 26.386(5) | 15.755(3) | 06 | 95.29(3) | 06 | 6184(2) | 4 | 1.294 | 0.984 | 2544 | 41702 | 10883 | | 0.956 | 0.0648, 0.1299 | 011000111 |
|----|--|----------------------|-------------------------|-----------------|----------------|-------------|--------------|----------------------------|--------------|-----------|----------------|-----------------|-----------------|---|-----------------------------|-------------------|--------|-------------|-------------|-------------|-------|--------------------------|-----------|
| 17 | $C_{47.50}H_{76}Fe_3N_2$ | $O_{16.50}$ | 1106.65 | 130(2) | Monoclinic | $P2_{1/n}$ | 12.0170(3) | 31.4880(7) | 19.0820(7) | 00.00 | 100.465(3) | 90.00 | 7100.4(4) | 4 | 1.035 | 5.278 | 2340 | 40942 | 13335 | | 0.996 | 0.0922, 0.2684 | |
| 16 | $C_{108}H_{218}Fe_{22}N_8O_{78}$ | | 4105.59 | 100(2) | Triclinic | <i>P</i> -1 | 15.139(3) | 15.192(3) | 22.806(5) | 76.867(4) | 74.721(4) | 62.049(3) | 4436.5(17) | 1 | 1.537 | 1.822 | 2118 | 34150 | 15040 | | 1.082 | 0.1020, 0.2354 | |
| 15 | C ₁₃₈ H ₂₈₅ Fe ₂₂ N ₁₁ | O_{78} | 4575.45 | 100(2) | Triclinic | <i>P</i> -1 | 15.211(2) | 19.157(3) | 20.098(3) | 97.015(4) | 100.774(4) | 108.767(4) | 5341.8(14) | 1 | 1.422 | 1.522 | 2386 | 38985 | 15804 | | 0.962 | 0.0744, 0.1538 | |
| 14 | C46H88Cl26Fe12N8 | O_{22} | 2695.12 | 100(2) | Monoclinic | C2/c | 32.910(8) | 10.291(3) | 27.489(7) | 06 | 101.702(5) | 06 | 9116.3(1) | 4 | 1.964 | 2.675 | 2386 | 46063 | 7711 | | 1.036 | 0.0815, 0.1829 | |
| 13 | $C_{44.50}H_{100.50}Fe_{12}$ | $N_{23.50}O_{30.50}$ | 2123.18 | 100(2) | Tetragonal | P4 | 27.599(6) | 27.599(6) | 11.270(3) | 06 | 06 | 06 | 8585(4) | 4 | 1.643 | 2.046 | 5392 | 94021 | 15134 | | 1.043 | 0.0895, 0.2239 | |
| | Empirical formula | | $Mr/g \text{ mol}^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $p(\mathbf{\mathring{A}})$ | <i>c</i> (Å) | a (grad) | β (grad) | γ (grad) | $V(\text{Å}^3)$ | Ζ | $\rho ({ m Mg}{ m m}^{-3})$ | $\mu \ (mm^{-1})$ | F(000) | Reflections | Independent | reflections | GOOF | $RI, wR2 [I>2\sigma(I)]$ | |

Table 2.3. Crystal data and details of structural determinations for 13-18

| 24 | $C_{115}H_{238}Fe_6N_{16}O_{39}$ | ${ m Y}_4$ | 3159.94 | 100(2) | Triclinic | <i>P</i> -1 | 16.227(5) | 18.474(6) | 28.510(9) | 107.056(5) | 91.859(5) | 109.972(5) | 7595(4) | 2 | 1.382 | 2.138 | 3328 | 78040 | | 24999 | | 1.034 | 0.1224, 0.2954 | 0.1855, 0.3333 |
|----|---|----------------------------------|-----------------|-----------------|----------------|-------------|-------------|---------------|--------------|-------------|----------------|-----------------|------------------|---|----------------------------|----------------------------|--------|-------------|-----------|-------------|-------------|-------|-------------------|--------------------|
| 23 | C ₁₁₈ H ₂₅₄ Fe ₆ Ho ₄ | $N_{16}O_{44}$ | 3596.18 | 100(2) | Triclinic | <i>P</i> -1 | 16.185(5) | 18.425(6) | 28.457(8) | 106.997(9) | 91.990(8) | 109.960(8) | 7542(4) | 2 | 1.584 | 2.710 | 3700 | 60601 | | 24625 | | 1.014 | 0.1235, 0.2795 | 0.1235, 0.2795 |
| 22 | $C_{114.50}H_{236}Fe_{6}Gd_{4}$ | $N_{16}O_{38.50}$ | 3417.28 | 100(2) | Triclinic | <i>P</i> -1 | 16.2377(12) | 18.5449(14) | 27.363(2) | 73.3260(10) | 89.287(2) | 68.8810(10) | 7325.0(9) | 2 | 1.549 | 2.435 | 3510 | 80052 | | 25794 | | 1.023 | 0.0483, 0.0932 | 0.0740, 0.1052 |
| 21 | $C_{115.50}H_{241}Dy_4Fe_6$ | $\mathrm{N}_{16}\mathrm{O}_{40}$ | 3479.33 | 100(2) | Triclinic | <i>P</i> -1 | 16.2194(19) | 18.445(2) | 28.537(3) | 106.928(2) | 92.016(2) | 109.823(2) | 7597.8(15) | 2 | 1.521 | 2.570 | 3572 | 82043 | | 26687 | | 1.110 | 0.0851, 0.1975 | 0.1047, 0.2087 |
| 20 | $C_{91}H_{187}Dy_{3}Fe_{6}N_{6}$ | O ₃₇ | 2780.05 | 100(2) | Triclinic | <i>P</i> -1 | 18.424(3) | 19.448(3) | 20.301(3) | 102.016(2) | 108.799(2) | 110.864(2) | 5990.2(14) | 2 | 1.541 | 2.625 | 2850 | 65236 | | 21094 | | 1.015 | 0.0587, 0.1345 | 0.1121, 0.1637 |
| 19 | C47.75H84.5Cl1.5Fe3 | N_3O_{22} | 2498.78 | 293(2) | Hexahonal | P6/mcc | 38.8452(8) | 38.8452(8) | 24.8241(7) | 06 | 06 | 120 | 32439.8(13) | 8 | 1.023 | 0.663 | 10552 | 69846 | | 4390 | | 1.006 | 0.0667, 0.1942 | 0.1390, 0.2464 |
| | Empirical formula | | $Mr/g mol^{-1}$ | Temperatura (K) | Crystal system | Space group | a (Å) | $b({ m \AA})$ | <i>c</i> (Å) | a (grad) | β (grad) | γ (grad) | $V({\rm \AA}^3)$ | Ζ | $ ho ({ m Mg}{ m m}^{-3})$ | $\mu \ (\mathrm{mm}^{-1})$ | F(000) | Reflections | collected | Independent | reflections | GOOF | R1, wR2 [I>2o(I)] | R1, wR2 (all data) |

Table 2.4. Crystal data and details of structural determinations for 19-24

| | 00 | $C_{201}H_{432}Eu_6Fe_{18}$ | $\mathrm{N}_{44}\mathrm{O}_{109}$ | 7126.94 | 100(2) | Triclinic | <i>P</i> -1 | 15.4184(6) | 23.1345(9) | 24.3653(1) | 78.522(1) | 82.093(1) | 76.833(1) | 8254.5(6) | 1 | 1.434 | 1.965 | 3664 | 89202 | | 28967 | | 1.008 | 0.0598, 0.1543 | 0.0945, 0.1839 |
|--------|------------|-------------------------------|-----------------------------------|-----------------|-----------------|----------------|-------------|--------------|-----------------|--------------|-----------|----------------|-----------------|------------|---|--------------------------|-------------------|--------|-------------|-----------|-------------|-------------|-------|----------------------------|--------------------|
| ç | 67 | $C_{212}H_{503}Fe_{18}N_{45}$ | $O_{134}Sm_6$ | 7734.96 | 100(2) | Trigonal | R-3 | 37.438(6) | 37.438(6) | 25.744(4) | 60 | 06 | 120 | 31249(11) | 3 | 1.233 | 1.509 | 12006 | 110848 | | 12210 | | 1.096 | 0.0533, 0.1430 | 0.1016, 0.1966 |
| | Q 7 | $C_{204}H_{443}Fe_{18}N_{44}$ | $O_{111.50}Tb_6$ | 7255.82 | 100(2) | Triclinic | <i>P</i> -1 | 15.7331(6) | 22.8661(8) | 24.5683(9) | 78.169(1) | 81.104(1) | 78.161(1) | 8408.1(5) | 1 | 1.433 | 2.073 | 3725 | 93463 | | 29596 | | 1.028 | 0.0581, 0.1493 | 0.0953, 0.1741 |
| Ę | 17 | $C_{194}H_{390}Fe_{18}Gd_{6}$ | $N_{43}O_{106}$ | 6970.27 | 100(2) | Triclinic | <i>P</i> -1 | 15.4512(18) | 23.102(3) | 24.516(3) | 78.394(3) | 81.559(4) | 77.193(4) | 8311.0(16) | 1 | 1.393 | 2.014 | 3555 | 77638 | | 23844 | | 1.023 | 0.0824, 0.2224 | 0.1767, 0.2752 |
| č | 07 | $C_{194}H_{409}Dy_{6}Fe_{18}$ | $N_{43}O_{104}$ | 6988.92 | 100(2) | Triclinic | <i>P</i> -1 | 15.3106(15) | 23.090(2) | 24.293(2) | 78.069(3) | 81.833(3) | 76.573(3) | 8132.8(14) | 1 | 1.427 | 2.212 | 3570 | 87050 | | 26779 | | 1.036 | 0.0783, 0.2076 | 0.1309, 0.2443 |
| L C | C7 | $C_{198}H_{474}Dy_6Fe_{18}$ | $N_{42}O_{132}$ | 7536.46 | 100(2) | Trigonal | R-3 | 37.390(6) | 37.390(6) | 25.583(4) | 90 | 06 | 120 | 30974(11) | 3 | 1.212 | 1.752 | 11628 | 107548 | | 12120 | | 1.100 | 0.0623, 0.1638 | 0.0948, 0.1853 |
| | | Empirical formula | | $Mr/g mol^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $b(\text{\AA})$ | <i>c</i> (Å) | a (grad) | β (grad) | γ (grad) | $V(Å^3)$ | Ζ | ho (Mg m ⁻³) | $\mu \ (mm^{-1})$ | F(000) | Reflections | collected | Independent | reflections | GOOF | R1, wR2 [$I>2\sigma(I)$] | R1, wR2 (all data) |

Table 2.5. Crystal data and details of structural determinations for 25-30

| | 37 | $C_{58}H_{120}Fe_4N_{10}O_{24}$ | Tb2 | 1882.87 | 100(2) | Monoclinic | $P2_{1/C}$ | 16.894(2) | 26.447(4) | 35.396(5) | 06 | 90.406(4) | 06 | 15814(4) | 8 | 1.582 | 2.554 | 7712 | <i>41139</i> | | 24452 | | 1.059 | 0.0971, 0.2268 | 0.1365, 0.2575 |
|---|----|---|-------------------------------------|-----------------|-----------------|----------------|-------------|--------------|---------------|-------------|-----------|----------------|-----------------|-------------------|---|------------------------|----------------------------|--------|--------------|-----------|-------------|-------------|-------|------------------------------|--------------------|
| | 35 | $\overset{\text{C}_{58}\text{H}_{120}\text{D}\text{y}_2\text{Fe}_{4}\text{N}_{10}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{\text{O}}{\overset{O}}{\overset{\text{O}}{\overset{O}}{\overset{O}}{\overset{O}{O$ | O ₂₄ | 1890.03 | 119(2) | Orthorhombic | Pbca | 17.12269(17) | 26.58764(20) | 35.1939(4) | 06 | 06 | 06 | 16022.1(3) | 8 | 1.567 | 2.620 | 7728 | 287005 | | 14102 | | 1.304 | 0.0554, 0.1034 | 0.0731, 0.1154 |
| ũ | 34 | C222.50H485Fe18N45 | Nd ₆ O _{114.50} | 7494.27 | 120(2) | Trigonal | <i>R</i> -3 | 33.3314(13) | 33.3314(13) | 30.2055(11) | 06 | 120 | 06 | 29062(2) | 3 | 1.285 | 1.285 | 11637 | 60292 | | 11430 | | 1.086 | 0.0738, 0.1953 | 0.1162, 0.2147 |
| | 33 | C ₂₁₂ H ₄₅₈ Dy ₆ Fe ₁₈ | N44 U 113 | 7412.50 | 100(2) | Triclinic | <i>P</i> -1 | 16.1487(9) | 21.1955(12) | 27.4800(18) | 98.613(2) | 93.2650(10) | 109.8890(10) | 8686.0(9) | 1 | 1.417 | 2.078 | 3806 | 48193 | | 29598 | | 1.015 | 0.0844, 0.1915 | 0.0844, 0.1915 |
| | 32 | C ₂₀₇ H ₄₅₇ Fe ₁₈ N ₄₅ O | $_{116}Y_{6}$ | 6971.91 | 100(2) | Triclinic | <i>P</i> -1 | 15.7078(12) | 22.8333(17) | 24.5202(18) | 78.380(2) | 81.161(2) | 78.225(2) | 8374.6(11) | 1 | 1.382 | 1.862 | 3644 | 92964 | | 29647 | | 1.008 | 0.0613, 0.1386 | 0.1283, 0.1489 |
| | 31 | C199H431Fe18H06 | $N_{44}O_{110.5}$ | 7203.73 | 100(2) | Triclinic | <i>P</i> -1 | 15.699(4) | 22.827(6) | 24.502(7) | 78.730(5) | 81.150(5) | 78.123(5) | 8367(4) | 1 | 1.430 | 2.233 | 3687 | 90535 | | 29441 | | 1.088 | 0.0819, 0.2022 | 0.1165, 0.2289 |
| | | Empirical formula | | $Mr/g mol^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $p({ m \AA})$ | c (Å) | a (grad) | β (grad) | γ (grad) | $V(\text{\AA}^3)$ | Ζ | $ ho~({ m Mg~m^{-3}})$ | $\mu \ (\mathrm{mm}^{-1})$ | F(000) | Reflections | collected | Independent | reflections | GOOF | R1, wR2 [$I > 2\sigma(I)$] | R1, wR2 (all data) |

Table 2.6. Crystal data and details of structural determinations for **31-35, 37**

| | 42 | $\frac{C_{85}H_{171.75}Dy_{4}Fe_{7}N_{6.75}}{O_{40.75}}$ | 2981.48 | 173(2) | Monoclinic | P21/c | 17.0512(5) | 18.7764(3) | 36.6927(11) | 06 | 92.347(3) | 06 | 11737.7(5) | 4 | 1.687 | 3.427 | 6004 | 169135 | | 20659 | | 1.009 | 0.0931, 0.2734 | 0.1193, 2909 |
|---|----|---|-------------------------|-----------------|----------------|-------------|--------------|-----------------|--------------|----------|----------------|-----------------|--------------|---|----------------------------|----------------------------|-------------|-------------|-----------|-------------|-------------|-------|--|-----------------------------------|
| | 41 | $\begin{array}{c} C_{58}H_{120}Dy_{2}Fe_{3}MnN_{10}\\ O_{24} \end{array}$ | 1889.12 | 100(2) | Orthorhombic | Pbca | 16.98138(12) | 26.54965(16) | 35.4422(3) | 06 | 06 | 06 | 15979.11(19) | 8 | 1.571 | 2.604 | 7720 | 566464 | | 14047 | | 1.032 | 0.0856, 0.2438 | 0.1099, 0.2541 |
| • | 40 | $C_{58}H_{120}Fe_4N_{10}O_{24}Tm_2$ | 1902.89 | 100(2) | Monoclinic | P21/c | 17.001(3) | 26.390(5) | 35.349(7) | 06 | 90.038(4) | 06 | 15860(5) | 8 | 1.594 | 3.000 | <i>1176</i> | 85916 | | 27884 | | 1.042 | 0.0756, 0.1495 | 0.1089, 0.1677 |
| | 39 | $C_{58}H_{120}Er_2Fe_4N_{10}O_{24}$ | 1899.55 | 100(2) | Monoclinic | $P2_{1/C}$ | 16.948(3) | 26.411(5) | 35.469(6) | 06 | 90.451(3) | 06 | 15876(5) | 8 | 1.589 | 2.876 | 7760 | 161663 | | 27933 | | 1.006 | 0.0816, 0.1911 | 0.1108, 0.2070 |
| | 38 | $C_{57}H_{116}Fe_4N_{10}O_{23}Y_2$ | 1742.85 | 100(2) | Monoclinic | $P2_{1/C}$ | 17.086(10) | 26.444(14) | 35.63(2) | 06 | 90.253(15) | 06 | 16096(16) | 8 | 1.438 | 2.201 | 7296 | 119514 | | 25030 | | 1.009 | 0.0819, 0.1745 | 0.1693, 0.2239 |
| | | Empirical formula | $Mr/g \text{ mol}^{-1}$ | Temperatura (K) | Crystal system | Space group | <i>a</i> (Å) | $b(\text{\AA})$ | <i>c</i> (Å) | a (grad) | β (grad) | γ (grad) | $V(x_3)$ | Ζ | $ ho ({ m Mg}{ m m}^{-3})$ | $\mu \ (\mathrm{mm}^{-1})$ | F(000) | Reflections | collected | Independent | reflections | GOOF | <i>R1</i> , <i>wR2</i> [<i>I</i> >2σ(<i>I</i>)] | <i>R1</i> , <i>wR2</i> (all data) |

Table 2.7. Crystal data and details of structural determinations for **38-42**

2.2. Synthesis of coordination homometallic Fe^{III} clusters

Precursors A [246], B [247] and C [248] were synthetized as described in literature.

[Fe₃O(piv)₆(H₂O)₃]·piv·2pivH (Precursor A)

The solution of $Fe(NO_3)_3 \cdot 9H_2O$ (10 g.) in 20 mL of pivalic acid was heating approx. 30 min till the evaporation of NO₂. The hot solution was slowly cooled down to room temperature and 120 mL EtOH were added afterwards. Obtained brown crystals were filtered and dried in the air. Yield: 70%. Elemental analysis for C₆₀H₁₁₀O₂₈Fe₆: C, 46.91; H, 8.18%. Found: C, 47.01; H, 7.78%. IR data (KBr pellet, cm⁻¹): 3438 brd, 2964 m, 2930 sh, 1699 sh, 1593 vs, 1486 vs, 1427 vs, 1231vs, 1207 sh, 788 w, 607 m.

[Fe₆O₂(OH)₂(piv)₁₂] (Precursor B)

The solution of $[Fe_3O(piv)_6(H_2O)_3]$ ·Piv·2PivH (5g.) in 15 ml of tetradecane was stirred at temperature range 210 - 220°C for 15 min. The hot solution was filtered and slowly cooled down to room temperature. Obtained yellow-brown crystals were filtered and dried in the air. Yield: 40%. Elemental analysis for C₆₀H₁₁₀O₂₈Fe₆: C, 44.60; H, 6.86%. Found: C, 44,81; H, 7,01%. IR data (KBr pellet, cm⁻¹): 3434 brd, 2963 m, 2929 sh, 2873 sh, 1696 m, 1585 vs, 1550 sh, 1484 vs, 1425 vs, 1379 sh, 1361 s, 1229 s, 1205 sh, 1168 w, 1031 w, 878 w, 871 w, 606 m, 444 m.

[Fe₁₄O₁₀(OH)₄(piv)₁₈] (Precursor C)

Precursor (A) (0.32 g, 0.2 mmol), 5 mL CH₂Cl₂ and 5 mL MeCN were placed in a sealed PTFE-lined steel autoclave and heated for 4 hours to 120°C and then allowed to slowly cool to room temperature over 48 hours. Black crystals were filtered off, washed with MeCN and dried in air. Yield: 49% (based on Fe). Elemental analysis for C₉₀H₁₆₆Fe₁₄O₅₀: C, 38.19; H, 5.91%. Found: C, 38.40; H, 5.97%. IR (KBr, cm⁻¹): 3633w, 3610w, 3440 br.w, 2962m, 2930m, 2872sh, 1590sh, 1547s, 1485s, 1459s, 1429vs, 1379s, 1362m, 1232s, 1031w, 892w, 787w, 736w, 599s, 551m, 509sh, 485sh, 452m, 438m.

$[Fe_{3}O(is)_{6}(H_{2}O)_{3}](NO_{3})\cdot 2(H_{2}O)\cdot 2(MeCN)(1)$

A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (20g.) in isobutyric acid 40 mL was heating till ca. half of solution was evaporated. After solution was cooled down to 40°C was added 70 mL EtOH. Resulting solution was left on the air for slow evaporation. One week later brown crystals were filtered off, washed with ethanol and dried on the air. Yield: ~ 30%. These brown crystals (3g) were dissolved in 100 mL MeCN and filtered through the filter paper. Obtained dark- brown

solution was placed into a fridge at -29 °C. After three days obtained brown crystals were filtered and washed by cooled MeCN, and dried on the air. Yield: ~ 90%. Elemental analysis for **1** without acetonitrile molecules, $C_{24}H_{52}NO_{21}Fe_3$: C, 33.56; H, 6.11; N, 1.63 %. Found: C, 33.79; H, 5.87; N, 1.56%. IR data (KBr pellet, cm⁻¹): 3423 m, 2969 m, 2929 sh, 2873 sh, 1588 vs, 1529 sh, 1474 s, 1428 s, 1382 m 1304 m, 1170 vw, 1099 w, 930 w, 767 vw, 606 m.

$[Fe_2O(is)_2(tpt)_2(H_2O)_2](NO_3)_2(2)$

To the solution of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot (H_2O)_2 \cdot (MeCN)_2$ (2) (0.082 g, 0.087 mmol) in 10 mL CH₃CN was added tpt (0.044 g, 0.14 mmol). The resulting solution was refluxing during 30 min and then filtered. The dark solution was left to evaporate slowly at room temperature. Red-brown crystals were obtained after 21 days, washed by MeCN and dried on the air. Yield: 0.008 g (6.79% based on Fe). Elemental analysis for C₄₄H₄₂N₁₄O₁₃Fe₂: C, 48.63; H, 3.89; N, 18.04%. Found: C, 48.54; H, 3.92; N, 18.25%. IR data (KBr pellet, cm⁻¹): 3416 brd, 3108 sh, 2969 sh, 1577 sh, 1559 vs, 1543 vs, 1490 m, 1439 w, 1395 sh, 1379 vs, 1328 m, 1303 sh, 1258 vw, 1012 m, 991 w, 852 m, 768 s, 677 m, 634 m, 613 sh.

$[Fe_4O_2(is)_7(dpa)_2](NO_3)(3)$

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.2 g, 0.233 mmol) and dpa (0.08 g, 0.46 mmol) in 10 mL THF was refluxing under ultrasonic treatment for 90 min (100 refluction) and then filtered. The filtrate was kept in a closed vial at room temperature. Next day black crystals suitable for X-ray analysis were filtered off, washed with hexane and dried in air. Yield: 0.13 g (58.58% based on Fe). Elemental analysis for C₄₈H₆₇N₇O₁₉Fe₄: C, 45.41; H, 5.31; N, 7.72%. Found: C, 45.99; H, 5.56; N, 7.24%. IR data (KBr pellet, cm⁻¹): 3313 w, 3203 w, 3081 sh, 2969 s, 2927 sh, 2872 sh, 1644 m, 1577 vs, 1545 sh, 1479 vs, 1422 vs, 1375 s, 1302 s, 1236 m, 1160 m, 1095 m, 1012 m, 928 w, 906 w, 838 w, 771 m, 686 m, 645 m, 570 w, 517 w.

[Fe₄O₂(piv)₈(bpm)] (4)

This compound was synthesized by using two different methods. Method A: A solution of 2,2'-bipyrimidine (0.032 g, 0.2 mmol) in MeCN (5 mL) was added to a solution of $[Fe_3O(piv)_6(H_2O)_3]piv \cdot 2pivH$ (0.230 g, 0.2 mmol) in 10 mL CH₂Cl₂. The resulting dark brown mixture was heated at reflux for 30 min. Black crystals of complex **4** suitable for X-ray analysis were separated by filtration after two weeks, washed with MeCN, and dried in air. Yield: 0.11 g, 60%. Elemental analysis for C₄₈H₇₈N₄O₁₈Fe₄: C, 47.16; H, 6.43; N, 4.58%. Found: C, 47.10; H, 6.68; N, 4.57%. IR data (KBr pellet, cm⁻¹): 3435 brd, 2962 vs, 2928 sh, 2870 sh, 1706 sh, 1566

vs, 1521 sh, 1484 vs, 1422 vs, 1377 s, 1362 s, 1227 s, 1169 w, 1112 w, 1098 w, 1030 w, 1012 w, 937 w, 906 w, 826 w, 814 w, 789 w, 764 w, 691 w, 657 m, 606 s, 518w, 439 m.

Method B: A solution of $[Fe_3O(piv)_6(H_2O)_3]piv 2pivH$ (0.230 g, 0.2 mmol) and 2,2_bipyrimidine (0.032 g, 0.2 mmol) in 4 mL MeCN was heated at 160 °C for 20 min in microwave reactor. Black crystals of 1a suitable for X-ray analysis were separated by filtration after 5 days, washed with MeCN, and dried in air. Yield: 0.142 g, 78%. Elemental analysis for $C_{48}H_{78}N_4O_{18}Fe_4$: C, 47.16; H, 6.43; N, 4.58%. Found: C, 47.13; H, 6.46; N, 4.55%. The identity of **4** was established by comparison of IR data as well as elemental and TG analysis.

$[Fe_4O_2(piv)_8(bpm)]$ ·3(MeCN) (5)

This compound was synthesized by using two different methods. **Method A:** A solution of 2,2'-bipyrimidine (0.032 g, 0.2 mmol) in 5 mL MeCN was added to a solution of $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.08 g, 0.05 mmol) in CH₂Cl₂ (5 mL). The resulting dark brown solution was allowed to stand at room temperature. Black crystals of complex **5** suitable for X-ray analysis were separated by filtration after one week, washed with MeCN, and dried in air. Yield 0.02 g, 22%. Elemental analysis for C₄₈H₇₈N₄O₁₈Fe₄ solvent free: C, 47.16; H, 6.43; N, 4.58%. Found: C, 47.51; H, 6.59; N, 4.40%. IR data (KBr pellet, cm⁻¹): 3435 brd, 2962 vs, 2928 sh, 2870 sh, 1706 sh, 1566 vs, 1521 sh, 1484 vs, 1422 vs, 1377 s, 1362 s, 1227 s, 1169 w, 1112 w, 1098 w, 1030 w, 1012 w, 937 w, 906 w, 826 w, 814 w, 789 w, 764 w, 691 w, 657 m, 606 s, 518 w, 439 m.

Method B: A solution of $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.161 g,0.1 mmol) and 2,2'-bipyrimidine (0.023 g, 0.15 mmol) in 4 mL MeCN was heated at 160 °C for 20 min in a microwave synthesizer. Black crystals of **5** were separated by filtration after 3 d, washed with MeCN, and dried in air; yield 0.102 g, 56%. Elemental analysis for C₄₈H₇₈N₄O₁₈Fe₄ solvent free: C, 47.16; H, 6.43; N, 4.58%. Found: C, 47.00; H, 6.59; N, 4.59%. The identity of **5** was established by comparison of IR data as well as elemental and TG analysis.

$[Fe_6O_2(OH)_2(is)_{10}(C_4H_7O_3)_2](HNO_3)_2 \cdot (HCOOH)_4 (6) \{Fe_3O\}$

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.082 g, 0.087 mmol) and striazine (0.028 g, 0. 34 mmol) in 6 mL MeCN and 6 mL CH₂Cl₂ was put under ultrasonic treatment for 1 hour and then filtered. The filtrate was kept in a closed vial at room temperature. After one week, red-brown crystals suitable for X-ray analysis were filtered off, washed with acetonitrile and dichloromethane and dried in vacuum. Yield: 0.007 g (19.33% based on Fe). Elemental analysis for C₅₂H₉₂N₂O₄₄Fe₆ (without solvent molecules): C, 34.92; H, 5.41; N, 1.56%. %. Found: C, 34.52; H, 5.63; N, 1.67%. IR data (KBr pellet ,cm⁻¹): 3362 brd, 2973 s, 2932 sh, 2873 sh, 1725 m, 1583 vs, 1473 s, 1425 vs, 1375 m, 1337 m, 1304 m, 1199 w, 1171 w, 1096 m, 992 w, 928 w, 839 w, 781 sh, 686 sh, 641 w, 572 w, 543 sh, 487 w.

[Fe₇O₄(OH)₂(piv)₁₁(bpm)₂(H₂O)] (7)

To a solution of $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.16 g, 0.1 mmol) in 10 mL dichloromethane and 5 mL acetonitrile, 2,2'-bipyrimidine (0.03 g, 0.18 mmol) was added. The resulting dark-brown solution was heated under reflux for 15 min. Black crystals suitable for X-ray analysis form after a week and were filtered off, washed with MeCN and dried in air. Yield: 0.06 g, 36%. Elemental analysis for C₇₁H₁₁₅N₈O₂₉Fe₇: C, 44.06; H, 5.99; N, 5.79. Found: C, 44.24; H, 5.80; N, 5.78%. IR data (KBr pellet, cm⁻¹): 3424 brd, 2960 m, 2927 m, 2870 sh, 1550 vs, 1484 s, 1422 vs, 1376 m, 1361 m, 1228 s, 1012 w, 866 w, 789 w, 764 w, 655 m, 604 m, 517 w, 488 m.

(mdeaH₃)₂[Fe₆O(thme)₄Cl₆]·0.5(MeCN)·0.5(H₂O) (8)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.066 g, 0.05 mmol), thmeH₃ (0.062 g, 0.51 mmol) and mdeaH₂ (0.079 g, 0.66 mmol) in 4 mL MeCN and 4 mL CH₂Cl₂ was stirring at room temperature for 30 min. Resulting solution was placed in a Teflon-lined stainless-steel and heated at 120 °C for 4 hours. Red-brown crystals suitable for X-ray analysis were filtered off, washed with acetonitrile and dried in air. Yield: 0.029 g (64.4% based on Fe). Elemental analysis for C₃₁H_{68.50}Cl₆N_{2.50}O_{17.50} Fe₆: C, 28.54; H, 5.29; N, 2.69 %. Found: C, 29.18; 29.38; H, 5.29; 5.22; N, 2.77; 2.71%. IR data (KBr pellet, cm⁻¹): 3414 brd, 2954 m, 2921 m, 2862 s, 1631 vw, 1463 w, 1398 vw, 1119 m, 1018 vs, 619 sh, 590 m, 521 vs, 474 w.

[Fe₈O₃(is)₉(tea)(teaH)₃]·(MeCN)·2(H₂O) (9)

To the solution of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.100 g, 0.1 mmol) in 5 mL MeCN was added teaH₃ (0.07 g, 0.469 mmol). The obtained solution was put under ultrasonic treatment for half of hour and then filtered. The filtrate was kept in a closed vial at room temperature. After three weeks, black crystals suitable for X-ray analysis were filtered off, washed with acetonitrile and dried in air. Yield: 0.06 g (69% based on Fe). Elemental analysis for C₆₂H₁₁₉N₅O₃₄Fe₈: C, 38.66; H, 6.23; N, 3.64. Found: C, 38.37; H, 5.79; N, 3.03%. IR data (KBr pellet, cm⁻¹): 3404 br.m, 2965 m, 2925 m, 2869 m, 1584 vs, 1472 s, 1429 s, 1391 m, 1375 m, 1348 m, 1305 m, 1262 sh, 1168 w, 1094 s, 1030 sh, 1004 sh, 926 m, 908 m, 840 w, 759 w, 738 w, 589 m, 517 m, 414 m.

[Fe₈O₃(is)₆(N₃)₃(tea)(teaH)₃](10)

Method A. The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.094 g, 0.1 mmol), NaN₃ (0.022 g, 0.33 mmol) and teaH₃ (0.055 g, 0.36 mmol) in 10 mL EtOH (MeOH or 1:1 EtOH/CH₂Cl₂ could also be used) was heated at reflux for 60 min and then filtered. The filtrate was kept in a closed vial at room temperature. The black hexagonal crystals suitable for X-ray analysis were filtered off the next day, washed with hexane and dried in air. Yield: 0.045 g (69% based on Fe) in EtOH; 74% in MeOH; 52% in EtOH/CH₂Cl₂.

Method B. The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.094 g, 0.1 mmol), NaN₃ (0.024 g, 0.36 mmol) and teaH₃ (0.053 g, 0.35 mmol) in 10 mL EtOH was put under ultrasonic irradiation for 32 min and then filtered. The filtrate was kept in a closed vial whose lid was pierced with several holes at room temperature. The black hexagonal crystals of **2** suitable for X-ray analysis were filtered off the next day, washed with hexane and dried in air. Yield: 0.045 g (69% based on Fe). Elemental analysis for for C₄₈H₉₃N₁₃O₂₇Fe₈: C, 33.30; H, 5.41; N, 10.52%. Found: C, 33.56; H, 5.47; N, 10.23%. IR (KBr pellet, cm⁻¹): 3416 br.m, 2969 m, 2925 m, 2865 m, 2068 vs, 1577 vs, 1471 s, 1429 s, 1391 m, 1375 sh, 1348 sh, 1311 m, 1098 s, 1071 m, 1038 sh, 1004 sh, 926 sh, 909 m, 875 w, 579 m, 515 m, 414 m.

[Fe₈O₃(is)₆(mdea)₃(N₃)₃(MeO)₃] (11)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.062 g, 0.065 mmol), NaN₃ (0.014 g, 0.21 mmol) and mdeaH₂ (0.1 g, 0.083 mmol) in 10 mL MeOH. The resulting solution was put under ultrasonic treatment for 1 hour and then filtered. The orange solution was filtered and left for slowly evaporation at room temperature. Red-brown crystals were obtained after one week. Yield: 0.015 g (24.19% based on Fe). Elemental analysis for C₄₂H₈₄N₁₂O₂₄Fe₈ (1588.01 g mol⁻¹): C, 31.76; H, 5.33; N, 10.58%. Found: C, 31.76; H, 5.29; N, 10.34%. IR data (KBr pellet, cm⁻¹): 3431 (br. m), 2967 m, 2921 m, 2870 m, 2811 sh, 2068 vs, 1578 vs, 1472 m, 1429 s, 1375 w, 1339 w, 1291 w, 1087 m, 1053 sh, 1001 w, 903 m, 877 w, 761 w, 628 sh, 584 m, 530 m.

$[Fe_{12}O_6(OH)_4(piv)_{10}(mdea)_4(mdeaH)_2]$ (12)

To the solution of precursor B $[Fe_{14}O_{10}(OH)_4(piv)_{18}]$ (0.1 g, mmol) in 10 mL Et₂O to the bottom of the vial was slowly added second layer - solution of mdeaH₂ (0.4 mg, mmol) in 2 mL MeCN. Closed vial with obtained two layered solutions was kept in the fridge. Red crystals suitable for X-ray analysis were obtained after nine months. Yield: 3.5 g (3.88 % based on Fe). Elemental analysis for C₆₂H₁₂₄N₆O₃₆Fe₁₂: C, 38.21; H, 6.33; N, 3.34%. Found: C, 37.76; H, 6.29; N, 3.24%. IR data (KBr pellet, cm⁻¹): 3423 (br. s), 2954 m, 2896 m, 2856 m, 1632 sh, 1581 vs, 1560 s, 1481 m, 1458 w, 1418 m, 1361 w, 1226 w, 1117 sh, 1068 m, 1036 m, 998 w, 898 w, 790 w, 666 w, 575 w, 465 w.

$[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4](NO_3)_{0.5}N_3 (MeO)_{0.5} \cdot 2.5(H_2O) (13)$

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.06g, 0.069 mmol), tedaH₄ (0.07 g, 0.29 mmol), NaN₃ (0.013g, 0.2 mmol) and mdeaH₂ (0.07g, 0.58 mmol) in 4 mL MeOH and 4 mL EtOH was stirring during 10 min. Resulting solution was placed in a Teflon-lined stainless-steel and heated at 120°C for 4 hours. Obtained solution was filtrated and kept under the room temperature. One week later red-brown crystals suitable for X-ray analysis were filtered off, washed with MeOH and dried in vaacum. Yield: 0.006 g (18.18% based on Fe). Elemental analysis for C_{44.50}H_{100.50}N_{23.50}O_{30.50}Fe₁₂: C, 25.17; H, 4.77; N, 15.5%. Found: C, 24.74; 25.26; H, 4.87; 4.96; N, 14.86;14.80%. IR data (KBr pellet, cm⁻¹): 3395 brd, 2861 s, 2068 vs, 1637 w, 1468 w, 1384 m, 1339 sh, 1268 w, 1096 s, 1057 s, 934 m, 911 sh, 740 w, 660 w, 613 sh, 497 m, 442 sh.

$[Fe_{12}O_6(teda)_4(Cl)_8] \cdot 6(CHCl_3)$ (14)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.066 g, 0.076 mmol), tedaH₄ (0.036 g, 0.152 mmol) and mdeaH₂ (0.029 g, 0.243 mmol) in 4mL chloroform and 4mL tetrahydrofuran was stirring during 5 min. Resulting solution was placed in a Teflon-lined stainless-steel and heated at 120°C for 4 hours. The obtained red-brown crystals suitable for X-ray analysis were filtered off, washed with CHCl₃ and dried in vacuum. Yield: 0.019 g (48.96% based on Fe). Elemental analysis for C₄₂H₈₂Cl₁₄N₈O₂₂Fe₁₂ (without four chloroform molecules): C, 22.75; H, 3.73; N, 5.05%. Found: C, 22.47; 22.36; H, 4.46; 4.64; N, 5.09; 5.08%. IR data (KBr pellet, cm–1): 3406 brd, 2872 s, 1631 m, 1469 m, 1418 vw, 1361 vw, 1316 vw, 1269 vw, 1089 vs, 1055 sh, 934 s, 909 m, 740 w, 634 s, 536 sh, 492 s.

[Fe₂₂O₁₆(OH)₂(is)₁₈(bdea)₆(EtO)₂(H₂O)₂]·2(EtOH)·5(MeCN)·6(H₂O) (15)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.084 g, 0.097 mmol), sca (0.02 g, 0.22 mmol) and bdeaH₂ (0.081 g, 0.5 mmol) in 10 mL EtOH was put under ultrasonic treatment for 1 hour and then filtered. The filtrate was kept in a closed vial at room temperature. Dark-brown crystals suitable for X-ray analysis were filtered off after one month, washed with hexane and dried in vacuum. Yield: 0.024 g (43.63% based on Fe). Elemental analysis for C₁₃₈H₂₈₅N₁₁O₇₈Fe₂₂: C, 36.2; H, 6.23; N, 3.37%. Found: C, 35.14; 35.14; H, 5.76; 5.75; N, 3.75; 3.72%. IR data (KBr pellet ,cm⁻¹): 3418 brd, 2963 s, 2927 sh, 2868 sh, 2086 vw, 1582 vs, 1543

vs, 1471 m, 1427 vs, 1364 w, 1303 w, 1169 vw, 1096 m, 1059 sh, 1024 sh, 905 w, 838 w, 759 w, 725 sh, 639 sh, 584 m, 520 w, 464 vw.

[Fe₂₂O₁₄(OH)₄(is)₁₈(mdea)₆(EtO)₂(H₂O)₂](NO₃)₂·EtOH·H₂O (16)

The solution of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.1 g, 0.1 mmol) and mdeaH₂ (0.032 g, 0.26 mmol) in 6 mL EtOH was stirring at room temperature for 2 hours and then filtered. The filtrate was kept in a closed vial at room temperature. Dark-brown crystals suitable for X-ray analysis were filtered off after two months, washed with hexane and dried in vacuum. Yield: 0.007 g (14.58% based on Fe). Elemental analysis for C₁₀₈H₂₁₈N₈O₇₈Fe₂₂: C, 31.60; H, 5.35; N, 2.73%. Found: C, 34.9; 34.69; H, 6.12; 6.61; N, 2.88; 3.74%. IR data (KBr pellet ,cm⁻¹): 3417 brd, 2966 s, 2924 sh, 2869 sh, 1582 vs, 1549 vs, 1471 m, 1426 vs, 1393 s, 1302 w, 1168 vw, 1094 m, 1055 sh, 1026 sh, 999 w, 902 w, 834 vw, 761 vw, 633 sh, 585 m, 533 m.

2.3. Synthesis of homometallic Fe^{III} carboxylate polymers

${[Fe_{3}O(piv)_{6}(CO_{2})(pyEt)] \cdot 0.5(pivH) \cdot 0.5(thf)}_{n}$ (17)

The mixture of Fe(NO₃)₃·9H₂O (0.54 g, 1.33 mmol) and pivalic acid (3.6 g, 35.24 mmol) was heating until evaporation NO. Then a solution of pyEt (0.12 g, 0.65 mmol) in 10 mL ethanol was added. The obtained row material was dissolved in 42 mL thf. Crystals suitable for X-ray analysis were separated by filtration in one week, washed with thf and dried in air. Yield, 0.182 g (38.29% based on Fe). Elemental analysis for $C_{52}H_{92}N_2O_{17}Fe_3$: C, 52.71; H, 7.82; N, 2.36%. Found: C, 53.32; H, 7.51; N, 2.34%. IR data (KBr pellet, cm⁻¹): 3430 w, 2961 m, 2928 sh, 2869 sh, 1589vs, 1484s, 1425 vs, 1378 m, 1362 m, 1228 m, 1072 w, 1023 w, 897w, 830 w, 787m, 604 m, 552 sh, 440 m.

${[Fe_4O_2(piv)_8(hmta)]_n(18)}$

A solution of hexamethylenetetramine (0.042 g, 0.3 mmol) in MeCN (5 mL) was added to a solution of $[Fe_3O(piv)_6(H_2O)_3]piv 2pivH$ (0.230 g, 0.2 mmol) in MeCN (10 mL). The resulting dark brown mixture was stirred for 2 h. Black crystals of complex **18** suitable for X-ray analysis were separated by filtration after three weeks, washed with hexane, and dried in air. Yield: 0.08 g (35% based on Fe). Elemental analysis for C₄₆H₈₄N₄O₁₈Fe₄: C, 45.87; H, 7.02; N, 4.65. Found: C, 46.05; H, 6.54; N, 4.54. IR data (KBr pellet, cm⁻¹): 2962 vs, 2930 sh, 2873 sh, 1574 sh, 1547 vs, 1512 m, 1485 vs, 1459 m, 1419 vs, 1375 m, 1362 m, 1250 m, 1228 s, 1056 w, 1024 m, 988 m, 905 w, 788 w, 768 w, 686 m, 603 m, 536 w, 435 m.

${[Fe_{3}O(piv)_{6}(4,4'-bpy)_{1.5}](OH) \cdot 0.75(CH_{2}Cl_{2}) \cdot n(H_{2}O)}_{n}(19)$

Compound $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.161 g, 0.10 mmol), s-triazine (0.032 g, 0.4 mmol), 4,4bpy (0.062 g, 0.4 mmol) and 8 mL CH₂Cl₂ were placed in a sealed PTFE-lined steel autoclave and heated to 120 °C for 4 h and then slowly cooled to room temperature over 48 hours. Darkgreen crystals of **19** suitable for a single-crystal X-ray diffraction analysis were filtered off, washed with CH₂Cl₂ and MeCN and dried in air. Yield: 0.082 g (38% based on Fe). Elemental analysis for C_{47.75}H_{84.5}Cl_{1.5}N₃O₂₂Fe₃: C, 43.60; H, 6.33; N, 3.49%. Found: C, 43.98; H, 6.82; N, 3.36%. IR data (KBr pellet, cm⁻¹): 3084 w, 2972 m, 2932 sh, 2872 sh, 1702 w, 1580 vs, 1483 s, 1458 sh, 1427 s, 1380 m, 1363 m, 1225 m, 1069 m, 1046 w, 1031 sh, 1013 w, 938 w, 897 w, 865 w, 815 m, 787 m, 730 w, 634 m, 605 s, 572 sh, 563 sh, 446 m.

2.4. Synthesis of heterometallic Fe^{III}-Ln^{III} carboxylate wheels

[Fe₆Dy₃(is)₉(bdea)₆(MeO)₆]·MeOH (20)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.12 g, 0.12 mmol), Dy(NO₃)₃·xH₂O (0.02g, 0.06 mmol), Sca (0.01 g, 0.11 mmol) and bdeaH₂ (0.02g, 0.2 mmol) in 12 mL MeOH was put under refluxing for 1 hour and then filtered. The filtrate was kept in a closed vial at room temperature. Two weeks later yellow crystals suitable for X-ray analysis were filtered off, washed with methanol and dried in vacuum. Yield: 0.029 g (10.28% based on Fe). Elemental analysis for C₉₀Dy₃Fe₆H₁₈₃N₆O₃₆: C, 39.33; H, 6.71; N, 3.05%. Found: C, 38.3; 38.07; H, 6.62; 6.91; N, 3.08; 3.01%. IR data (KBr pellet, cm⁻¹): 3438 brd, 2961 s, 2929 sh, 2873 sh, 1550 vs, 1471 s, 1423 vs, 1372 m, 1289 m, 1256 sh, 1166 w, 1096 s, 1049 s, 1013 sh, 981 sh, 902 m, 835 w, 748 w, 660 sh, 565 m, 467m.

A series of $[Fe_6M_4(is)_8(bdea)_{10}(N_3)_2] \cdot x(solvents)$ wheels (where $M^{III} = Dy (21)$, Gd (22), Ho (23), Y (24))

$[Fe_6Dy_4(is)_8(bdea)_{10}(N_3)_2] \cdot 3.5(MeOH) \cdot 0.5(H_2O)$ (21)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.082 g, 0.087 mmol), Dy(NO₃)₃ ·xH₂O (0.063 g, 0.18 mmol), NaN₃ (0.02 g, 0.3 mmol) and bdeaH₂ (0.273 g, 1.69 mmol) in 10 mL MeOH was put under ultrasonic treatment for 1 hour and then filtered. The yellow filtrate was kept in a closed vial at room temperature. After four days the yellow crystals suitable for X-ray analysis were filtered off, washed with methanol and dried in vacuum. Orange filtrate was left at room temperature. Yield: 0.018 g (18% based on Fe). Elemental analysis for C_{115.50}H₂₄₁Dy₄Fe₆N₁₆O₄₀: C, 39.87; H, 6.98; N, 6.44%. Found: C, 39.62; 39.64; H, 6.80; 6.82; N, 6.59; 6.57%. IR data (KBr pellet, cm⁻¹): 3423 brd, 2960 vs, 2929 sh, 2871 sh, 2076 vs, 1586 vs, 1543 s, 1474 s, 1426 s, 1371 m, 1286 m 1257 sh, 1167 w, 1088 vs, 1045 sh, 1007 sh, 910 m, 847 w, 759 w, 659 sh, 581 m, 475 m.

Next compounds have been synthesized in the same manner as **21** using corresponding lanthanide nitrates: $Gd(NO_3)_3 \cdot 6H_2O$, $Ho(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$.

$[Fe_6Gd_4(is)_8(bdea)_{10}(N_3)_2] \cdot 2.5(MeOH)$ (22)

(Yield: 0.03 g, 30% based on Fe). Elemental analysis for $C_{114.50}H_{236}Fe_6Gd_4N_{16}O_{38.50}$: C, 40,25; H, 6,96; N, 6,56%. Found: C, 39.79; 39.73; H, 6.99; 6.89; N, 6.58; 6.68%. IR data (KBr pellet, cm⁻¹): 3427 brd, 2958 s, 2931 sh, 2871 sh, 2075 m, 2036 sh, 1583 m, 1541 sh, 1470 sh, 1411 w, 1383 s, 1285 w, 1165 w, 1083 s, 1043 sh, 898 w, 835 vw, 582m.

$[Fe_{6}Ho_{4}(is)_{8}(bdea)_{10}(N_{3})_{2}] \cdot 2(MeOH)$ (23)

(Yield: 0.012 g, 11 % based on Fe). Elemental analysis for C₁₁₈H₂₅₄Fe₆Ho₄N₁₆O₄₄: C, 39.39; H, 7.12; N, 6.23%. Found: C, 39.37; 39.57; H, 6.31; 6.73; N, 6.59; 6.58%. IR data (KBr pellet, cm⁻¹): 3424 brd, 2960 s, 2927 sh, 2871 sh, 2076 vs, 1741 sh, 1587 vs, 1544 s, 1473 m, 1427 m, 1371 m, 1286 w, 1166 w, 1089 vs, 1045 sh, 1008 vw, 910 m, 848 vw, 759 vw, 660 sh, 581 m, 476m.

[Fe₆Y₄(is)₈(bdea)₁₀(N₃)₂]·3(MeOH) (24)

(Yield: 0.018 g, 20% based on Fe). Elemental analysis for C₁₁₅H₂₃₈Fe₆N₁₆O₃₉Y₄: C, 43,71; H, 7,59; N, 7,09%. Found: C, 43.31; 43.71; H, 7.25;7.59; N, 7.33;7.09%. IR data (KBr pellet, cm⁻¹): 3424 brd, 2960 s, 2927 sh, 2871 sh, 2076 vs, 1742 sh, 1587 vs, 1544 s, 1473 m, 1427 m, 1371 m, 1286 w, 1167 w, 1089 vs, 1045 sh, 1007 vw, 910 m, 848 vw, 759 vw, 660 sh, 582 m, 477m.

A series of $[Fe_{18}Ln_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot x$ (solvents) wheels (where $Ln^{III} = Dy$ (25), Dy (26), Gd (27), Tb (28), Sm (29), Eu (30), Ho (31), Y (32))

$[Fe^{III}_{18}Dy^{III}_{6}(is)_{12}(teaH)_{18}(tea)_{6}(N_{3})_{6}] \cdot (MeCN) \cdot 8(H_{2}O) (25)$

To the solution of $[Fe_3O(is)_6(H_2O)_3]NO_3 \cdot 2(MeCN) \cdot 2(H_2O)$ (0.082 g, 0.087 mmol) in EtOH (6 mL) was added a solution of $Dy(NO_3)_3 \cdot 6(H_2O)$ (0.031 g, 0.09 mmol), sodium azide (0.02 g, 0.3 mmol) and triethanolamine (0.26 g, 1.47 mmol) in MeOH (6 mL). The resulting solution was treated under ultrasonic irradiation for one hour and 15 minutes. Filtered mixture was left for slowly evaporation of the mother solution. This gave yellow crystals of the first polymorph **23**. Yield: 0.028 g (25.72% based on Fe). Elemental analysis for $C_{198}H_{474}N_{42}O_{132}Dy_6Fe_{18}$: C, 31.55; H 6.34; N 7.81; Dy, 12.93; Fe, 13.33. Found: C, 32.53, 32.47; H, 5.59, 5.90; N, 8.31, 8.28; Dy,

12.9; Fe, 14.5. IR data (KBr pellet, cm–1): 3423 brd, 2964 sh, 2864 s, 2064 vs, 2036 sh, 1639 vw, 1565 m, 1471 w, 1415 w, 1359 w, 1284 vw, 1162 sh, 1096 vs, 898 m, 750 vw, 560 vw, 469 vw.

[Fe^{III}₁₈Dy^{III}₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·(MeCN)·8(H₂O) (26)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.083 g, 0.087 mmol) Dy(NO₃)₃ ·xH₂O (0.064 g, 0.18 mmol), NaN₃ (0.025 g, 0.38 mmol) and teaH₃ (0.26 g, 1.74 mmol) in MeOH and MeCN (1:1, 12 mL) was put under ultrasonic treatment for 35 min and then filtered. The filtrate was kept in a closed vial at room temperature. After five days the yellow crystals suitable for X-ray analysis were filtered off, washed with methanol and dried in vacuum. Yield: 0.03 g (29.71% based on Fe) . Elemental analysis for C₁₉₂H₄₀₆N₄₂O₁₀₄Dy₆Fe₁₈: C, 33.19; H, 5.89; N, 8.47; Dy, 14.03; Fe, 14.47 %. Found: C, 32.01; H, 5.63; N, 8.08; Dy, 13.7; Fe, 14.3 %. IR data (KBr pellet, cm⁻¹): 3423 brd, 2964 sh, 2864 m, 2064 vs, 2036 sh, 1630 sh, 1567 m, 1471m, 1416 m, 1359m, 1284 w, 1163vw, 1996 vs, 898 m, 750 vw, 595 vw, 457 w.

Next compounds (27-32) have been synthesized in the same manner as 26 using corresponding lanthanide nitrates: $Dy(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot xH_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, $Ho(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$.

$[Fe^{III}_{18}Gd^{III}_{6}(is)_{12}(teaH)_{18}(tea)_{6}(N_{3})_{6}]\cdot(MeCN)\cdot10(H_{2}O)$ (27)

(Yield: 0.02 g, 19.8% based on Fe). Elemental analysis for $C_{194}H_{413}N_{43}O_{106}Gd_6Fe_{18}$: C, 33.32; H, 5.95; N, 8.61; Gd, 13.5; Fe, 14.4%. Found: C, 33.44, 33.46; H, 5.63, 6.27; N, 8.28, 8.33; Gd, 13.4; Fe, 12.5. IR data (KBr pellet, cm⁻¹): 3423 brd, 2962 str, 2920 sh, 2854 m, 2064 m, 2036 sh, 1570 m, 1473 str, 1471 w, 1415 w, 1359 w, 1281 w, 1164 w, 1075 m, 898 m, 748 sh, 560 vw.

[Fe^{III}₁₈Tb^{III}₆(Is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·2(MeCN)·8(MeOH)·7.5(H₂O) (28)

(Yield: 0.17 g, 16.22% based on Fe). Elemental analysis for C₂₀₄H₄₄₃N₄₄O_{111.5}Tb₆Fe₁₈: C, 33.77; H, 6.15; N, 8.49; Tb, 13.15; Fe, 13.9%. Found: C, 32.97, 33.08; H, 5.62, 6.00; N, 8.29, 8.17; Tb, 13.4; Fe, 14.3%. IR data (KBr pellet, cm⁻¹): 3423 brd, 2972 sh, 2964 s, 2063 vs, 2036 sh, 1569 m, 1472 m, 1415 m, 1358 m, 1284 w, 1163 sh, 1086 vs, 897 m, 591 w, 559 w, 460 w

$[Fe^{III}_{18}Sm^{III}_{6}(is)_{12}(teaH)_{18}(tea)_{6}(N_{3})_{6}] \cdot 6(MeOH) \cdot 21(H_{2}O) (29)$

(Yield: 0.017 g, 6.21% based on Fe). Elemental analysis for C₁₉₈H₄₅₆N₄₂O₁₂₃Sm₆Fe₁₈: C, 32.57; H, 6.29; N, 8.06%. Found: C 33.13, 33.22; H, 5.42, 5.87; N, 8.33, 8.31%. IR data (KBr pellet, cm⁻¹): 3426 brd, 2960 sh, 2920 sh, 2852 m, 2064 m, 2036 sh, 1629 w, 1565 m, 1469 w, 1414 m, 1359 w, 1283 vw, 1075 s, 898 m, 488 vw.

$[Fe^{III}_{18}Eu^{III}_{6}(is)_{12}(teaH)_{18}(tea)_{6}(N_{3})_{6}] \cdot (MeCN) \cdot 2(MeOH) \cdot 9(H_{2}O) (30)$

(Yield: 0.02 g, 19.75% based on Fe). Elemental analysis for C₁₉₆H₄₁₉N₄₃O₁₀₇Eu₆Fe₁₈: C, 33.59; H, 6.03; N, 8.59%. Found: C, 33.8, 33.7; H, 6.38, 6.36; N, 8.81, 8.67%. IR data (KBr pellet, cm⁻¹): 3340 brd, 2962 sh, 2920 sh, 2853 m, 2065 m, 2036 sh, 1631 w, 1568 m, 1470 w, 1415 w, 1359 w, 1284 vw, 1076 s, 898 m, 560 vw, 689 vw.

[Fe^{III}₁₈Ho^{III}₆(is)₁₂(teaH)₁₈(tea)₆ (N₃)₆]·(MeCN)·3(MeOH)·11(H₂O) (31)

(Yield: 0.017 g, 16.45% based on Fe). Elemental analysis for $C_{197}H_{427}N_{43}O_{110}Ho_6Fe_{18}$: C, 33.08; H, 6.02; N, 8.42%. Found: C, 31.91, 34.96; H, 5.82, 6.24; N, 7.47, 7.08%. IR data (KBr pellet, cm⁻¹): 3423 brd, 2964 sh, 2864 s, 2063 vs, 2036 sh, 1571 m, 1472 m, 1416 m, 1359 w, 1285 w, 1164 sh, 1076 vs, 898 m, 593 vw, 559 vw, 459 vw.

[Fe^{III}₁₈Y^{III}₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·2(MeCN)·2(MeOH)·14(H₂O) (32)

(Yield: 0.017 g, 17.4% based on Fe). Elemental analysis for $C_{1938}H_{432}N_{44}O_{112}Y_6Fe_{18}$: C, 35.18; H, 6.44; N, 9.12%. Found: C, 33.5, 33.68; H, 6.12, 6.11; N, 8.35, 8.40%. IR data (KBr pellet, cm⁻¹): 3324 brd, 2963 sh, 2928 sh, 2863 s, 2064 vs, 2036 sh, 1544 m, 1471 m, 1416 m, 1359 w, 1284 w, 1164 sh, 1076 vs, 898 m, 830 vw, 750 vw, 593 vw, 559 vw, 462 vw.

$[Fe^{III}_{18}Dy^{III}_{6}(piv)_{12}(teaH)_{18}(tea)_{6}(N_{3})_{6}] \cdot 4(MeOH) \cdot 2(MeCN) \cdot 12.5(H_{2}O) (33)$

To the solution of $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.051 g, 0.088 mmol), $Dy(NO_3)_3 \cdot 6(H_2O)$ (0.072 g, 0.2 mmol), sodium azide (0.016 g, 0.246 mmol) and triethanolamine (0.266 g, 1.78 mmol) in MeOH and MeCN (1:1, 12 mL) was put under ultrasonic treatment for 35 min and then filtered. Filtrate was left for slowly evaporation of the mother solution. Yield: 28 g (38.35% based on Fe).

[Fe₁₈Nd₆(piv)₁₂(teaH)₁₈(tea)₆(N₃)₆]·3(MeCN)·12.5(MeOH)·6(H₂O) (34)

To the solution of $[Fe_6O_2(OH)_2(piv)_{12}]$ (0.085 g, 0.05 mmol), Nd(NO₃)₃·6(H₂O) (0.068 g, 0.155 mmol), sodium azide (0.017 g, 0.26 mmol) and triethanolamine (0.258 g, 1.72 mmol) in MeOH and MeCN (1:1, 14 mL). The resulting solution was treated under ultrasonic irradiation for 35 minutes. Filtrate was left for slowly evaporation of the mother solution. This gave yellow crystals of **32**. Yield: 0.016 g (13.33% based on Fe). Elemental analysis for C₂₀₄H₄₁₄N₄₂O₉₆Nd₆Fe₁₈: C, 35.70; H 6.08; N 8.57. Found: C, 35.98, 35.87; H, 6.09, 6.18; N, 8.31, 8.28. IR data (KBr pellet, cm⁻¹): 3416 brd, 2956 s, 2863 vs, 2065 vs, 1636 sh, 1585 m, 1562 s, 1482 m, 1411 s, 1358 m, 1259 sh, 1224 m, 1160 sh, 1095 vs, 898 m, 790 w, 748 w, 602 m, 559 sh, 458 w.

2.5. Synthesis of heterometallic Fe^{III}-Ln^{III} carboxylate clusters

A series of $[Fe_4Ln_2(OH)_2(is)_6(bdea)_4(N_3)_2] \cdot 2(MeOH)$ (where $Ln^{III} = Dy$ (35), Gd (36), Tb (37), Er (38), Y (39), Tm (40)) clusters

[Fe₄Dy₂(OH)₂(is)₆(bdea)₄(N₃)₂]·2(MeOH) (35)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.082 g, 0.087 mmol), Dy(NO₃)₃ ·xH₂O (0.063 g, 0.18 mmol), NaN₃ (0.02 g, 0.3 mmol) and bdeaH₂ (0.273 g, 1.69 mmol) in 10 mL MeOH was put under ultrasonic treatment for 1 hour and then filtered. The yellow filtrate was kept in a closed vial at room temperature. After four days the yellow crystals of {Fe₆Dy₄} **21** were filtered off and orange filtrate was left at room temperature. After one week formed orange crystals of **35** suitable for X-ray analysis were filtered off, washed with methanol and dried in vacuum. Yield: 0.021 g (21% based on Fe). Elemental analysis for C₅₈H₁₂₀Dy₂Fe₄N₁₀O₂₄: C, 36.86; H, 6.40; N, 7.41%. Found: C, 36.45; 36.45; H, 6.24; 6.25; N, 7.40; 7.42%. IR data (KBr pellet, cm⁻¹) : 3441 brd, 2961 m, 2930 sh, 2870 sh, 2061 vs, 1605 m, 1564 s, 1470 m, 1411 m, 1360 w, 1331 w, 1280 m, 1168 sh, 1083 m, 1038 sh, 986 vw, 914 w, 825 w, 634 sh, 586 m, 546 w.

Next compounds (**36-38**) have been synthesized in the same manner as **35** using corresponding lanthanide nitrates: $Gd(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$.

$[Fe_4Gd_2(OH)_2(is)_6(bdea)_4(N_3)_2] \cdot 2(MeOH)$ (36)

(Yield: 0.02 g, 24%). Elemental analysis for $C_{57}H_{116}N_{10}O_{23}Gd_2Fe_4$: C, 37.06; H, 6.33; N, 7.58%. Found: 36.96; 37.00; H, 6.28; 6.27; N, 7.50; 7.55%. IR data (KBr pellet, cm⁻¹): 3377 brd, 2961 m, 2930 sh, 2871 sh, 2061 vs, 1603 m, 1558 s, 1470 m, 1409 m, 1360 w, 1331vw, 1280 w, 1168 sh, 1084 m, 1038 sh, 985 vw, 914 m, 824 w, 759 vw, 632 sh, 583 m, 544 w.

[Fe₄Tb₂(OH)₂(is)₆(bdea)₄(N₃)₂]·2(MeOH) (37)

(Yield: 0.041g, 31.29% based on Fe). Elemental analysis for $C_{57}H_{116}N_{10}O_{23}Tb_2Fe_4$: C, 37. 02; H, 6.32; N, 7.44%. Found: 36.15; H, 6.39; N, 7.49%. IR data (KBr pellet, cm⁻¹): 3440 brd, 2962 m, 2930 sh, 2870 sh, 2061 vs, 1603 m, 1564 s, 1470 m, 1410 m, 1360 w, 1331vw, 1279 w, 1168 sh, 1083 m, 913 m, 825 w, 758 vw, 632 sh, 585 m, 544 w.

[Fe₄Y₂(OH)₂(is)₆(bdea)₄(N₃)₂]·2(MeOH) (38)

(Yield: 0.047 g, 51% based on Fe). Elemental analysis for $C_{57}H_{116}Fe_4N_{10}O_{23}Y_2$: C, 39.97; H, 6.94; N, 8.03%. Found: 39.25; 39.25; H, 6.84; 6.85; N, 8.08; 8.10%. IR data (KBr pellet, cm⁻¹):

3439 brd, 2962 m, 2930 sh, 2870 sh, 2061 vs, 1600 m, 1567 s, 1470 m, 1413 m, 1360 w, 1280 w, 1168 sh, 1084 m, 985 vw, 930 w, 825 vw, 638 sh, 585 w, 547 w.

[Fe₄Er₂(OH)₂(is)₆(bdea)₄(N₃)₂]·2(MeOH) (39)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.083 g, 0.096 mmol), Er(NO₃)₃·5H₂O (0.068g, 0.153 mmol), NaN₃ (0.02 g, 0.3 mmol) and bdeaH₂ (0.273 g, 1.69 mmol) in 10 mL MeOH was put under ultrasonic treatment for 1 hour and then filtered. The yellow filtrate was kept in a closed vial at room temperature. After twelve days formed white precipitate was separated from the solution. Orange crystals suitable for X-ray analysis after ten days were filtered off, washed with methanol and dried in vacuum. Yield: 0.04 g (32% based on Fe). Elemental analysis for C₅₈H₁₂₀Er₂Fe₄N₁₀O₂₄: C, 36.67; H, 6.37; N, 7.37%. Found: C, 36.09; 36.09; H, 6.23;6.23; N, 7.4; 7.39%. IR data (KBr pellet, cm⁻¹): 3426 brd, 2961 m, 2930 sh, 2870 sh, 2061 vs, 1607 m, 1567 s, 1470 m, 1412 m, 1360 w, 1331 vw, 1280 w, 1168 sh, 1085 m, 985 vw, 913 w, 825 vw, 638 sh, 585 m, 546 w.

[Fe₄Tm₂(OH)₂(is)₆(bdea)₄(N₃)₂]·2(MeOH) (40)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.083 g, 0.086 mmol) Tm(NO₃)₃·5H₂O (0.065 g, 0.146 mmol), NaN₃ (0.018 g, 0.38 mmol) and bdeaH₂ (0.284 g, 1.76 mmol) in 10 mL MeOH was put under ultrasonic treatment for 1 hour and then filtered. The yellow filtrate was kept in a closed vial at room temperature. After two weeks formed white precipitate was separated from the solution. Next day orange crystals suitable for X-ray analysis were filtered off, washed with methanol and dried in vacuum. Yield: 0.041 g (32% based on Fe). Elemental analysis for C₅₈H₁₂₀Fe₄N₁₀O₂₄Tm₂: C, 36.58; H, 6.36; N, 7.36%. Found: C, 35.87; 35.87; H, 5.90; 6.17; N, 7.58;7.18%. IR data (KBr pellet, cm⁻¹): 3425 brd, 2962 m, 2930 sh, 2870 sh, 2061 vs, 1607 m, 1567 s, 1470 m, 1412 m, 1360 w, 1331 vw, 1280 w, 1168 sh, 1085 m, 985 vw, 913 m, 825 w, 760 vw, 633 sh, 586 m, 547 w.

$[Fe^{III}_{3}Mn^{III}Dy^{III}_{2}(OH)_{2}(is)_{6}(bdea)_{4}(N_{3})_{2}] \cdot (MeOH)$ (41)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.062 g, 0.072 mmol), Dy(NO₃)₃ ·xH₂O (0.1 g, 0.1 mmol), $[Mn(is)_2]$ (0.02 g, 0.08 mmol), NaN₃ (0.014 g, 0.215 mmol) and bdeaH₂ (0.01 g, 0.062 mmol) in 12 mL MeOH was put under refluxing for 1 hour and then filtered. The orange filtrate was kept in a closed vial at room temperature. Two weeks later black crystals suitable for X-ray analysis were filtered off, washed with methanol and dried in air. Yield: 0.036 g (26.86% based on Fe). Elemental analysis for C₅₇H₁₁₆N₁₀O₂₃Dy₂MnFe₃: C, 36.86; H, 6.29; N, 7.54; Dy, 17.5; Mn, 2.96; Fe, 9.02%. Found: C, 36.4; 36.32; H, 6.37; 6.07; N, 7.52; 7.46; Dy, 20; Mn, 3.7; Fe, 9.6%. IR data (KBr pellet, cm⁻¹): 3431 brd, 2961 m, 2930 sh, 2869 sh, 2059 vs, 1604 m, 1571 s, 1470 m, 1407 m, 1360 w, 1279 w, 1168 sh, 1086 m, 913 w, 825 vw, 759 sh, 585 m, 547 w.

[Fe₇Dy₄O₄(OH)₃(is)_{9.25}(bdea)₆(NO₃)_{0.75}(H₂O)] (42)

The mixture of $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (0.12 g, 0.12 mmol), Dy(NO₃)₃·xH₂O (0.02g, 0.06 mmol), Sca (0.01 g, 0.11 mmol) and bdeaH₂ (0.02g, 0.2 mmol) in 12 mL MeOH was put under refluxing for 1 hour and then filtered. The filtrate was kept in a closed vial at room temperature. Two weeks later were obtained yellow crystals. These crystals have been left in the mother solution for six months. During this time yellow crystals completely dissolve and start to grow red - brown crystals of **41** suitable for X-Ray analysis. Yield: 0.008 g (13.55 % based on Fe). Elemental analysis for C₈₉H₁₇₇N₆O₃₉Dy₄Fe₇: C, 35.67; H, 5.95; N, 2.8%. Found: C, 34.09, 34.13; H, 5.83, 5.83; N, 3.50, 3.48%. IR data (KBr pellet, cm⁻¹): 3429 brd, 2960 m, 2925 sh, 2861 sh, 1587 s, 1536 s, 1473 m, 1430 s, 1374 w, 1292 w, 1169 sh, 1093 m, 1033 w, 897 w, 848 vw, 759 sh, 603 m, 558 sh, 511 w.

2.6. Conclusions to the Chapter 2

- The rational design using crystal engineering strategies led to the formation of 42 new homo- and heterometallic Fe^{III} and Fe/4f coordination compounds employing different carboxylate and/or O-based and N-based ligands.
- The preparation of the compounds was carried out by using pre-synthesized precursors, different reaction conditions, various methods of synthesis, molar ratio of reactants and involving different multitopic organic ligands into a reaction.
- Structures, composition and thermal properties of homo- and heterometallic Fe^{III} and Fe/4f coordination compounds were determined using single-crystal X-ray analysis diffraction, infrared spectroscopy, elemental and thermogravimetrical analyses.
- Magnetic properties of the obtained compounds were determined by the method magnetochemistry, including dc (direct current) and ac (alternating current) measurements.

3. HOMOMETALLIC POLYNUCLEAR Fe^{III} CLUSTERS AND COORDINATION POLYMERS

The most promising approach in the creation of high-nuclearity coordination compounds is based on the assembling of molecular "building blocks", or the "bottom-up assembly". In such case, varying of the size, connectivity, charge and functionality of complex "building blocks" and/or ligands allows us to achieve the targeted properties of final product.

Polynuclear Fe/Fe-4f complexes may be obtained by assembling of suitable presynthesized metal-containing building blocks and different organic ligands. From this, μ_3 -oxo trinuclear Fe^{III} pivalates or isobutyrates, [Fe₃(μ_3 -O)(O₂CR)₆(H₂O)₃]⁺, are especially universal building blocks, which may be used to prepare a diverse range of polynuclear complexes. It needs to be mentioned that such trinuclear species display synthetic convenience, i.e. the presence of a vacant coordination site at the periphery of the complex to which another complex fragment can be attached. Moreover, their terminal and carboxylate ligands frequently are labile and can be partially substituted providing an opportunity to assemble the metallic clusters into extended networks.

In the dissertation a number of homometallic Fe^{III} compounds {Fe₂} (**2**), {Fe₄} (**3-5**) [249], {Fe₆} (**6**, **8** [250]), {Fe₇} (**7**) [251], {Fe₈} (**9-11**) [252], {Fe₁₂} (**13**, **14**) and {Fe₂₂} (**15**, **16**) compounds [250], and oxo-trinuclear {Fe₃O} (**17**, **19** [253]) and oxo-tetranuclear {Fe₄O₂} (**18**) [249] cluster-based coordination polymers were synthesized by the reaction of trinuclear, [Fe₃O(O₂CR)₆(H₂O)₃]⁺ (R = (CH₃)₃C (**1**) [252], (CH₃)₂CH (precursor **A**) or hexanuclear [Fe₆O₂(OH)₂(piv)₁₂] (precursor **B**) carboxylates with *N/O*-containing organic ligands: tpt, dpa, 4,4'-bpy, bpm, str, teaH₃, mdeaH₂, bdeaH₂, pyEt, tedaH₄, thmeH₃ and hmta (Figure 3.1) under various reaction conditions. Cluster {Fe₁₂} (**12**) was derived from the tetradecanuclear [Fe₁₄O₁₀(OH)₄(piv)₁₈] (precursor **C**) using liquid-liquid diffusion method with mdeaH₂ ligand.



Fig. 3.1. Structures of the selected organic ligands used in the preparation of coordination compounds.

hmta

3.1. Di-, tri-, tetra, hexa-, hepta-, octa-, dodeca-, docosanuclear Fe^{III} clusters with N,Odonor ligands

bpm

The structure and composition of the synthesized homometallic Fe^{III} coordination compounds were determined and characterized by a single-crystal X-ray diffraction analysis (1-19), infrared spectroscopy (1-19), thermogravimetric (1-11, 13-15, 18-19) and elemental analyses (1-19). Magnetic properties of 4, 5, 7-11, 13-16, 18-19 compounds were investigated.

Crystal engineering implies the use of organic ligands and chemical complexes in accordance with their coordination capacity. Thus, taking into the consideration that smaller clusters are good approximations for larger clusters, trinuclear isobutyrate cluster (1) was selected as a starting material for the construction of a number of polynuclear homo- and heterometallic clusters. The interaction of μ_3 -oxo trinuclear iron(III) carboxylate (1 or A) or hexanuclear pivalate (B) cluster with various *N*-containing chelating ligands resulted in di-, tetra-, hexa- and heptanuclear homometallic carboxylate-based clusters (Figure 3.2).

$$\{Fe_{3}O\} (1) \xrightarrow{tpt}{MeCN, reflux} [Fe_{2}O(is)_{2}(tpt)_{2}(H_{2}O)_{2}](NO_{3})_{2}(2)$$

$$\{Fe_{3}O\} (1) \xrightarrow{dpa}{thf, US} [Fe_{4}O_{2}(is)_{7}(dpa)_{2}](NO_{3})(3)$$

$$\underbrace{str}{MeCN/CH_{2}Cl_{2}, US} [Fe_{6}O_{2}(OH)_{2}(is)_{10}(C_{4}H_{7}O_{3})_{2}](HNO_{3})_{2} \cdot (HCOOH)_{4} (6)$$

$$\{Fe_{3}O\} (A) \xrightarrow{bpm}{MeCN/CH_{2}Cl_{2}, reflux} [Fe_{4}O_{2}(piv)_{8}(bpm)] (4)$$

$$\{Fe_{6}O_{2}\} (B) \xrightarrow{bpm}{MeCN, microwave} [Fe_{4}O_{2}(piv)_{8}(bpm)] \cdot 3(MeCN) (5)$$

$$\underbrace{bpm}{MeCN/CH_{2}Cl_{2}, reflux} [Fe_{7}O_{4}(OH)_{2}(piv)_{11}(bpm)_{2}(H_{2}O)] (7)$$

Fig. 3.2. Shematic representation of synthesis of homometallic 2-7 clusters.

The $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(H_2O) \cdot 2(MeCN)$ (1) cluster was obtained by the heating of Fe(NO₃)₃·9H₂O in excess of isobutyric acid (isH) followed by addition of ethanol solvent with further recrystallization in MeCN [252]. Compounds $[Fe_2O(is)_2(tpt)_2(H_2O)_2](NO_3)_2$ (2) and $[Fe_7O_4(OH)_2(piv)_{11}(bpm)_2(H_2O)]$ (7) were obtained as a result of the reaction of precursor (1) or precursor (**B**) with tpt or bpm ligand under reflux. The ultrasonic treatment of the precursor (1) with dpa (in thf) or str (CH₂Cl₂/MeCN) leads to the formation of clusters [Fe₄O₂(is)₇(dpa)₂]NO₃ (3) and $[Fe_6O_2(OH)_2(is)_{10}(C_4H_7O_3)_2](HNO_3)_2 \cdot (HCOOH)_4$ (6) (where $C_4H_8O_3 =$ 2hydroxyisobutyric acid), respectively. During the reaction, s-triazine ligand was modified into formic acid, because str is sensitive to hydrolysis in alcohol and other hydroxyl containing compounds [254] and isobutyric group under acid condition was converted in 2hydroxyisobutyric acid. The reaction of the precursor (A) with bpm in CH₂Cl₂/MeCN gave a complex 4 that was isolated in around 60% yield. Complex $[Fe_4O_2(piv)_8(bpm)]$ (4) has also been made by microwave irradiation and crystalline material appears after five days in higher yield (ca. 80%). Using a hexanuclear precursor (**B**) as a starting material and a similar preparative procedure (both in solution and under microwave heating) afforded the solvated [Fe₄O₂(piv)₈(bpm)]·3MeCN (5). Employment of the microwave-assisted reaction in the preparation of 5 clearly improves its yield (56%) in comparison with the solution method (22%).

The IR spectra of **1**, **2** and **6** contain the O–H stretching vibration at 3423, 3415 and 3362 cm⁻¹, caused by the presence of water molecules and hydroxyl groups, respectively. The IR spectra of **1** – **7** display strong peaks of carboxylate groups of isobutyrates/pivalates appear in the region of 1578 - 1533 cm⁻¹ (asymmetric stretching vibrations) and at 1479 - 1397 cm⁻¹

(symmetric stretching vibrations). The C–H asymmetric and symmetric stretching vibrations of carboxylates (1 - 7) are observed in the range of 2973 – 2869 cm⁻¹, whereas a doublet of asymmetric and symmetric bending vibrations for methyl (3 - 5 and 7) appears at 1422 – 1360 cm⁻¹ and 1474-1304 cm⁻¹ (1). In the case of complexes 2, 4, 5 and 7, the C=N stretching vibrations of aromatic ring of the tpt (2), bpm (4, 5, 7) ligands overlap with the asymmetric stretching bands of the carboxylates. The C=N stretching vibrations and N–H stretching vibrations of dpa (3) appear at 1644 cm⁻¹ and 3313 - 3304 cm⁻¹, respectively (Annexe 3, Figures A3.1 – A3.6).

The TGA curves of **1** and **2** showed the first step of a weight loss corresponds to release of two water molecules and NO_3^- group for cluster **1** (found: 11.20%; calcd: 11.42%) and two coordinated aqua ligands for compound **2** (found: 3.02%; calcd: 3.31%). Two molecules of acetonitriles in cluster **1** were evaporated during a filtration of crystals. Next step for **2** is accompanied by an exothermic peak at 249 °C that indicates the weight loss of two nitrate groups and two isobutyrate groups (found: 22.35%; calcd: 26.4%), while compound **1** loses three water molecules and one carboxylate ligand (found: 15.78%; calcd: 16.42%). The last consecutive steps of compound **1** are accompanied by two endothermic peaks at 225 °C and 273 °C that indicate the weight loss of five carboxylate groups (found: 49.86%; calcd: 50.7%), while compound **2** decomposes with the slow release of two tpt ligands (found: 53.9%; calcd: 57.4%) Thus, compounds completely decomposes with the formation of expected iron oxides (calcd: 26.9% for **1**, 21.3% for **2**) (Annexe 4, Figures A4.1, A4.2).

TGA curves of **3**, **4** and **5** showed a first weight loss in a temperature range 25-170 °C for compound **3**, 220-300 °C for **4**, 100-300 °C for **5** that corresponds to the removal of NO_3^- group and one isobutyrate ligand for compound **3** (found: 12.21%; calcd: 11.74%), a bpm molecule for **4** (found 12.4%, calcd. 12.9%), three solvate acetonitrile molecules and a bpm ligand for cluster **5** (20.2%, calcd. 20.95%). The following three weakly resolved steps above 550 °C (**3**) and 300 – 600 °C (**4**, **5**) indicate the weight loss of two dpa ligands and six isobutyrate groups (for **3**, found: 68.53%; calcd: 68.2%) and eight pivalic molecules with a total weight loss of 64.8% for **4** (calcd. 66.2%) and 56.8% for **5** (calcd. 60.1%) to the final product (found: 19.26% for **3**, 22.7% for **4** and 22.9% for **5**; calcd. 25.13% for **3**, 26.1% for **4** and 23.7% for **5**) (Annexe 4, Figures A4.3-A4.5).

The TGA curves of **6** and **7** show a sequence of all-endothermal mass loss steps: 70 - 180 °C (for **6**) and 80–217 °C (for **7**) indicates the loss of four formic acids for compound **6** (found: 10.1%; calcd: 10.28%) and the loss of the H₂O and one pivalate ligand for **7** (found: 5.5%, calcd:

6.2%); 180 - 280 °C loss of two HNO₃ molecules and four isobutyrates for **6** (found: 25.19%; calcd: 26.53%) and above 217 °C for **7** the loss of one pivalate and a bpm ligand (found: 13.5%, calcd: 13.4%); 280-400 °C corresponds to six isobutyrates and two 2-hydroxyisobutyrates for **6** (found: 38.73%; calcd: 40.71%) and 298–340 °C loss of nine pivalates and one bpy ligand for **7** (found: 57.5%, calcd: 55.3%) with residual weight of 25.98% (**6**) and 23.5% (**7**) suggests the final product of iron oxides (calcd: 26.78% (**6**) and 24.63% (**7**)) (Annexe 4, Figures A4.6, A4.7).

The single-crystal X-ray diffraction analysis showed that compound **1** crystallizes in the triclinic space group *P*-1. Three Fe atoms form equilateral triangle with the O atom in the centre (Figure 3.3). The Fe–(μ_3 -O) distances are equal to 1.899(2) and 1.899(1) Å. Each pair of Fe atoms is bridged by bidentate isobutyrate ligand. Three water molecules complete an octahedral environment of Fe centers. Selected bond distances in **1** are given



Fig. 3.3. Structure of $[Fe_3O(is)_6(H_2O)_3]^+$ cation in **1**. Color definition: Fe – green spheres, O – red, N – blue, C – grey balls. Hydrogen atoms, anions and solvent molecules are omitted.

Single-crystal X-ray analysis revealed that compound **2** crystallizes in the monoclinic space group $P2_1/n$ and consists of two [Fe(is)(tpt)(H₂O)]²⁺ units that are parallel to each other and located into an opposite direction (Figure 3.4 a). These units are interconnected via μ_2 -O²⁻ sandwiched between them. The Fe···Fe distance is 3.549(2) Å, and Fe-(μ_2 -O) distance is 1.7746(9) Å. The angle Fe- μ_2 -O-Fe is 180°. Each Fe^{III} atom has a N₃O₄ coordination environment by two O atoms from chelating isobutyrate, three N atoms from tpt ligand, one O atom from aqua ligand and one common O atom sandwiched between. The Fe–N distances range from 2.021(6) to 2.089(3) Å and Fe–O distances range from 1.774(5) to 2.164(1) Å.

Compound 2 has intermolecular O–H···O hydrogen bonds of 1.97(4) and 1.89(4) Å between dinuclear cations and NO₃⁻ anions shown in Figure 3.4 (b). Selected bond distances of dinuclear Fe^{III} compound are given in Annexe 1, Table A1.1.



Fig. 3.4. Structure of $[Fe_2O(is)_2(tpt)_2(H_2O)_2]^{2+}$ cation in **2** (a). View of intermolecular O–H···O hydrogen bonds (dotted turquoise lines) in **2** (b). Color definition: Fe – green spheres, N – blue, O – red, C – grey balls.

A single-crystal X-ray diffraction analysis showed that cluster **3** crystallizes in the monoclinic space group C2/c and comprises a central $\{Fe_4(\mu_3-O)_2\}^{8+}$ core (Figure 3.5 a). Seven isobutyrate groups additionally bridge four Fe^{III} atoms in the cluster cation. Two molecules of 2,2'-dipyridylamine coordinate chelating to peripheral Fe^{III} centres. The distance between inner Fe^{III} atoms bridged by two μ_3 -oxides equals 2.852(8) Å. Two iron atoms adopt a distorted octahedral O₆ and the remaining two N₂O₄ geometry with the Fe–O distances in the range of 1.828(2) - 2.082(2) Å, and the Fe–N bonds are 2.147(3) and 2.164(4) Å. The N–Fe–N chelate angles are equal to 81.96(1) and 83.22(1)°. Fe…Fe distances are in the range 2.853(1) – 3.474(1) Å. Selected bond distances in **3** are given in Annexe 1, Table A1.1.





Fig. 3.5. Structure of $[Fe_4O_2(is)_7(dpa)_2]^+$ cation in **3** (a). View of clusters **3** that are linked by intermolecular hydrogen bonds of the N–H···O type (b). Dotted turquoise lines show hydrogen bonds. Hydrogens are omitted for clarity.Fe – green spheres, N – blue, O – red, C – grey balls.

In cluster **3**, N–H···O hydrogen bonds of 2.87 and 3.03 Å between tetranuclear cations and NO_3^- anions connect adjacent clusters (Figure 3.5 b).

Single-crystal X-ray analysis demonstrated that compounds **4** and **5** have the same composition of the $[Fe_4O_2(piv)_8(bpm)]$ cluster moiety but differ by the function of one pivalate carboxylate group, the connectivity of the ligands, and the solvent molecules. (Figure 3.6). The Fe1 and Fe3 atoms occupy the body sites, and Fe2 and Fe4 atoms reside in the wingtip sites. The two body ions bridged by two μ_3 -oxides have an Fe1...Fe3 separation of 2.909(1) Å. The four Fe atoms in **4** (Figure 3.6 a) are coplanar within 0.099 Å and the μ_3 -oxygen atoms O1 and O2 occupy opposite positions from this plane. The dihedral angle between the planes Fe1/Fe3/Fe2 and Fe1/Fe3/Fe4 is 172.9°. The O1 and O2 atoms deviate from these planes by 0.454 and 0.460 Å, respectively, thus having a flattened pyramidal arrangement of bonds. Each iron atom is six-coordinate and has a distorted octahedral coordination environment. The three iron ions (Fe1, Fe3, Fe4) are O₆-coordinated, while the remaining iron atom has an N₂O₄ coordination environment that arises from a μ_3 -oxygen atom, a chelating bpm molecule, and three bridging pivalate ligands.

The asymmetric unit of **5** contains two similar complexes. The molecular structure of one of them (complex A) is shown in Figure 3.6 (b). Unlike **4**, only one piv anion acts as a chelate ligand and the other seven have bidentate bridging functions. Moreover, **4** and **5** differ in their connectivity. The additional carboxylate bridge between the two body atoms Fe1 and Fe3 leads to shortening (in comparison with **4**) of the Fe1…Fe3 distance up to 2.866(2) Å. In **4**, two pairs
of pivalate carboxylate groups bridge only one body iron atom (Fe3) with two iron atoms (Fe2 and Fe4) in the wing position, whereas in **5** the double carboxylate bridges link each body iron atom with only one iron atom in the wing position. The Fe^{III} atoms in **5** have a distorted octahedral coordination. In both complexes, the one iron atom has a N₂O₄ coordination environment that arises from a chelating bpm ligand, three bridging pivalate ligands, and a μ_3 -oxygen atom. The remaining iron atoms are all O₆-coordinated. Selected bond distances in **4** and **5** are given in Annexe 1, Table A1.1.



Fig. 3.6. Structure of $[Fe_4O_2(piv)_8(bpm)]$ **4** (a) and **5** (b). Hydrogen atoms and solvent molecules are omitted. Pivalates groups that differ by function are highlighted. Fe – green spheres, N – blue, O – red, C – grey balls.

The single X-ray analysis revealed that compound **6** crystallizes in the monoclinic space group $P2_1/n$. Cluster **6** consists of two triangular identical Fe₃(µ₃-O) fragments (Fe–O bond lengths for both are 1.909(3), 1.958(4) and 1.869(3) Å), where three iron(III) ions are held by µ₃-O^{2–} group (Figure 3.7 a). Further, two triangular fragments are interconnected through two bridging µ₂-OH[–] groups (Fe–O for both are 1.965(3) and 1.984(4) Å). Fe…Fe distances in {Fe₃O} fragments are 2.918(1), 3.211(1) and 3.598(1) Å. Additionally, iron atoms in each triangle are linked via three carboxylate groups and one 2-hydroxyisobutyrate ligand. Each of isobutyrates coordinates to a pair of Fe^{III} ions in a *syn,syn*– η^1 : η^1 :µ₂ bridging mode. The formed *in-situ* 2-hydroxyisobutyrate ligand coordinates at the periphery to the two neighboring iron centers, displaying a η^2 : η^1 :µ₂–bonding mode. All Fe^{III} sites are six-coordinated, adopting a slightly distorted octahedral O₆ geometry. Selected bond distances in **6** are given in Annexe 1, Table A1.1. Single-crystal X-ray analysis of **7** revealed discrete heptanuclear molecules (Figure 3.7 b) with seven crystallographically independent Fe^{III} atoms. All iron sites are hexacoordinated with distorted octahedral O₆ (five Fe atoms) or N₂O₄ (two Fe atoms) environments. Fe–O bond lengths range from 1.817(2) to 2.167(3) Å, Fe–N bonds from 2.170(3) to 2.242(3) Å. Each complex contains two interlocked tetranuclear [Fe₄(μ_3 -O)₂] butterfly-type cores composed of two edge-sharing {Fe₃(μ_3 -O)} triangles (Figure 3.7 b), crucial building blocks for the assembly of frustrated spin structures.



Fig. 3.7. Structure of $[Fe_6O_2(OH)_2(is)_{10}(C_4H_7O_3)_2]^{2-}$ (6) (a) and $[Fe_7O_4(OH)_2(piv)_{11}(bpm)_2(H_2O)]$ (7) (b). Two C₄H₇O₃ groups in 6 are highlighted in yellow. In core structure of 7 the two cornersharing {Fe₄(μ_3 -O)₂} groups are emphasized in transparent yellow triangles. Fe – green spheres, N – blue, O – red, C – grey balls.

These tetranuclear groups share a common iron atom, which serves as a "wingtip" site for the first {Fe₄O₂} group and occupies the "body" position in the other one. The two pairs of "body" iron ions bridged by two μ_3 -oxides are separated by 2.930(1) and 2.849(1) Å, representing the shortest Fe…Fe contacts in this compound. The two {Fe₄(μ_3 -O)₂} cores are additionally bridged by two protonated μ_2 -O sites (O5/O5A). Nine pivalate ligands bind in bidentate bridging modes, whereas one is chelating and one is monodentate-bound to Fe7. Intramolecular hydrogen bonds are formed between the water ligand bound to Fe5 and two neighboring pivalates (O…O: 2.76–2.84 Å), and between the uncoordinated O site of the monodentate pivalate and μ_2 -OH (O…O: 2.85 Å). Selected bond distances in **7** are given in Annexe 1, Table A1.1.

The magnetic susceptibility measurements of **4** and **5** compounds showed the presence of strong antiferromagnetic interactions between iron ions in **4** and **5**. Given the butterfly-type

arrangement of **4** and **5** clusters, we can use the following Hamiltonian to describe the system [Equation (1)] $\hat{H} = -J_{bb}(S_A \cdot S_B) - J_{wb}(S_A \cdot S_C + SA \cdot S_D + S_B \cdot S_C + S_B \cdot S_D)$ (1). Magnetochemical analysis of the reported Fe₄ butterfly clusters shows that the antiferromagnetic interactions between wing-body Fe^{III} ions are slightly stronger in **5** ($J_{wb} = -88.7 \text{ cm}^{-1}$) in comparison with wing-body interactions in **4** ($J_{wb} = -72.2 \text{ cm}^{-1}$) (Figure 3.8).



Fig. 3.8. (a) Plot of $\chi(T)$ (black includes a paramagnetic impurity, gray does not) and $\chi T(T)$ for **5**, with a fit from the matrix diagonalization routine with g = 2.00 (fixed), $J_{bb} = 0$ cm⁻¹ (fixed), and $J_{wb} = -88.7$ cm⁻¹. (b) The same treatment for **4**, with g = 2.00 (fixed), $J_{bb} = 0$ cm⁻¹ (fixed), and $J_{wb} = -72.2$ cm⁻¹.

Magnetic susceptibility measurements of **7** (2 – 290 K, 0.1 – 5.0 Tesla; Figure 3.9) indicate strong antiferromagnetic coupling between the seven Fe^{III} atoms (3d⁵, ⁶A₁ ground term, S = 5/2) resulting in an S = 5/2 ground state. At room temperature, $\chi_m T$ only approaches 7.1 cm³·K·mol⁻¹, much smaller than the expected spin-only value for seven isolated Fe^{III} ions of 30.6 cm³·K·mol⁻¹ (g = 2.0). With decreasing T, $\chi_m T$ decreases steadily to reach a plateau below 50 K with $\chi_m T \approx$ 4.4 cm³·K·mol⁻¹, close to the spin-only value for one isolated Fe^{III} ion of 4.375 cm³·K·mol⁻¹. Given the multitude of exchange pathways, a simplified Heisenberg model spin Hamiltonian ($\hat{H} = -J_1(S_A \cdot S_B) - J_2(S_A \cdot S_C + S_A \cdot S_D + S_B \cdot S_C + S_B \cdot S_D)$) was used to assess the effective exchange energies for the two dominant exchange pathways of the {Fe₇O₆} core (J_1 : Fe–(μ_3 -O)–Fe; J_2 : Fe–(μ_3 -O)²–Fe) and yields $J_1 = 49.0$ cm⁻¹, $J_2 = 22.5$ cm⁻¹ (g = 1.995) [255]. The field-dependent magnetization at 2.0 K concurs with a Brillouin expression for an S = 5/2 ground state.



Fig. 3.9. Temperature dependence of $\chi_m T$ of **7** at 0.1 Tesla; inset: field-dependent magnetization at 2.0 K (experimental data: circles, best fits to models: light gray lines, horizontal line: expected value for one isolated S = 5/2 center).

Highnuclear Fe^{III} coordination clusters. The reaction of a trinuclear iron (III) isobutyrate with amino/polyalcohol ligands leads to the formation a range of structures with beautiful architectures. N/O-containing alkoxide arms ligands adopt chelating and bridging modes and they are good candidates that are facilitating the formation of highnuclear Fe^{III} products. In Figure 3.10 shown the way amino/polyalcohol ligands can assemble {Fe₃O} fragments into hexa-, octa-, dodeca- and docosanuclear iron(III) clusters.

Fig. 3.10. Schematic representation of synthesis of homometallic 8-16 clusters.

A hexanuclear compound $(mdeaH_3)_2$ [Fe₆O(thme)₄Cl₆]·0.5(MeCN)·0.5(H₂O) (8), and two $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4](NO_3)_{0.5}N_3(MeO)_{0.5} \cdot 2.5(H_2O)$ dodecanuclear (13)and $[Fe_{12}O_6(teda)_4(Cl)_8] \cdot 6(CHCl_3)$ (14) have been synthesized by the solvothermal reaction of precursor (1) and mdeaH₂ with thmeH₃, tedaH₄ or tedaH₄/NaN₃, respectively. The interaction of acetonitrile solution with theaH₃ 1 in under ultrasonic irradiation gave $[Fe_8O_3(is)_9(tea)(teaH)_3]$ ·MeCN·2(H₂O) (9) cluster. The adding of sodium azide to the previous reaction in ethanol solution under reflux resulted in cluster [Fe₈O₃(is)₆(tea)(teaH)₃(N₃)₃] (10). The interaction of 1 with mdeaH₂ ligand in a ultrasonic bath gave crystals of $[Fe_8O_3(is)_6(mdea)_3(N_3)_3(MeO)_3]$ (11). The slow diffusion of diethyl ether solution containing precursor (C) and acetonitrile solution containing mdeaH₂ ligand in two layered system resulted in compound $[Fe_{12}O_6(OH)_4(piv)_{10}(mdea)_4(mdeaH)_2]$ (12). The reaction of 1 with bdeaH₂ or $mdeaH_2$ under ultrasonic irradiation resulted gave at room in or $[Fe_{22}O_{16}(OH)_2(is)_{18}(bdea)_6(EtO)_2(H_2O)_2] \cdot 2(EtOH) \cdot 5(MeCN) \cdot 6(H_2O)$ (15)and $[Fe_{22}O_{14}(OH)_4(is)_{18}(mdea)_6(EtO)_2(H_2O)_2](NO_3)_2 \cdot EtOH \cdot H_2O(16)$, respectively.

The IR-spectra of 8-16 show the O–H stretching vibrations observed in the region 3431-3395 cm⁻¹ which correspond to alcohol groups of mdeaH₃ ligand (8), water molecules (9), OH groups of doubly deprotonated teaH ligands (10, 11), alcohol groups of mdeaH ligand (12), solvate molecules and hydroxyl groups (13, 14) and hydroxy groups as well as water and ethanol molecules (15, 16). The C–H asymmetric and symmetric stretching vibrations are observed in the region 2969 – 2856 cm⁻¹ for thme^{2–} and mdea^{2–} groups (8), methyl, methylene -(CH₂)- and methyne >(CH)- groups of is[–] and polyalcohol ligands (9-11, 15 and 16). Strong bands in the region 1484-1463 cm⁻¹ are ascribed to the C–H asymmetric bending vibrations for alkyl groups (9-16), whereas their symmetric bending vibrations appear in the region 1398 – 1302 cm⁻¹. Strong peaks of the coordinated asymmetric and symmetric stretching vibrations of isobutyrate groups for 9-12, 15 and 16 clusters are observed in the region 1632 – 1542 cm⁻¹ and 1429 – 1413 cm⁻¹, respectively. An intensive peak at 2068 cm⁻¹ corresponds to N≡N stretching vibrations of azide anions in 10, 11 and 13 (Annexe 3, Figures A3.7- A3.15).

TGA/DTA curves of **9-11** showed that cluster **9** loses the organic ligands (three molecules of the aminoalcohol ligand and nine pivalates) in two steps from 120 to 400 °C; the total first weight loss of 64.3% (calcd: 63.1%) is accompanied by an endothermic peak at 229 °C. The decomposition of the remaining tea³⁻ ligand takes place in the interval from 570 to 770 °C. Cluster **10** is stable up to 120 °C, and then it starts to decompose in three weakly resolved steps until approx. 450 °C. The first two steps of the TGA curve of **10** are associated with an

endothermic peak at 205 °C with a weight loss up to 230 °C; this corresponds to removal of the three azido groups and one carboxylate ligand (found: 13.8%; calcd: 12.3%). The third step for **10** is the loss of three teaH²⁻ and five isobutyric groups (found: 45.6%; calcd: 45.4%). After a plateau extending to 540 °C, further heating of **10** instigates a fourth weight loss of 8.1% until 630 °C, and this corresponds to removal of the remaining aminoalcohol ligand (calcd: 8.4%) to give the oxides with a total weight loss of 67.5% (calcd: 68.7%). The TGA data show that cluster **11** is the least stable compound. It remains stable up to 180 °C followed by the loss of all organics in three unresolved steps until ~400 °C, with a total weight loss of 57.9% (calcd: 61.1%) to the final metal oxides. The decomposition is accompanied by one exothermic peak at 234 °C and one endothermic peak at 279 °C (Annexe 4, Figures A4.9-A4.11).

The first step of the TGA curves of **8**, **13** and **14** shows weight loss below 100°C (for **8**) and 150 °C (for **13**, **14**), corresponding to the loss of acetonitrile and water molecules for cluster **8** (found: 2.1%; calcd: 2.3%), nitrate and azide anions, methoxy groups and water molecules for **13** (found: 7.1%; calcd: 6.3%), and one solvent chloroform molecule for cluster **14** (found: 5.4%; calcd: 5.7%). The compound **14** loses its 5 solvent chloroform molecules at room temperature (accoding to elemental analysis). The next step for clusters **8** and **13** is accompanied with an endothermic peak (at 265 °C) for **8** and an exothermic peak (at 250 °C) for **13**. This step indicates the loss of two (mdeaH₃⁺) ligands and six chlorides for **8** (found: 14.9%; calcd: 13.8%) and the loss of four azide and four methoxy groups for **13** (found: 14.9%; calcd: 13.8%), while compound **14** releases of five chloride groups (found: 8.22%; calcd: 8.44%). The two last steps of decomposition until 680 °C (**8**), 600°C (**13**) or 750°C (**14**) correspond to loss of four thme³⁻ ligands for cluster **8** (found: 35.8%; calcd: 35.9%), four teda⁴⁻ groups for **13** (found: 48.6%; calcd: 49.3%), leading to formation of the final product of iron oxides (calcd: 24.5% (**8**), 30.1% (**13**) and 38.02 (**14**)) (Annexe 4, Figures A4.8, A4.12, A4.13).

Note, according to elemental analysis the compound **15** loses its solvent molecules (ethanol and acetonitrile) during drying of the crystals under vacuum. The TGA curve of **15** showed that the compound releases two coordinated and six solvent water molecules on the first step from 100 C° to 190 C° (found: 3.1%, calcd: 3.4%). The following step up to 400 °C corresponds to release of two ethoxy, six bdea^{2–} groups and sixteen isobutyrates (found: 56.9%, calcd: 57.01%). In the last step up to 650 C° the rest of two isobutyrate ligands are burnt (found: 4.1%, calcd: 4.1%) leading to the formation of iron oxides (calcd: 37.4%) (Annexe 4, Figure A4.14).

A single-crystal X-ray diffraction analysis showed that compound **8** crystallizes in the tetragonal space group *I*-42*d* and consists of an anionic hexametalate $[Fe_6O(thme)_4Cl_6]^{2-}$ cluster, two outersphere protonated mdeaH₃⁺ moieties and solvent molecules. The source of chloride groups that coordinate to the cluster is chloroform. In the anionic cluster with *C*₂ molecular symmetry a central μ_6 -oxo atom resides on two-fold axis and is surrounded by six Fe^{III} centres to form an octahedron (Figure 3.11).



Fig. 3.11. Structure of an anionic $[Fe_6O(thme)_4Cl_6]^{2-}$ cluster in **8** (a) and polyhedral representation of six Fe^{III} ions (b). Color scheme: Fe – light green, Cl – lavender, O – red, C – grey spheres.

Twelve alkoxo groups of four triply deprotonated thme^{3–} ligands additionally bridge the Fe^{III} atoms: each of thme^{3–} ligands coordinates in a $\eta^2:\eta^2:\eta^2-\mu_3$ mode with each oxygen bridging two metal sites. The remaining coordination site at each Fe^{III} centre is occupied by Cl[–] ligand. All Fe^{III} atoms in **8** are six-coordinated and adopt an octahedral O₅Cl environment by a terminal chloride and five oxygen atoms: one central μ_6 -O atom and four O atoms from two neighbouring thme^{3–} ligands. The bond distances from each Fe^{III} atom to the central μ_6 -O atom vary from 2.223(1) to 2.264(11) Å, and other Fe–O bond distances are in the range of 1.978(7) – 2.005(8) Å. The Fe–Cl bond distances are in the range 2.266(5) – 2.292(3) Å. Selected bond distances in **8** are given in Annexe 1, Table A1.1.

The single-crystal X-ray analyses of **9-11** showed that these compounds have similar structures, but differ by composition and solvate molecules. Cluster **9** crystallizes in the monoclinic space group $P2_1/n$, complex **10** in cubic space group Pa-3, whereas compound **11** in triclinic space group P-1. Their cores comprise two central axial Fe^{III} ions bridged by three μ_4 -O²⁻, and each μ_4 -O²⁻ furthermore bridges two peripheral Fe^{III} ions in pair, resulting in one of the

three "blades" of the propeller (Figure 3.12 a, b and c). The central pair of iron ions in (9) and (10) represents the axle of the propeller with Fe–Fe distances of 2.83 Å (9 and 10) and 2.79 Å (11). Additionally, Fe^{III} ions are bridged by nine carboxylate groups (9) or six carboxylate groups (10) and four triethanolamine ligands: three doubly deprotonated (teaH^{2–}) and one triply deprotonated (tea^{3–}) or six isobutyrate groups (11), three mdea^{2–} ligands and three methoxy groups. Three monodentate azide ligands completing the structure of 10 or 11. In 9-11 each Fe atom is six-coordinated and has a distorted O₆ or O₅N octahedral coordination environment. Selected bond distances in 9-11 are given in Annexe 1, Table A1.1.



Fig. 3.12. Structure of [Fe₈O₃(is)₉(tea)(teaH)₃] (9) (a), [Fe₈O₃(is)₆(tea)(teaH)₃(N₃)₃] (10) (b) and [Fe₈O₃(is)₆(mdea)₃(N₃)₃(MeO)₃] (11) (c). Color definition: Hydrogens and solvent molecules are omitted. Fe – green spheres, N – blue, O – red, C – grey balls.

Cluster $[Fe_{12}O_6(OH)_4(piv)_{10}(mdea)_4(mdeaH)_2]$ (12) crystallizes in the triclinic space group *P*-1 and has its own symmetry C_i . Single-crystal X-ray analysis of 12 showed that twelve Fe^{III} atoms are bridged by six μ_3 -O²⁻ ions, four μ_2 -OH⁻ groups, four mdea²⁻, two mdeaH⁻ ligands and ten carboxylates (Figure 3.13 a). Twelve iron atoms form six {Fe₃O} non-equilateral triangles with a central μ_3 -oxygen. Fe...Fe distances in triangles are in the range from 2.941(2) to 3.571(2) Å. The Fe-(μ_3 -oxo) distances vary from 2.941(2) to 3.571(2) Å. Twelve iron ions are six-coordinated, six of them (Fe1, Fe3, Fe6) have coordination environment with NO₅ donor set and other six (Fe2, Fe4, Fe5) are surrounded by six oxygen atoms. Fe–N bond distances are 2.234(6), 2.318(7) and 2.273(6) Å.



Fig. 3.13. Structure of [Fe₁₂O₆(OH)₄(piv)₁₀(mdea)₄(mdeaH)₂] (12) (a) and a view of intramolecular hydrogen bonds of the O–H…O type in 12 (b). Dotted turquoise lines show hydrogen bonds. Hydrogen are omitted. Fe – green spheres, N – blue, O – red, C – grey balls.

Two pivalates are monodentate and eight pivalates are bridging towards the two nearby iron(III) ions. Each of N-methyldiethanolamine ligand binds three neighboring iron atoms in a three-dentate N/O-chelating form. The presence of uncoordinated C=O group of carboxylates and μ_2 -OH⁻ groups (O9 and O21) results in intramolecular O-H···O hydrogen bonds of 2.687(7) Å (Figure 3.13 b). Two mdeaH⁻ ligands participate as a donors in the formation of intramolecular O-H···O hydrogen bonds (2.701(6) Å) with coordinated oxygen of pivalate group. Selected bond distances in **12** are given in Annexe 1, Table A1.1.

Single-crystal X-ray diffraction analysis revealed that complex $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4](NO_3)_{0.5}N_3(MeO)_{0.5} \cdot 2.5(H_2O)$ (13) crystallizes in the tetragonal space group P4, whereas complex $[Fe_{12}O_6(teda)_4(Cl)_8] \cdot 6(CHCl_3)$ (14) crystallizes in the monoclinic space group C2/c. Both complexes have a saddle-like non-coplanar {Fe₁₂} ring arrangement. The structure of 13 consists of $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4]^{2+}$ cation and for charge balance there are a half of NO₃⁻, a half of MeO⁻ and N₃⁻ anions. The dodecanuclear 14 complex is a neutral-charged compound and consists of neutral [Fe₁₂O₆(teda)₄(Cl)₈] clusters and solvent chloroform molecules. The core structure of 13 can be considered as the arrangement of two near-planar {Fe₆} areas (deviation 0.20° between planes) of twelve Fe^{III} atoms that are bridged by four μ_4 -O²⁻ ions, two hydroxyl μ_2 -OH⁻ groups and four teda⁴⁻ ligands, whereas four N_3^- and four methoxy MeO⁻ groups are completed the coordination spheres of Fe^{III} atoms (Figure 3.14 a). Two N-atoms of teda⁴⁻ coordinate chelating to metal atom and each of O-atoms of four hydroxy groups coordinates bridging to neighboring metal atoms. Each teda⁴⁻ ligand is quadruple-coordinated and demonstrates $\eta^2:\eta^2:\eta^2:\eta^2:\eta^1:\eta^1-\mu_6$ bringing mode. Eight Fe^{III} centres (Fe1, Fe2, Fe4, Fe5, Fe7, Fe8, Fe10, and Fe11) are hexa-coordinated with a distorted octahedral geometry: four of them have an O₆ donor set, whereas the other four have an O₅N coordination environment with Fe–O bond distances of 1.913(15) – 2.171(17) Å and Fe–N bond distances of 1.97(2) - 2.05(2) Å. The O₆ donor set comprises two oxygen atoms of two different teda⁴⁻ ligands, two oxygen atoms of μ_4 -O²⁻ group, one oxygen atom from methoxy group (μ_2 -MeO⁻) and one oxygen atom from hydroxy (μ_2 -OH⁻) group. The O₅N donor set is made up from three O atoms of two teda⁴⁻ ligands, one O atom from methoxy group, one O atom from μ_4 -O²⁻ group and one N atom from azide. Remaining four Fe^{III} centres (Fe3, Fe6, Fe9, and Fe12) are heptacoordinate with distorted pentagonal bipyramidal geometry and an O₅N₂ donor set, made up from two N atoms and four O atoms of teda⁴⁻ ligand, and one O atom of μ_4 -O²⁻ group (Fe–O, 1.922(17) - 2.272(15) Å; Fe-N, 2.25(2) - 2.319(18) Å). The outer azide anions in 13 form O–H···N hydrogen bonds of 2.75(4) and 2.73(4) Å with hydroxyl groups of neighboring clusters $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(OMe)_4]^{2+}$ to generate a cationic hydrogen-bonded {Fe₁₂} cluster-based chain as shown in Figure 3.14 c.

The core of cluster **14** is essentially the same as that in **13** e.g. has the saddle-like form with two planar Fe₆ layers. Twelve Fe^{III} atoms linked via four μ_4 -O²⁻ ions, and four teda⁴⁻ ligands except that hydroxyl and methoxy groups are replaced by μ_2 -O²⁻ and μ_2 -Cl⁻ ligands, respectively, to give [Fe₁₂O₆(teda)₄(Cl)₄]⁴⁺ unit with a {Fe₁₂O₆}²⁴⁺ core (Figure 3.14 b).



(c)

Fig. 3.14. Structure of $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4]^{2-}$ an anionic cluster in **13** (a) and $[Fe_{12}O_6(teda)_4(Cl)_8]$ (**14**) (b). A hydrogen-bonded chain (N atoms of bridging azide and O atoms of OH groups emphasized as blue and red balls) in **13** (c). Hydrogen bonds are shown as light blue dotted lines.

The coordination of four mono-dentate chlorides to Fe^{III} atoms completes the structure of **14**. Note, the asymmetric unit of **14** consists of six Fe ions, two tead^{4–} ligands, four chlorides,

tree oxo-groups and three solvent chloroform molecules. Four Fe^{III} centers are hexa-coordinated, displaying a distorted octahedral coordination environment. Two of them (Fe2 and Fe4) comprise an O₄Cl₂ coordination environment involving three O atoms of teda^{4–}, one O atom of μ_4 -O^{2–} group and two chlorides, whereas the other two Fe^{III} centers (Fe1 and Fe5) have an O₅Cl donor set including one O atom from teda^{4–} ligand, two O atoms from μ_4 -O^{2–} groups and one O atom from μ_2 -O^{2–} group. The Fe–O bond distances are in the range of 1.937(6) – 2.289(7) Å and Fe–Cl bond distances are equal 2.337(3) – 2.603(3) Å. Remaining two Fe^{III} centres (Fe3 and Fe6) are hepta-coordinated with a distorted pentagonal bipyramidal geometry, having an O₅N₂ donor set, made up from two N and four O atoms of teda^{4–} ligand and one O atom of μ_4 -O^{2–} group (Fe–O, 1.936(6) - 2.304(7) Å; Fe–N, 2.272(8) - 2.348(8) Å). Selected bond distances in **13** and **14** are given in Annexe 1, Table A1.1.

Single-crystal X-ray diffraction analysis revealed that complexes $[Fe_{22}O_{16}(OH)_2(is)_{18}(bdea)_6(EtO)_2(H_2O)_2] \cdot 2(EtOH) \cdot 5(MeCN) \cdot 6(H_2O)$ (15)and $[Fe_{22}O_{14}(OH)_4(is)_{18}(mdea)_6(EtO)_2(H_2O)_2](NO_3)_2 \cdot EtOH \cdot H_2O(16)$ crystallize in the triclinic space group P-1 and their cores have C_i . symmetry. The structures of 15 and 16 consist of 22 Fe centers (with 11 crystallographically independent sites) that form a $\{Fe_{22}(\mu_4-O)_8(\mu_3-O)_6(\mu_2-O)_8(\mu_3-O)_6(\mu_3-O)_8(\mu_3 O_{2}(\mu_{2}-OH)_{2}(\mu_{2}-EtO)_{2}$ core in **15**, and a {Fe₂₂($\mu_{4}-O$)₈($\mu_{3}-O$)₆($\mu_{2}-OH$)₄($\mu_{2}-EtO$)₂} core in **16**. Additional bridges between Fe^{III} atoms are provided by 18 isobutyrate and six bdea²⁻ (15) (Figure 3.15 a) or $mdea^{2-}$ (16) ligands that are situated at the periphery of the molecules. A terminal H₂O ligand completes the coordination sphere of two Fe atoms.

The {Fe₂₂} core in **15** and **16** can be formally constructed from three layers of two types. The upper and bottom {Fe₈} layers consist of eight Fe^{III} atoms interlinked by three μ_4 -O atoms to form three edge-sharing [Fe₄(μ_4 -O)] tetrahedra, with shortest Fe–Fe distances of 2.834(2) Å in **15** and 2.849(2) Å in **16**, resembling a propeller with three tilted blades (Figure 3.15 b). Each {Fe₈} layer is connected to the central {Fe₆} layer via three μ_3 -O and three isobutyrate bridges. The central {Fe₆} layer itself comprises two μ_4 -O, two μ_2 -EtO groups, and μ_2 -O or μ_2 -OH bridges. Four Fe atoms form a central [Fe₄(μ_4 O)₂(μ_2 -O)₂(μ_2 -EtO)₂]²⁺ fragment, to which two additional Fe atoms are attached as shown in Figure 3.15 (c). These two Fe atoms are pentacoordinated with an O₅ donor set, whereas all other Fe atoms have distorted NO₅ or O₆ octahedral environments (Fe–O: 1.838(5)–2.143(5), Fe–N: 2.200(10)–2.258(8) Å, consistent with those of the above-mentioned clusters and the reported Fe₂₂ species [203]). Selected bond distances in **15** and **16** are given in Annexe 1, Table A1.1.



Fig 3.15. Structure of $[Fe_{22}O_{16}(OH)_2(is)_{18}(bdea)_6(EtO)_2(H_2O)_2]$ (15) (a). View of sub-units within complex: Fe₈ unit (b) and central Fe₆ unit (c). Atoms of hydrogen are omitted for clarity. Fe – green spheres, N – blue, O – red, C – grey balls.

The magnetic susceptibility data of $(mdeaH_3)_2[Fe_6O(thme)_4Cl_6]\cdot 0.5(MeCN)\cdot 0.5(H_2O)$ (8) are presented as $\chi_m T vs. T$ and $M_m vs. B$ curves in Figure 3.16.



Fig. 3.16. Temperature dependence of the product $\chi_m T$ at 0.1 Tesla, and molar magnetization M_m vs. applied magnetic field *B* at 2.0 K (inset) of **8**.

At 290 K, the value of $\chi_m T$ is 11.13 cm³ K mol⁻¹ at 0.1 T, which is well below the spinonly value of six non-coupled high-spin Fe^{III} centers (26.26 cm³ K mol⁻¹, $S_{eff} = 5/2$, $g_{iso} = 2$). Decreasing temperature, the $\chi_m T$ values continuously decrease down to 0.07 cm³ K mol⁻¹ at 2.0 K. At this temperature, the molar magnetization is an almost linear function of the applied magnetic field, reaching 0.2 $N_A \mu_B$ at 5.0 T. These observations are in line with dominant antiferromagnetic exchange interactions between the six Fe^{III} centers, and minor paramagnetic impurities.

The low-field temperature-dependent magnetic susceptibility data of three octanuclear propeller-like clusters **9–11** are depicted in Figure 3.17 (a) as open circles (do not take into account blue circle). Due to the similar structures of **9–11**, the simulated exchange parameters differ by small amounts from one compound to another. Therefore, the coupling scheme that is applied in the fit to the effective spin Hamiltonian is explained using the example of compound **11**.



Fig. 3.17. Temperature dependence of the magnetic susceptibility χ_m of **9–11** at 0.1 Tesla; inset: temperature dependence of the corresponding effective magnetic moment $\mu_{eff}(a)$. Coupling scheme of **9–11** using the example of compound **11**: (left) front view, (right) side view (b).

The calculations of *wxJFinder* show that 15 of the 28 exchange interaction parameters are negligible. 12 of the remaining 13 parameters are divided into four categories, each represented by three (almost) identical parameters. Thus, all compounds are described by effective Hamiltonians that contain five independent exchange parameters *Ji* as depicted in Figure 3.17 (b) (notation: $\hat{H}_{ex} = \sum_{k < l} -2J_i \hat{S}_k \cdot \hat{S}_l$). The resulting fit parameters are shown in the Table 3.1 and the corresponding curves as straight lines in Figure 3.17 (a).

According to the Heisenberg model employed here, all compounds are characterized by a single ferromagnetic (J_1) and otherwise antiferromagnetic independent exchange interaction parameters J_i (S = 5/2, $g_{iso} = 2.0$). The magnetochemical studies showed that for **9–11**, antiferromagnetic exchange interactions dominate along the edges of the propeller while a moderate ferromagnetic interaction is found along the propeller axis.

| | 9 | 10 | 11 |
|----------------------------|-------|-------|-------|
| $g_{ m eff}$ | 2 | 2 | 2 |
| J_1 / cm $^{-1}$ | +35.8 | +25.3 | +16.0 |
| J_2 / cm $^{-1}$ | -22.8 | -22.0 | -17.5 |
| $J_3 /{ m cm}^{-1}$ | -22.6 | -22.0 | -17.0 |
| J_4 / cm $^{-1}$ | -14.7 | -16.4 | -11.8 |
| J_5 / cm $^{-1}$ | -8.5 | -6.1 | -38.1 |
| $J_6 /{ m cm}^{-1}$ | NA | NA | -7.5 |
| ρ / % | 0.58 | 0.11 | 0.19 |
| <i>SQ</i> / % ^a | 0.6 | 1.5 | 1.6 |

Table 3.1. Magnetochemical analysis details of 9-11

The magnetic properties of the {Fe₁₂} compounds **13** and **14** are analyzed on the basis of the $\chi_m T vs. T$ and $M_m vs. B$ plots shown in Figure 3.18. As expected from structure, the data of both compounds share common features, and the $\chi_m T$ curves are qualitatively similar: at 290 K, $\chi_m T = 22.40$ and 24.30 cm³ K mol⁻¹ for **13** and **14**, respectively, at 0.1 T. Again, these values are well below the spin-only value of twelve non-interacting high-spin Fe^{III} centers (52.52 cm³ K mol⁻¹).

Cooling the compounds yielded decreasing $\chi_m T$ values that reach 0.22 (13) and 0.86 cm³ K mol⁻¹ (14) at 2.0 K. The molar magnetizations at 2.0 K show larger deviations from each other: for 13, M_m is almost linear in *B* up to 5.0 T taking a maximum value of 0.8 $N_A \mu_B$. For 14, a distinct change of the slope is observed at about 1.5 T: steeper for lower fields, and less so for higher fields, for which the slopes of the $M_m vs. B$ curves of 13 and 14 are eventually the same

(ca. B > 3 T). Therefore, both compounds are characterized by dominant antiferromagnetic exchange interactions between the twelve iron centers of each compound.



Fig. 3.18. Temperature dependence of the product $\chi_m T$ at 0.1 Tesla, and molar magnetization M_m vs. applied magnetic field *B* at 2.0 K (inset) of **13** (blue circles) and **14** (black circles).

The magnetic data of the {Fe₂₂} compounds (**15** and **16**) are shown in Figure 3.19. As for **13** and **14**, the $\chi_m T vs. T$ curves are similar as expected from the molecular structures. They exhibit a room temperature value of $\chi_m T = 32.93$ (**15**) and $32.56 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ (**16**) at 0.1 T, which are distinctly below the spin-only value of 22 non-interacting high-spin Fe^{III} centers of 96.29 cm³ K mol⁻¹. The values continuously decrease by decreasing temperature.



Fig 3.19. Temperature dependence of the product $\chi_m T$ at 0.1 Tesla, and molar magnetization M_m vs. applied magnetic field *B* at 2.0 K (inset) of **15** (green circles) and **16** (brown circles).

At 2.0 K, they reach a value of 0.98 and 0.37 cm³ K mol⁻¹ for **15** and **16**, respectively. At this temperature, the molar magnetization as a function of the applied field of **15** is concave up to ca. 1.5 T, reaching 0.9 $N_A \mu_B$, which is indicative of small paramagnetic impurities. For **16**, the concave segment of the curve is barely noticeable, therefore indicating almost negligible paramagnetic impurities. The M_m versus B curve is thus essentially a convex curve with a maximum value of 1.7 $N_A \mu_B$ at 5.0 T. On the basis of both observations, the ground state of **16** is most likely characterized by a total effective spin of $S_{tot} = 0$. Magnetic measurements revealed strong antiferromagnetic coupling between the Fe^{III} spin centers in both clusters.

3.2. Homometallic Fe^{III} carboxylate coordination polymers with *N*-bridging ligands

Oxo-polynuclear coordination clusters have well-defined molecular structures that make them unique building blocks in supramolecular construction of the extended networks. The employing such clusters with N,N'-donor bridging ligands (4,4'-bpy, bpm, pyEt, hmta) can give 1D, 2D and 3D coordination polymers (CP's) with different topology. Clusters act as "nodes" and organic ligands as "linkers". Bridging ligands occupy apical positions in the cluster replacing axillary ligands (H₂O, EtO⁻ *etc.*), and extending to multidimensional CPs. Several synthetic approaches towards the preparation of CPs exist but hydro(solvo)thermal method considers to be one of the most effective methods for growing 3D CP's or porous metal organic frameworks.

The recrystallization in tetrahydrofuran of a viscous mass, obtained from the reaction of precursor (**A**) and pyEt led to formation of $\{[Fe_3O(piv)_6(HCO_2)(pyEt)]\cdot 0.5(pivH)\cdot 0.5(thf)\}_n$ (**17**) (Figure 3.20). Treatment of $[Fe_3O(piv)_6(H_2O)_3]piv\cdot 2pivH$ (**A**) with hmta in acetonitrile solution gave a 1D coordination polymer $\{[Fe_4O_2(piv)_8(hmta)]\}_n$ (**18**) (Figure 3.20) [249]. Solvothermal reaction of hexanuclear precursor (**B**) with 4,4'-bpy ligand in the presence of str-template gave green crystals of 3D CP $\{[Fe_3O(piv)_6(4,4'-bpy)_{1.5}](OH)\cdot 0.75(CH_2Cl_2)\cdot n(H_2O)\}_n$ (**19**) [253] (Figure 3.20).

$$\{Fe_{3}O\}(\mathbf{A}) \xrightarrow{\text{pyEt}} \{[Fe_{3}O(\text{piv})_{6}(CO_{2})(\text{pyEt})] \cdot 0.5(\text{pivH}) \cdot 0.5(\text{thf})\}_{n}(\mathbf{17})$$

$$\{Fe_{6}O_{2}\}(\mathbf{B}) \xrightarrow{\text{hmta}} \{[Fe_{4}O_{2}(\text{piv})_{8}(\text{hmta})\}_{n}(\mathbf{18})$$

$$\{Fe_{6}O_{2}\}(\mathbf{B}) \xrightarrow{4.4' \cdot \text{bpy+str}}_{\text{MeCN/CH}_{2}Cl_{2}, \text{ HT}} \{[Fe_{3}O(\text{piv})_{6}(4,4' \cdot \text{bpy})_{1.5}](OH) \cdot 0.75(CH_{2}Cl_{2}) \cdot n(H_{2}O)\}_{n}(\mathbf{19})$$



The infrared spectra of **17-19** showed the C–H stretching vibrations of pivalate groups appear in the region $2964 - 2868 \text{ cm}^{-1}$, and strong single band in the region $1483 - 1482 \text{ cm}^{-1}$, and a doublet in the region $1378 - 1360 \text{ cm}^{-1}$, which correspond to asymmetric and symmetric bending vibrations for methyl and methylene -(CH₂)- groups of pivalates and pyEt ligands, respectively. Strong peaks of asymmetric and symmetric vibrations of the coordinated carboxylate groups are observed in the region $1582 - 1544 \text{ cm}^{-1}$ and $1457 - 1415 \text{ cm}^{-1}$, respectively. The C=N stretching vibration of aromatic rings was observed at 1714 cm^{-1} in **17**. Several well-separated strong and sharp bands at 1250, 1056, 1024, and 987 cm⁻¹ can be assigned to the C–N stretching modes of the coordinated hmta in **18**. The IR spectrum of **19** displays the O–H stretching vibration at 3139 cm^{-1} (Annexe 3, Figures A3.16 - A3.18).

The TGA curves of coordination polymers **18** and **19** showed that polymer **18** is stable up to 200°C, while polymer **19** shows a first weight loss as soon as heating begins. A first weight loss up to 300°C for **18** corresponds to the release of three carboxylate ligands (found: 32.8%, calcd: 33.6%) and for polymer **19** until 180°C, corresponding to the removal of 0.75 dichloromethane and eight water solvent molecules (found: 10.5%, calcd: 11.5%). The following last steps show the decomposition of a hmta and five remaining piv⁻ ligands 52.7 % for **18** (found: 52.7%, calcd: 53.6%) and six pivalate and 4,4'-bpy for polymer **19** (found: 77.0%, calcd: 74.3 %) to give the expected homometallic oxides (found: 14.6% for **18** and 12.5% for **19**; calcd: 13.3% for **18** and 12.29% for **19**) (Annexe 4, Figures A4.15, A4.16).

X-ray analysis revealed that **17** crystallizes in the monoclinic space group $P2_1/n$. Complex **17** consists of the trinuclear [Fe₃O(O₂CCMe₃)₆(HCO₂)] clusters bridged by 1,2-bis(4pyridyl)ethane into 1D coordination polymer of "zig-zag"- type chain (Figure 3.21). The Fe^{III} centers have NO₅ or O₆ donor sets adopting a slightly distorted octahedral coordination environment. Two Fe atoms (F1, Fe2) are coordinated by a μ_3 -oxo atom, four oxygen atoms from bridging pivalate ligands, and a nitrogen atom of 1,2-bis(4-pyridyl) ethane, whereas the remaining one (Fe3) binds a μ_3 -oxo atom and five oxygen atoms of carboxylates. The Fe– μ_3 -oxo bond distances are 1.882(3), 1.893(3) and 1.952(3) Å. Fe-O_{carb} bond distances vary between 1.987(6) and 2.032(5) Å, and Fe–N bond distance is 2.190(4) Å. Selected bond distances in **17** are given in Annexe 1, Table A1.1. The presence of pivalic acid in external sphere leads to the formation of a short intermolecular O–H···O hydrogen bond of 2.517 Å with the coordinated monodentate HCO₂ group. At the same time, the monocoordinated HCO₂ group participates in the formation of intermolecular O–H···O hydrogen bonds (2.581 and 2.666 Å) with pyEt ligand. Interestingly, the packing of coordination polymer **17** results in tube-like channels of diamiter *ca*. 1 nm shown in Figure 3.21 (b).



(b)

Fig. 3.21. A view of an one-dimensional chain in 17 (a). Hydrogen atoms and solvent molecules are omitted. Tube-like channels of diameter *ca*. 1 nm in 17 (b). Fe – green spheres, N – blue, O – red, C – grey balls.

X-ray analysis of **18** revealed that $[Fe_4O_2(piv)_8]$ cluster moieties are linked into infinite zigzag chains by the bridging hmta ligand. Figure 3.22 shows a crystallographically independent repeating unit and a zigzag chain in **18**. Four iron atoms are joined into a butterfly $\{Fe_4(\mu_3-O)_2\}^{8+}$ core by two μ_3 -oxygen atoms and seven bidentate bridging piv⁻ ligands. The coordination spheres of two iron atoms are made of six oxygen atoms that come from four carboxylate groups and two μ_3 -O atoms, whereas the remaining wingtip iron ions present a NO₅ distorted octahedral coordination that arises from one μ_3 -O atom, one nitrogen atom of hmta, and four oxygen atoms of four bridging piv⁻ ligands or two bridging and one chelating piv⁻ ligand. The $\{Fe_4(\mu_3-O)_2\}^{8+}$ core is nonplanar and the Fe1/Fe2/Fe3 and Fe1/Fe3/Fe4 planes form a dihedral angle of 160.5°. Atoms O1 and O2 are displaced from these planes by 0.308 and 0.323 Å, respectively. The

wingtip Fe2 atom is bridged by two pairs of carboxylate groups with the body atoms Fe1 and Fe3, whereas wingtip Fe4 is bridged to the body atoms Fe1 and Fe3 only by two single carboxylate groups (Figure 3.22 a). Therefore, the distances Fe2…Fe3 [3.311(1) Å] and Fe2…Fe1 [3.323(1) Å] are shorter than Fe4…Fe1 [3.402(2) Å] and Fe4…Fe3 [3.440(1) Å]. The inner Fe1 and Fe3 atoms have two oxo bridges and one carboxylate bridge. Selected bond distances in **18** are given in Annexe 1, Table A1.1.



Fig. 3.22. Structure of **18** (a). Simplified view of the chain along the *a* axis in **18** (b). Piv groups and hydrogen atoms are omitted for clarity.

Single-crystal X-ray analysis revealed that coordination polymer **19** crystallizes in the hexagonal space group P6/mcc. The structure comprises two types of identical but symmetryindependent $[Fe^{III}_{3}O(piv)_{6}]^{+}$ cluster moieties covalently cross-linked by 4,4'-bpy spacer ligands into a 3D cationic network, with a cluster/spacer stoichiometry of 2:3. One of the symmetryindependent trinuclear $[Fe^{III}_{3}O(piv)_{6}]$ moieties resides on a mirror plane and another one occupies a special position of the 6 fold inversion axis thus having C_s and C_{3h} crystallographic symmetries, respectively, and their ratio in the structure is 3:1. Neighboring 2-fold symmetry related clusters connected by 4,4'-bpy are approximately coplanar and the planes through their Fe₃O cores form a dihedral angle of 6.5°, while neighboring symmetry independent clusters connected by another 4,4'-bpy ligand are mutually perpendicular. The latter pair of clusters may be regarded as a pseudo-tetrahedral four-connected binodal building block (Figure 3.23). Such building blocks constitute a rare binodal unifom (8,3)-c (**etc**) network, Figure 3.23 (b). Selected bond distances in **19** are given in Annexe 1, Table A1.1.



Fig. 3.23. Pseudo-tetrahedral four-connected binodal building block in **19** (a). The *tert*-butyl group of piv ligands and H atoms are omitted for clarity. The 6-fold interpenetration of (8,3)-c networks viewed along the *c* axis (b). Fragments of individual networks are specified by different colours.

Magnetic measurements of **18** indicate the presence of strong antiferromagnetic interactions between body-body Fe^{III} ions with J_{bb} equals to -22 cm^{-1} , whereas the interaction between Fe-containing clusters is negligible through hmta ligand (Figure 3.24).



Fig. 3.24. Plot of $\chi(T)$ (black includes a paramagnetic impurity, gray does not) and $\chi T(T)$ for **18**.

All intracluster couplings are described by a Heisenberg-type exchange Hamiltonian, assuming an isosceles spin triangle: $\hat{H}_{ex} = -2J_I (\hat{S}_I \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - 2J_2 \hat{S}_I \cdot \hat{S}_3$. Intercluster interactions are taken into account by the molecular field approximation, expressed as $\chi_m^{-1} = \chi_m'^{-1} - \lambda_{mf}$ where χ_m' denotes the molar susceptibility of a discrete {M₃} spin cluster and λ_{mf} the molecular field parameter. Magnetic dc measurements showed that the $\chi_m T$ value of **19** at T = 290 K (7.54 cm³ K mol⁻¹) is smaller than the expected spin-only value of 13.1 cm³ K mol⁻¹ for three isolated S = 5/2 centers ($g_{iso} = 2.0$) (Figure 3.25).



Fig. 3.25. Temperature dependence of χmT for **19** at 0.1 T; solid lines, least-squares fits to the employed phenomenological models. Inset, temperature dependence of the reciprocal susceptibility.

This value and the low-field susceptibility data for compound **19** indicates predominate antiferromagnetic magnetic exchange interactions between the spin centers, mediated by the

central μ_3 -O-bridge and the 4,4'-bpy linkers. A least-squares fit (Figure 3.25) yields $J_1 = -0.1$ cm⁻¹, $J_2 = -27$ cm⁻¹, and $\lambda_{mf} = -0.609$ mol cm⁻³ (SQ = 1.2% for T ≥ 10 K). Both inter- and intracluster exchange interactions of 3D CP **19** are antiferromagnetic as expected.

3.3. Conclusions to the Chapter **3**

- Homometallic Fe^{III} coordination compounds with different structure topology were synthesized, among them 16 homometallic iron(III) clusters, two 1D and one 3D coordination polymers based on {Fe₃O}- and {Fe₄O₂}-type carboxylate clusters.
- Three-dimensional coordination polymer {[Fe₃O(piv)₆(4,4'-bpy)_{1.5}](OH)·0.75(CH₂Cl₂)·n(H₂O)}_n (19) possesses a 6-fold interpenetrated network with rare (8,3)-c (etc) topology.
- Thermogravimetric measurements showed thermal stability of coordination complexes, revealing that the decomposition of molecular clusters begins approx. at 50 °C, except compounds 5, 9, 11, 18, whose decomposition starts from temperatures above 180-200°C.
- Magnetic direct-current measurements of the analyzed compounds revealed predominant antiferromagnetic intracluster interactions in homometallic compounds {Fe₄} (4, 5), {Fe₇} (7), {Fe₆} (8), {Fe₁₂} (13, 14), {Fe₂₂} (15, 16)), and oxo-tetranuclear {Fe₄O₂} (18) and oxo-trinuclear {Fe₃O} (19) cluster-based coordination polymers.
- Magnetic studies of propeller-like {Fe₈O₃} clusters (9-11) revealed both antiferromagnetic exchange interactions dominate along the edges of the propeller and a moderate ferromagnetic interaction along the propeller axis.

4. HETEROMETALLIC POLYNUCLEAR Fe^{III}-Ln^{III} CARBOXYLATE COMPOUNDS

The most succesfull approach to highnuclear mixed metal Fe^{III}-4f^{III} coordination clusters and wheels relies on the reaction of tri- or hexanuclear Fe^{III} carboxylate precursors and lanthanide(III) salts with tri- or tetratopic (butyldiethanolamine and triethanolamine) ligands that capable to bridge both 3d and 4f metal ions in one system [256]. Varying precursors and organic ligands at the presence of azide or dicyanamide under reflux or ultrasonic treatment in methanol solution a number of heterometallic wheels (nona-, deca- and tetracosanuclear) and clusters (hexa- and undecanuclear) were obtained.

A heterometallic wheels {Fe₆Dy₃} (20), {Fe₆Ln₄} (21-24), {Fe₁₈Ln₆} (25-34) [257] and clusters {Fe₄Dy₂} (35-40), {Fe₃MnDy₂} (41), {Fe₇Dy₄} (42) were synthesized from the reaction of [Fe₃O(is)₆(H₂O)₃]NO₃·2(MeCN)·2(H₂O) (1) with the different combination of organic ligands such as mdeaH₂, teaH₃, sodium azide and/or sodium dicyanamide under reflux or ultrasonic irradiation in MeOH/MeCN or EtOH/MeOH solutions. Figure 4.1 shows synthetic routes for preparation of Fe-4f coordination systems: wheels and clusters.



Fig. 4.1. The schematic representation of the synthesis of heterometallic wheels and clusters (**20-42**).

4.1. Nona-, deca-, tetracosanuclear Fe^{III}-Ln^{III} carboxylate wheels

The nonanuclear heterometallic wheel $[Fe_6Dy_3(is)_9(bdea)_6(MeO)_6]$ ·MeOH (20) was prepared by the reaction of precursor (1) with dysprosium(III) nitrate hexahydrate and bdeaH₂ in

methanol solution at the presence of sodium dicyanamide under reflux conditions (see the above Figure 4.1). The ultrasonic irradiation of precursor (1), lanthanide nitrate (where $M^{III} = Dy, Gd$, Ho, Y), sodium azide with bdeaH₂ or teaH₃ in MeOH or mixed solution (MeOH/MeCN or MeOH/EtOH) under ultrasonic irradiation series of decanuclear produces a $[Fe_6M_4(is)_8(N_3)_2(bdea)_{10}] \cdot x(solvents)$ wheels $(M = Dy (21, 3.5(MeOH) \cdot 0.5(H_2O)))$, Gd (22, 2.5(MeOH)), Ho (23, 2(MeOH)), Y (24, 3(MeOH)) and a series of unprecedented large heterometallic [Fe₁₈M₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·x(solvents) wheels (M = Dy (25, 26), Gd (27), Heterometallic Tb (28), Sm (29), Eu (**30**), Ho (**31**), Y (**32**)), respectively. $[Fe_{18}M_6(piv)_{12}(teaH)_{12}(tea)_{13}(N_3)_6]$ x(solvents) (where M = Dy (33) and Nd (34)) pivalate wheels were synthesized using a hexanuclear precursor (B) as a starting material and a similar preparative procedure.

The infrared spectra of **20-32** and **34** display the O–H stretching vibration in the region $3438 - 3416 \text{ cm}^{-1}$ caused by the presence of methanol molecules (**20-24**), uncoordinated hydroxyl groups of teaH²⁻ and solvent EtOH or H₂O molecules (**25-32**, **34**). Spectra of all compounds showed strong peaks of asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups appear in the region $1587 - 1562 \text{ cm}^{-1}$ and $1427 - 1411 \text{ cm}^{-1}$, respectively. The C–H asymmetric and symmetric stretching vibrations of methyl, methylene - (CH₂)- and methyne >(CH)- groups of carboxylates and polyalcohol ligands are observed in the range of $2964 - 2860 \text{ cm}^{-1}$, along with strong single bands in the region $1483 - 1470 \text{ cm}^{-1}$ and $1383 - 1316 \text{ cm}^{-1}$, which correspond to asymmetric and symmetric bending vibrations for alkyl groups methyl and methylene, respectively. The characteristic intensive peaks in the range of $2076 - 2036 \text{ cm}^{-1}$ correspond to N≡N stretching vibration of azide ligands in **21-32** and **34** compounds (Annexe 3, Figures A3.19-A3.32).

TGA curves of **20-24** showed that compounds **21-24** display similar thermal decomposition behavior and release solvent molecules before 220 °C, while compound **20** loses its methanol solvent molecule up to 180 °C (found: 1.16%; calcd: 1.15%). On further heating, the wheels start to decompose in several weakly resolved steps where compound **20** to loses six methoxy groups and organic ligands until 480°C (**20**) (found: 66.33%; calcd: 69.24%), while wheels **21-24** lose azides and organic ligands before 550°C (found: 65.95%; calcd: 69.95%) to the final metal oxide products (found: 32.48% for **20** and 33.15% for **21-24**; calcd: 32.95% for **20** and 34.55 for **21-24**) (Annexe 4, Figure A4.17-A4.21).

Note, according to elemental analyses clusters 25-32 lose theirs solvent molecules during drying of the crystals under vacuum. TGA curves of 25–32 showed that all compounds exhibit

similar thermal behavior and release the remaining guest molecules before 190°C (found: 2.2%). The following two consecutive steps above 650 °C correspond to release of all carboxylate, azido, and tea^{3–} groups, and also the main part of teaH^{2–} ligand (found: 55.91%, calcd: 60.63%). In the last stage burns the rest of two deprotonated teaH^{2–} ligands (found: 8%, calcd: 8.43%) leading to formation of the final product of iron and lanthanide oxides (calcd: 32.02%) (Annexe 4, Figures A4.22, A4.29).

X-Ray data showed that compound $[Fe_6Dy_3(is)_9(bdea)_6(MeO)_6]$ ·MeOH (**20**) crystallizes in the triclinic space group *P*-1 and cluster has C_{3i} symmetry. The core of **20** consists of six Fe^{III} ions and three Dy^{III} ions that are held by nine *syn*,*syn*- η^1 : η^1 : μ_2 bridging isobutyrates, six aminoalcohol ligands and six methoxy groups forming almost ideal ring-type structure with interleaving two Fe^{III} ions and one Dy^{III} ion (Figure 4.2).



Fig. 4.2. Structure of $[Fe_6Dy_3(is)_9(bdea)_6(MeO)_6]$ (20): top view (a) and side view (b). Hydrogen atoms and solvent molecules are omitted. Fe – green, Dy – yellow spheres, N – blue, O – red, C – grey balls.

The coordination geometry around iron atoms can be described as a distorted octahedron with O₆ donor set (two oxygen atoms of two different carboxylates, an oxygen atom of an aminoalcohol ligand and three oxygen atoms of methoxy groups). Fe–O bond distances ranging from 1.950(1) to 2.070(7) Å. Three Dy ions are eight-coordinated and have N₂O₆ coordination environment, where two nitrogen and four oxygen donors are coming from two N-butyldiethanolamine ligands and other two oxygen donors from carboxylates. The Dy–O_{bdea} bond distances are in the range between 2.274(9) and 2.329(6) Å, and Dy–O_{carb} bond distances are in the range of 2.330(2) – 2.357(9) Å. Dy–N bond distances are in the range of 3.057(3) – 4.127(5)

Å and Fe···Dy distances are between 3.352(1) and 3.373(9) Å. Selected bond distances in **20** are given in Annexe 1, Table A1.1.

Compounds $[Fe_6M_4(is)_8(N_3)_2(bdea)_{10}]$ ·MeOH (M = Dy (21), Gd (22), Ho (23), Y (24)) are isomorphous crystallize in the triclinic space group *P*-1 and clusters have C_{2i} symmetry. Singlecrystal X-ray analysis showed that 21-24 comprise wheel-shaped decanuclear $[Fe_6M_4(is)_8(N_3)_2(bdea)_{10}]$ ·clusters built from six Fe^{III} and four M^{III} ions, which are linked by four bridging carboxylates and ten aminoalcohol ligands into a saddle–like structure with a cavity shown in Figure 4.3. Four remaining isobutyrates coordinate chelating to M^{III} ions. The coordination sphere of two Fe^{III} ions is completed by monodentate azide ligand.

Each Fe^{III} atom is six-coordinated and adopts distorted octahedral NO₅ (Fe1, Fe2, Fe4, Fe5) or N₂O₄ (Fe3 and Fe6) geometries. All M^{III} atoms are eight-coordinated with a dodecahedral NO₇ distorted geometry. Fe…M and Fe…Fe distances are in the range 3.352(3) -3.521(10) Å and 3.1576(28) - 6.0792(21) Å, respectively. Selected bond distances in **21-24** are given in Annexe 1, Table A1.1.



Fig 4.3. Structure of [Fe₆Dy₄(is)₈(N₃)₂(bdea)₁₀] (21) (a) and the polyhedra representation of metal atoms in 21 (b). Hydrogen atoms and solvent molecules are omitted. Fe – green,
M - yellow spheres, N – blue, O – red, C – grey balls.

Single crystal X-ray analysis showed that **26-28**, **30-33** clusters crystallize in the triclinic space group *P*-1 and compounds have C_i molecular symmetry. Compounds **25**, **29** and **34** crystallize in the *R*-3 space group and clusters have C_{3i} symmetry. The compounds consist of six {Fe₃M} building units organized in a {Fe₁₈M₆} cyclic structure as shown in Figure 4.4. The core of **25–34** involves 18 Fe^{III} and 6 M^{III} ions interconnected by six isobutyrates and 24 aminoalcohol ligands into a ring with alternating three Fe^{III} and one M^{III} ions. The wheels are

slightly puckered with the Fe^{...}Fe^{...}Fe angle of *ca*. 140° and Fe^{...}M^{...}Fe angle of ca. 114° and form the hole of ca. 1 nm (Figure 4.5), while the external diameter of ultra-large wheels is *ca*. 3.7 nm. The crystal structures of ultra-large wheels display infinite channel formation filled by solvents molecules (Figure 4.5) parallel to the crystal *c* axis for **25**, **29** and **34**, and along the *a* axis for the remaining ones. Upon removal of neutral solvent molecules, the triclinic crystal structures reveal a large total potential solvent accessibile volume of ca. 27%, and trigonal one ca. 44% per unit cell volume, as calculated by PLATON.27. The volume of a unit cell in the crystal of clusters varies from 8132 to 31249 Å³.



Fig. 4.4. Structure of [Fe₁₈Dy₆(is)₁₂(teaH)₁₂(tea)₁₂(N₃)₆] (26) (a). Polyhedra representation of {Fe₃Dy} unit (b). Color definition: Fe – light green, Dy – yellow spheres, N – blue, O – red, C – grey balls. Hydrogen atoms and solvent molecules are omitted.

All Fe centers in **25–34** are six-coordinated adopting a distorted octahedral geometry: 12 Fe atoms have a NO₅ donor set and the remaining six Fe atoms have N₂O₄ donor set. The Fe atoms having a NO₅ donor set are coordinated by one O atom from bridging isobutyrate, four O atoms from three aminoalcohol ligands and one N atom from a doubly deprotonated teaH^{2–}, or by five O atoms from one tea^{3–} and two doubly deprotonated teaH^{2–}, and a N atom of tea^{3–}, while N₂O₄ coordination geometry arises from four O atoms from three aminoalcohols, one N atom from a doubly deprotonated teaH^{2–} and one azide N atom.

All Fe–O bond distances in **25–32** are in the range of 1.900(4) - 2.313(2) Å (Fe–O_{carb}: 1.935(2) - 2.106(2) Å, and Fe–O_{alc}: 1.900(4) - 2.013(4) Å). The Fe–N_{azide} distances range from 2.021(6) to 2.089(3) Å, whereas the Fe–N_{alc} distances are distinctly longer, 2.205(5) - 2.357(3)

Å. All M atoms are eight-coordinated having a distorted square antiprismatic NO₇ environment with M–O distances of 2.275(8) - 2.456(1) Å and M–N distances of 2.602(7) - 2.697(1) Å through five O atoms from two teaH^{2–} and one tea^{3–} ligands, a one N atom from tea^{3–} and O atoms of the bridging and monodentate carboxylate moieties. The Fe…Fe distances along the wheels are in the range of 3.162(3) - 3.222(4) Å, and M…Fe distances are 3.354(1) - 3.534(1) Å. The neighbouring along ring metals polyhedra in **26-35** share common O-O edge. Selected bond distances in **25-33** are given in Annexe 1, Table A1.1.



Fig. 4.5. Formation of infinite channels in trigonal crystal structures of 25, 29 and 34 along the *c* axis (a). Formation of infinite channels in triclinic crystal structures of 26-28 and 30-33 along the *c* axis (b).

The magnetic properties of **20** were investigated by both dc and ac measurements. The dc magnetic data of {Fe₆Dy₃} (**20**) are presented as $\chi_m T$ vs. *T* and M_m vs. *B* curves in Figure 2.2.1.5 a. At 290 K, the value of $\chi_m T$ is 63.25 cm³ K mol⁻¹ which is below the range 65.29–68.41 cm³ K mol⁻¹ expected for six Fe³⁺ and three Dy³⁺ non-interacting center [258]. $\chi_m T$ continously decreases to 22.98 cm³ K mol⁻¹ by lowering temperature to 2.0 K. These observations reveal predominant antiferromagnetic exchange interactions within the compound. The molar magnetizations M_m reaches 16.6 $N_A \mu_B$ at 2.0 K and 5 T. The M_m vs. *B* curve exhibits a distinct slope in the measured range, preventing a more accurate characterization of the exchange interactions. Ac measurements of **20** show out–of–phase magnetic susceptibility χ_m " signals up to 3.6 K at zero bias field (see Figure 4.6 b). We, therefore, analyze the data in terms of a generalized Debye expression [259] by simultaneously fitting the χ_m ' vs. *f* and χ_m " vs. *f* data at

each temperature. In agreement with a single Orbach relaxation process with an effective energy barrier $U_{eff} = (3.6 \pm 0.2) \text{ cm}^{-1}$, and attempt time $\tau_0 = (4.9 \pm 0.6) \times 10^{-6} \text{ s}$.



Fig. 4.6. Dc magnetic data of {Fe₆Dy₃} (**20**); temperature dependence of $\chi_m T$ at 0.1 Tesla; inset: molar magnetization M_m vs. magnetic field B at 2.0 K (a). Ac plot of {Fe₆Dy₃} (**20**): Cole-Cole plot of out-of-phase vs. in-phase molar magnetic susceptibility (b).

The magnetic properties of 21-24 were investigated by both dc and ac measurements. The data of compounds $\{Fe_6Dy_4\}$ (21), $\{Fe_6Gd_4\}$ (22), $\{Fe_6Ho_4\}$ (23) and $\{Fe_6Y_4\}$ (24) in static magnetic fields are shown in Figure 4.7 (a). The $\chi_m T$ vs. T curve of compound {Fe₆Y₄} 24 is characterized by a value of 21.63 cm³ K mol⁻¹ at 290 K, and continously decreases by lowering temperature to 6.61 cm³ K mol⁻¹ at 2.0 K. Both observations reveal dominant antiferromagnetic exchange interactions since six non-interacting Fe^{III} centers are expected to behave as spin =5/2 centers (g = 2) yielding an almost constant value of approximately 26.26 cm³ K mol⁻¹ in the whole temperature range. The diamagnetic Y^{3+} centers are exchanged by Gd^{3+} centers, i.e. nearly pure spin-7/2 centers ($g \approx 1.993$ [258]), in 22. At 290 K, $\chi_m T = 53.86$ cm³ K mol⁻¹ is well below 57.55 cm³ K mol⁻¹ expected for six Fe³⁺ and four Gd³⁺ non-interacting centers revealing predominant antiferromagnetic exchange interactions. The other two compounds of this series (21 and 23) reveal a similar behavior although the lower temperature behavior is affected by anisotropy effects of Dy³⁺ (21), and Ho³⁺ (23) centers, respectively. At 290 K, $\chi_m T =$ 78.50 cm³ K mol⁻¹ (21) and 76.83 cm³ K mol⁻¹ (23) are at the lower limits of or below the values expected for six Fe³⁺ and four respective Ln³⁺ non-interacting centers, therefore indicating predominant antiferromagnetic exchange interactions: 78.30-82.46 cm³ K mol⁻¹ and 79.33-81.41 cm³ K mol⁻¹, respectively [258].

Ac measurements show out–of–phase magnetic susceptibility χ_m " signals only for **21** up to 2.8 K at zero bias field (Figure 4.7 b).



Fig. 4.7. Dc magnetic data of {Fe₆M₄} (**21-24**) compounds; (a): temperature dependence of $\chi_m T$ at 0.1 Tesla; (b): ac data of {Fe₆Dy₄} (**21**).

The magnetic properties of 25-32 were investigated by both dc and ac measurements. Analysis of **32** (comprising diamagnetic yttrium centers instead of lanthanides) reveals the magnetism of the Fe^{III} constituents. In a first approximation, these form six linear Fe₃ trimers, separated by the Y^{III} centers. Assuming a symmetric cluster and normalizing the data to such a linear trimer results in the magnetic properties shown in Figure 4.8 (a) as open circles. All observations combined indicate predominant antiferromagnetic exchange interactions within each Fe₃ unit (*S*=5/2).

Potential interactions between neighboring Fe₃ groups are accounted for by an (isotropic) molecular field approach. The best fit (SQ = 4.1%) reproduces the experimental data as shown in Figure 4.8 (a), yielding $J_{\text{Fe3}} = -12.4 \text{ cm}^{-1}$ ($H_{\text{ex}} = -2J\text{Fe}_3$ ($S_1 \cdot S_2 + S_2 \cdot S_3$), g = 2.0) for both intratrimer exchange interaction energies and $\lambda_{\text{mf}} = -0.412 \text{ mol cm}^{-3}$, that is, $zJ_{\text{inter}} = -0.21 \text{ cm}^{-1}$.

The magnetic data of **32** are compared to the data for **25–31** in Figure 4.8 (b). It is reasonable to infer from this almost constant difference for all compounds including **32** that it mainly arises from the antiferromagnetic interactions within the Fe^{III} "chains" discussed before. Additionally, the $\chi_m T$ curves of **26**, **27**, **28** and **31** also show ferromagnetic interactions within the ring structure revealed by the distinct maxima at approximately 3–4 K. In case of **29** and **30**, no maxima are observed which is due to the almost temperature independent paramagnetism (TIP)–like behavior of the Sm^{III} centers (**29**, multiplets characterized by very close energy levels) and Eu^{III} centers (**30**, $m_J = 0$ ground state), respectively [258].

In addition to the dc measurements, 25-32 were measured in an ac magnetic field in absence of a static field. Only 26 and 28 show any out-of-phase signal and thus slow relaxation above 2.0 K and below 1500 *Hz* (Figure 4.8 c, d).



Fig. 4.8. Magnetic properties of **32**, normalized to a Fe^{III}₃ unit: temperature dependence of $\chi_m T$ at B = 0.1 T (\circ : experimental data, straight lines: calculated data ($S_{eff} = 5/2$ spin system)); inset: molar magnetization M_m vs applied field B at T = 2.0 K. (a). Temperature dependence of $\chi_m T$ at B = 0.1 Tesla of **25-32** (b). Temperature dependence of out-of-phase magnetic susceptibility χ''_m of **26** (c) and **28** (d) in absence of a static field B.

4.2. Hexa- and undecanuclear Fe^{III}-Ln^{III} carboxylate clusters

The ultrasonic treatment of precursor (1) with $M(NO_3)_3 \cdot xH_2O$ (where $M^{III} = Dy$, Gd, Tb, Y, Er, Tm), sodium azide and bdeaH₂ in methanol solution resulted in a series of hexanuclear $[Fe_4M_2(\mu_3-OH)_2(is)_6(bdea)_4(N_3)_2]\cdot 2(MeOH)$ clusters (where M= Dy (**35**), Gd (**36**), Tb (**37**), Y (**38**), Er (**39**), Tm (**40**)). Thhe reaction of precursor (1) with Dy(NO_3)_3 \cdot xH_2O, sodium azide, bdeaH₂ and manganese(II) isobutyrate in methanol solution under reflux conditions gives black crystals of $[Fe_3MnDy_2(\mu_3-OH)_2(is)_6(bdea)_4(N_3)_2]\cdot 2MeOH$ (**41**) cluster. The reaction of precursor (1) with dysprosium(III) nitrate, sodium dicyanamide and bdeaH₂ in methanol under refluxing resulted in yellow crystals of heterometallic nonanuclear { Fe_6Dy_3 } (**20**) wheel. During six

months yellow crystals completely dissolved and started to grow red – brown crystals of an undecanuclear $[Fe_7Dy_4O_4(OH)_3(is)_{9.25}(bdea)_6(NO_3)_{0.75}(H_2O)]$ (42) cluster.

The IR spectra **35-42** revealed strong peaks in the region $1588 - 1558 \text{ cm}^{-1}$ and $1430 - 1407 \text{ cm}^{-1}$, which arise from the asymmetric and symmetric stretching vibrations of the coordinated isobutyrate groups, respectively. The presence of solvate methanol molecules in **35-41**, and hydroxy groups and aqua ligand in **42** gives the O–H stretching vibration of in the region $3449 - 3373 \text{ cm}^{-1}$. In the range of $2962 - 2861 \text{ cm}^{-1}$ appear the C–H asymmetric and symmetric stretching vibrations of methyl, methylene and methyne groups of carboxylates and butyldiethanolamine ligands, whereas the asymmetric and symmetric bending vibrations for these groups produce a strong single band in the region $1473 - 1471 \text{ cm}^{-1}$ and a doublet in the region $1371 - 1361 \text{ cm}^{-1}$, respectively. The C=O stretching vibrations of the monocoordinated carboxylates in **35-42** are observed in the region $1607 - 1600 \text{ cm}^{-1}$. An intensive peak at 2059 (for **41**) and 2061 cm⁻¹ (for **35-40**) corresponds to N=N stretching vibrations of azide ligands. (Annexe 3, Figures A3.33 - A3.40)

TGA curves of clusters **35-41** showed that all compounds display similar thermal decomposition behavior and release solvent molecules before 150 °C. On further heating, the clusters start to decompose in several weakly resolved steps until 500 °C to lose organic ligands and azides (found: 64.30%; calcd: 67.66%) with residual weight of 35.7% (calcd: 35.15%) (Annexe 4, Figures A4.30-A4.36).

Single-crystal X-ray diffraction measurements revealed that clusters **35-41** are isostructural, but crystallize in different space groups: **35, 36** and **41** crystallize in the orthorombic *Pbca* space group, while **37-40** crystallize in the monoclinic $P_{2_1/c}$ space group. All clusters **35-40** built up from four Fe^{III} and two M^{III} ions that are connected by the six is⁻ and four bdea²⁻ ligands (Figure 4.9 a). The core of hexanuclear clusters consisting of {Fe₄M₂} array comprises two {Fe₂M} triangles that are linked to each other through the two bridging (μ_3 -OH⁻) ligands with a M^{...}M distance of 3.815(1) - 3.910(3) Å. Additionally, two (end-on) azide ligands coordinate to two peripheral Fe^{III} ions and two monodentate carboxylates complete the coordination spheres of two M ions. Four isobutyrate ligands are bidentate and coordinate to each pair of Fe and M ions in a *syn*,*syn*- η^1 : η^1 : μ_2 bridging mode, while two remaining coordinate to M1 and M2 ions in a monodentate manner. Cluster **41** has the same structure as **35**, but differ by the type of metal centers and consists of {Fe₃MnDy₂} array.

All Fe centers in 35-40 are six-coordinated adopting a distorted octahedral geometry: two peripheral Fe atoms (Fe3 and Fe6) have a N₂O₄ donor set and the remaining two Fe atoms (Fe4

and Fe5) have NO₅ donor set, whereas each Ln atom is eight-coordinated and has O_8 donor set. Selected bond distances in **35**, **37-41** are given in Annexe 1, Table A1.1.



Fig. 4.9. Structure of [Fe₄Dy₂(OH)₂(is)₆(bdea)₄(N₃)₂]·(35) (a). View of inter- and intramolecular OH…O hydrogen bonds. Hydrogen bonds shown as dotted turquoise lines (b). Color definition:
Fe – light green, Dy – yellow spheres, N – blue, O – red, C – grey balls. Hydrogen atoms and solvent molecules are omitted for clarity.

The presence of hydroxo groups in clusters gives strong intramolecular O–H···O hydrogen bonds of 2.630(2) Å and 2.661(2) Å with an uncoordinated oxygen of C=O group of isobutyrates. Methanol molecules participate in the formation of intermolecular O–H···O hydrogen bonds of 2.721(2) Å and 2.738(2) Å (Figure 4.9 b).

Single-crystal X-ray analysis diffraction showed that $[Fe_7Dy_4O_4(OH)_3(is)_{9.25}(bdea)_6$ (NO₃)_{0.75}(H₂O)] cluster crystallizes in the monoclinic space group $P2_1/c$ and consists of seven iron(III) ions and four dysprosium(III) ions bound via four μ_4 –O and three μ_3 –OH groups, six isobutyrates and six N-butyldiethanolamine ligands. The coordination environment of Dy ions is completed by the coordination of two chelating carboxylate and one nitrate groups, one monodentate aqua and one monodentate carboxylate groups (Figure 4.10 a). The coordination mode of isobutyrates is divided into three categories: the first coordinates in chelating mode to three Dy^{III} ions, the second coordinates to one Fe^{III} and one Dy^{III} ions in *syn,syn*– η^1 : η^1 : μ_2 bridging mode, while remaing isobutyrate coordinates monodentate to Dy ion. Coordination environment of iron atoms is represented as distorted octahedral geometry, four iron centers (Fe1, Fe4, Fe5, Fe7) have a NO₅ donor set and the other three iron centers (Fe2, Fe3 and Fe6) have an O₆ coordination environment. Two Dy^{III} centers (Dy1 and Dy3) possess a distorted

monocapped square antiprism (NO₈ donor set) and two other Dy^{III} ions (Dy2 and Dy4) have a distorted square antiprism geometry (O₈ donor set) (Figure 4.10 b). Selected bond distances in **42** are given in Annexe 1, Table A1.1.



Fig. 4.10. Structure of [Fe₇Dy₄O₄(OH)₃(is)_{9.25}(bdea)₆ (NO₃)_{0.75}(H₂O)] (42) (a) and metallic core in 42 (b). Color definition: Fe – light green, Dy – yellow spheres, N – blue, O – red, C – grey balls. Hydrogen atoms are omitted for clarity.

Dc magnetic data of compounds {Fe₄Dy₂} (**35**), {Fe₄Gd₂} (**36**), {Fe₄Tb₂} (**37**), {Fe₄Y₂} (**38**), {Fe₄Er₂} (**39**) and{Fe₄Tm₂} (**40**) are depicted as symbols in Figure 4.11 (a). The $\chi_m T$ value of **38** is 14.01 cm³ K mol⁻¹ at 290 K, continuously decreases by lowering temperature and almost vanishes at 2.0 K (0.04 cm³ K mol⁻¹). Comparing these values to the expectation 17.51 cm³ K mol⁻¹ for four non–interacting Fe^{III} centers ($S_{Fe} = 5/2$, g = 2) reveals dominant antiferromagnetic exchange interactions within the compound. Taking into account the structure of **38**, the outer Fe^{III} centers form well isolated dimers. Each dimer is therefore characterized by two Fe^{III} centers that show strong antiferromagnetic interactions. They form $S_{total} = 0$ units as indicated by the $M_m vs$. *B* curve at 2.0 K since M_m is zero at all applied magnetic fields (0–5 T).

Replacing the diamagnetic Y^{III} centers by Gd^{III} centers in **36**, $\chi_m T$ is 29.24 cm³ K mol⁻¹ at 290 K. This value is below 33.15 cm³ K mol⁻¹ expected for four Fe^{III} and two Gd^{III} ($S_{Gd} = 7/2$, $g \approx 1.993$ [258]) non–interacting centers revealing predominant antiferromagnetic exchange interactions. $\chi_m T$ continously decreases by lowering temperature, exhibiting a steeper slope compared to **38** at T < 15 K, thus indicating futher antiferromagnetic exchange interactions due to either Fe^{III}–Gd^{III} or Gd^{III}–Gd^{III} interactions, or potentially both. At 2.0 K and 5 T, the molar magnetization is 13.7 $N_A \mu_B$ indicating saturation close to the value 14.0 $N_A \mu_B$ which is expected

for two Gd^{III} non-interacting centers, therefore revealing small lanthanide-transition metal and/or even smaller lanthanide-lanthanide exchange interactions [258].



Fig. 4.11. Dc magnetic data of {Fe₄M₂} compounds; (a): temperature dependence of $\chi_m T$ at 0.1 Tesla; (b): ac data of {Fe₄Dy₂} (**35**): Cole-Cole ($\chi_m'' vs. \chi_m'$) at zero static bias field.

This series consists of four further compounds characterized by $M^{III} = Dy^{III}$ (35), Tb^{III} (37), Er^{III} (**39**), and Tm^{III} (**40**), respectively. The $\chi_m T$ values at 290 K (41.16 cm³ K mol⁻¹ (**35**), 37.15 cm³ K mol⁻¹ (**37**), 36.37 cm³ K mol⁻¹ (**39**), 27.32 cm³ K mol⁻¹ (**40**) are for all compounds lower the respective values expected for four Fe^{III} and two respective M^{III} non-interacting centers: $43.53-45.61 \text{ cm}^3 \text{ K mol}^{-1}$, $41.04-41.53 \text{ cm}^3 \text{ K mol}^{-1}$, $39.61-40.08 \text{ cm}^3 \text{ K mol}^{-1}$, and 31.57 cm³ K mol⁻¹, respectively [258]. Therefore, the exchange interaction between the centers of the compounds are predominantly antiferromagnetic. By lowering temperature, $\chi_m T$ continously decreases for all compounds which is partially due to the antiferromagnetic interaction and partially due to the thermal depopulation of the m_J states. For T < 15 K, the $\chi_m T$ vs. T curves show two different patterns: either $\chi_m T$ rapidly drops down (37) as for 36 or $\chi_m T$ shows a minimum (35, 39, 40). Since the latter are unincisive, they may be due to very small ferromagnetic interactions or paramagnetic impurities. The molar magnetizations $M_{\rm m}$ at 2.0 K and 5 T (10.5 $N_A \mu_B$ (35), 11.1 $N_A \mu_B$ (37), 9.0 $N_A \mu_B$ (39), 7.1 $N_A \mu_B$ (40)) are all below the maximum contributions of two respective lanthanides $(2 \times g_J \cdot J: 20 N_A \mu_B, 18 N_A \mu_B, 18 N_A \mu_B, 18 N_A \mu_B)$ 14 $N_A \mu_B$, respectively). Since the slopes of M_m vs. B curves are still distinct regarding lanthanides, the m_J ground state cannot be definitely determined and even maximum m_J cannot be excluded.

Ac measurements show out–of–phase magnetic susceptibility χ_m'' signals only for 35 up to 5.5 K at zero bias field (see Figure 4.11 b). Due to the shape of the semi-logarithmic plot of τ vs. 1/T, a single, dominant Orbach relaxation process is considered using $\tau = \tau_0 \times \exp(U_{\text{eff}}/(k_BT))$.
The least-squares fit of the data yields an effective energy barrier of $U_{\text{eff}} = (9.7 \pm 0.2) \text{ cm}^{-1}$ and an attempt time of $\tau_0 = (1.1 \pm 0.2) \times 10^{-6} \text{ s}$. These values represent a common effective energy barrier as well as a common attempt time in comparison to other Fe-Ln SMMs [256].

The {Fe₃MnDy₂} (**41**) is isostructural to compound **35** of the archetype {Fe₄Ln₂} except for the replacement of a single Fe^{III} center by a Mn^{III} center which results in slighly different magnetic properties. Elemental analysis revealed that the cluster contains of three iron, one manganese and two dysprosium atoms. The dc magnetic data are presented as $\chi_m T vs. T$ and M_m *vs. B* curves in Figure 4.12 (a). At 290 K, $\chi_m T$ is 41.97 cm³ K mol⁻¹ which is slightly below the range 42.15–44.36 cm³ K mol⁻¹ that is expected for three Fe^{III}, one Mn^{III} and two Dy^{III} non– interacting center [258].



Fig. 4.12. (a): Dc magnetic data of {Fe₃MnDy₂}; temperature dependence of $\chi_m T$ at 0.1 Tesla; inset: molar magnetization $M_m vs$. magnetic field *B* at 2.0 K. (b): Ac magnetic data of {Fe₃MnDy₂} (**41**).

By lowering temperature, $\chi_m T$ continously decreases to 22.98 cm³ K mol⁻¹ at 2.0 K. Both observations reveal predominant antiferromagnetic exchange interactions within the compound. At 2.0 K and 5 T, the molar magnetizations M_m reaches 12.6 $N_A \mu_B$. The $M_m vs$. B curve shows a distinct slope, therefore disallowing further, more accurate characterization of the exchange interactions.

Ac measurements of **41** show out–of–phase magnetic susceptibility χ_m'' signals up to 4.4 K at zero bias field (see Figure 4.12 b).

The magnetic dc data of {Fe₇Dy₄} (**42**) are shown in Figure 4.13 (a) as the field dependence of the molar magnetization $M_{\rm m}$ and the temperature dependence of the product of molar magnetic susceptibility and temperature $\chi_{\rm m}T$. The $\chi_{\rm m}T$ vs. T curves exhibit 66.42 cm³ K mol⁻¹ and 65.42 cm³ K mol⁻¹ at 290 K for 0.1 and 1.0 Tesla, respectively. These

values are well below the range 82.68 – 86.84 cm³ K mol⁻¹ that is expected [258] for seven Fe^{III} and four Dy^{III} non–interacting centers indicating dominant antiferromagnetic exchange interactions potentially between two or more Fe^{III} centers. These values stay almost constant down to $T \approx 50$ K, only decreasing by 1–2 cm³ K mol⁻¹. Cooling beyond 50 K reveals maxima at both applied magnetic fields indicating the presence of ferromagnetic exchange interaction pathways. The maximum at 1.0 T is smaller in comparison to 0.1 T due to the different splits of energy states owing to the Zeeman interaction as also indicated by the deviation from linearity in the magnetization curve for $B \ge 0.5$ T at 2.0 K. At this temperature, the M_m vs. B curve shows a distinct slope, and M_m increases to 28.13 $N_A \mu_B$ at 5 T.

Ac measurements of **42** show out–of–phase magnetic susceptibility χ_m'' signals up to 12 K at zero bias field (see Figure 4.13 b). In agreement with a single Orbach relaxation process with effective energy barrier $U_{eff} = (15.0 \pm 0.2) \text{ cm}^{-1}$, and attempt time $\tau_0 = (3.7 \pm 0.2) \times 10^{-6}$ s. These values represent common values for Fe-Ln SMMs [256].



Fig. 4.13. Dc magnetic data of {Fe₇Dy₄} (42); molar magnetization M_m vs. magnetic field B at 2.0 K; inset: temperature dependence of χ_mT at 0.1 T (open green circles) and 1.0 T (open blue circles) (a). Ac magnetic data of {Fe₇Dy₄} (42): Cole-Cole plot of out-of-phase vs. in-phase molar magnetic susceptibility (b).

4.3. Conclusions to the Chapter 4

• Twenty two heterometallic Fe^{III} -4f^{III} coordination compounds were designed and successfully synthesized. Among them two series of decanuclear { Fe_6M_4 } (21-24) and tetracosanuclear { $Fe_{18}M_6$ } (25-34) wheel-type clusters; and a series of hexanuclear { Fe_4M_2 } (35-40) condensed clusters.

- It was found that the heterometallic wheels {Fe₆Dy₃}(20), {Fe₆M₄}(M^{III} = Dy (21), Gd (22), Ho (23), Y(24)), {Fe₁₈M₆}(M^{III} = Dy (25, 26, 33), Gd (27), Tb (28), Ho (29), Sm (30), Eu (31), Y (32) and Nd (34)) are constructed from the smaller {Fe₃M}, {Fe₂M} or {Fe₃M₂} unit that expanding to highnuclear clusters.
- A series of the largest heterometallic tetracosanuclear 3d/4f wheels, {Fe₁₈M₆}(M^{III} = Dy (25, 26, 33), Gd (27), Tb (28), Ho (29), Sm (30), Eu (31), Y (32) and Nd (34)), currently known was prepared.
- Thermogravimetric measurements showed thermal stability of coordination complexes, revealing that the decomposition of molecular clusters begins approx. at 50 °C, except compounds 21-24, 42 whose decomposition starts from temperatures above 180-200°C.
- Magnetic dc measurements of the analyzed compounds revealed predominant antiferromagnetic intracluster interactions in heterometallic wheel-shaped {Fe₆Dy₃} (20), {Fe₆M₄} (M^{III} = Dy (21), Gd (22), Ho (23), Y(24)), {Fe₁₈M₆} (M = Sm (29), Eu (30), Ho (31), Y(32)), and condensed {Fe₄M₂} (M = Dy (35), Gd (36), Tb (37), Y (38), Er (39), Tm (40)) and {M₄Dy₂}-type (41) (M = Fe, Mn) compounds. Additionally, ferromagnetic exchange interactions were found in the ring structures {Fe₁₈Ln₆} (Ln = Dy (26), Gd (27), Tb (28)) and condensed {Fe₇Dy₄} cluster 42.
- The out-of-phase signals detected in alternate-current susceptibility plot suggests the presence of slow magnetic relaxation of wheels: {Fe₆Dy₃} (20), {Fe₆Dy₄} (21), {Fe₁₈Dy₆} (26), {Fe₁₈Tb₆} (28) and clusters: {Fe₄Dy₂} (35), {M₄Dy₂} (M^{III} = Fe, Mn) (41), {Fe₇Dy₄} (42).
- An effective energy barrier (U_{eff}) and attempt time (τ₀) have been calculated for nonanuclear {Fe₆Dy₃} (20), hexanuclear {Fe₄Dy₂} (35) and undecanuclear {Fe₇Dy₄} (42) clusters

OVERALL CONCLUSIONS AND RECOMMENDATIONS

The *solved scientific problem* in this thesis lies in the fact that the optimal and effective synthetic conditions for the obtaining of cluster-based coordination polymers with porosity and Fe^{III}/Fe^{III} -4f carboxylate clusters that showed slow magnetic relaxation, using of pre-synthesized carboxylate precursor and *N*,*O* - donor organic ligands have been found.

Generalizing obtained scientific and practical results of research, presented in the thesis the following conclusions and recommendations can be made:

- 1. An extensive series of homo- and heterometallic Fe^{III} and Fe^{III} -4f compounds with different nuclearity ranging from di-, tri- tetra-, hexa-, hepta-, octa-, nona-, undeca-, dodeca- up to docosa- and tetracosanuclear cores, metal ratio and coordination topology have been obtained by employing the different synthetic strategies and various bridging and chelating multitopic organic ligands such as carboxylates and *N*,*O*-donor ligands.
- 2. The structure-directed potential of semiflexible amino alcohols and carboxylate bridging ligands has been successfully applied to the preparation of a new family of the currently largest d/f coordination wheels, namely the tetracosanuclear [Fe₁₈M₆(is)₁₂(Htea)₁₈(tea)₆(N₃)₆]·*n*(solvent) (M^{III} = Dy (**25**, **26**), Gd (**27**), Tb (**28**), Sm (**29**), Eu (**30**), Ho (**31**) and Y (**32**)) compounds.
- 3. The use of different O,N-donor bridging ligands leaded to the formation of one- and threedimensional coordination networks by connection the {Fe₃O}- and {Fe₄O₂}-type carboxylate clusters.
- 4. The use of modern analytical methods such as IR spectroscopy, single-crystal X-ray diffraction, thermal analysis and magnetochemistry were used to study the physico-chemical properties and structural features of the synthesized compounds.
- 5. Detailed studies of magnetic properties of a large number of new synthesized Fe^{III}/Fe^{III}-4f clusters and cluster-based coordination polymers were performed that allowed to establish the nature of magnetic interactions between metal ions in these compounds.
- 6. Magnetic measurements revealed predominant antiferromagnetic intracluster interactions in homometallic compounds {Fe₄} (**4**, **5**), {Fe₇} (**7**), {Fe₆} (**8**), {Fe₁₂} (**13**, **14**), and {Fe₂₂} (**15**, **16**)), oxo-tetranuclear {Fe₄O₂} (**18**) and oxo-trinuclear {Fe₃O} (**19**) cluster-based coordination polymers, as well as in heterometallic wheel-shaped {Fe₆Dy₃} (**20**), {Fe₆M₄} (**21-24**), {Fe₁₈M₆} (**25-32**) and condensed {Fe₄M₂} (**35-40**), {M₄Dy₂} (**41**) (M^{III} = Fe, Mn) and {Fe₇Dy₄} (**42**) compounds. Additionally, ferromagnetic exchange interactions were found in the ring structures {Fe₁₈Ln₆} (Ln^{III} = Dy (**25**, **26**), Gd (**27**), Tb (**28**), Ho (**31**)) and

condensed cluster {Fe₇Dy₄} (**42**). In a series of {Fe₈O₃} (**9-11**) propeller-like clusters magnetic studies revealed the presence of antiferromagnetic exchange interactions dominating along the edges of the propeller, while a moderate ferromagnetic interaction is found along the propeller axis.

- 7. The wheel-shaped charge-neutral {Fe₆Dy₃}-(**20**), {Fe₆Dy₄}- (**21**), {Fe₁₈Dy₆}- (**26**), {Fe₁₈Tb₆}- (**28**) type coordination clusters and the condensed {Fe₄Dy₂}- (**35**), {M₄Dy₂}(M^{III} = Fe, Mn) (**41**) and {Fe₇Dy₄}- (**42**) type coordination clusters were found to exhibit slow magnetization relaxation.
- 8. Ac measurements of 20 and 42 show out–of–phase magnetic susceptibility χm'' signals up to 3.6 K and 12 K, respectively at zero bias field, which indicates a slow relaxation of magnetization, with an energy barrier of U_{eff} = (3.6 ± 0.2) cm⁻¹ (20), (9.7 ± 0.2) cm⁻¹ (35) and (15.0 ± 0.2) cm⁻¹ (42), and an attempt time of τ₀ = (4.9 ± 0.6)×10⁻⁶ s (20), (1.1 ± 0.2)×10⁻⁶ (35) and (3.7 ± 0.2)×10⁻⁶ s (42).
- 9. The structural and magnetic data of the obtained polynuclear Fe^{III} clusters have been used for the development of *wxJFinder* program to calculate Heisenberg coupling constants *J* in the $Fe^{III}(\mu_{2+n}-O)Fe^{III}$ system.

PRACTICAL RECOMMENDATIONS

For the construction of Fe^{III} porous coordination polymers, it is recommended to use in the reaction of Fe^{III} oxo-bridged polynuclear carboxylate building units with bridging *N*-organic ligands under hydro(solvo)thermal reactions.

In order to prepare new polynuclear heterometallic Fe^{III}-Ln^{III} compounds, it is recommended the use of ligands that are capable of simultaneously bridging and also providing different coordination pockets for both the 3d (e.g. N-donor ligands) and the 4f metal ions (e.g. O-donor ligands), giving special emphasis to carboxylates and aminopolyalcohols as ligands. Such processes should be assisted by co-ligands that additionally can bridge or complete the coordination spheres of the metal ions.

In order to achieve a better understanding of the magnetic properties of polynuclear heterometallic Fe^{III}-Ln^{III} compounds and the contribution of the 3d metal ions to the SMM properties it is necessary to use in their preparation diamagnetic ions such as Y^{III} or Gd^{III}, which are magnetically isotropic.

The obtained porous materials such as Fe^{III} coordination polymers and carboxylate clusters are recommended for studying their absorption properties and the influence of various guest molecules on changing magnetic properties.

REFERENCES

- Kaplan J., Ward D. M. The essential nature of iron usage and regulation. In: Curr Biol., 2013, vol. 23(15), R642–R646.
- 2. Urdampilleta M. et al. Supramolecular spin valves. In: Nat. Mater., 2011, vol. 10, p. 502–506.
- 3. Murrie M. Cobalt(II) single-molecule magnets. In: Chem. Soc. Rev., 2010, vol. 39, p. 1986-1995.
- 4. Yang C.-I., Zhang Z.-Z., Lin S.-B. A review of manganese-based molecular magnets and supramolecular architectures from phenolic oximes. In: Chem. Soc. Rev., 2015, vol. 289–290, p. 289-314.
- 5. Gatteschi D., Sessoli R., Cornia A. Single-molecule magnets based on iron(III) oxo clusters. In: Chem. Commun., 2000, p. 725-732.
- 6. Wernsdorfer W. et al. Exchange-biased quantum tunnelling in a supramolecular dimer of singlemolecule magnets. In: Nature, 2002, vol. 416, p. 406–409.
- Barra A. L., Gatteschi D., Sessoli R. High-frequency EPR spectra of [Fe₈O₂(OH)₁₂(tacn)₆]Br₈: A critical appraisal of the barrier for the reorientation of the magnetization in single-molecule magnets. In: Chem. Eur. J., 2000, vol. 6, 1608-1614.
- 8. Sessoli R. et al. Magnetic bistability in a metal-ion cluster. In: Nature, 1993, vol. 365, p. 141-143.
- 9. Palii A. et al. Beyond the spin model: exchange coupling in molecular magnets with unquenched orbital angular momenta. In: Chem. Soc. Rev., 2011, vol. 40, p. 3130-3150.
- 10. Lis T. Preparation, structure, and magnetic properties of a dodecanuclear mixed-valence manganese carboxylate. In: Acta Cryst B, 1980, vol. 36, p. 2042-2046.
- Sessoli R. et al. High-spin molecules: [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄]. In: J. Am. Chem. Soc., 1993, vol. 115 (5), p. 1804-1816.
- Osa Sh. et al. A Tetranuclear 3d–4f single molecule magnet: [Cu^{II}LTb^{III}(hfac)₂]₂. In: J. Am. Chem. Soc., 2004, vol. 126 (2), p. 420-421.
- Piquer L. R., Sañudo E. C. Heterometallic 3d–4f single-molecule magnets. In: Dalton Trans., 2015, vol. 44, p. 8771-8780.
- 14. Feltham H. L. C., Brooker S. Review of purely 4f and mixed-metal nd-4f single-molecule magnets containing only one lanthanide ion. In: Coord. Chem. Rev., 2014, vol. 276, p. 1–33.
- 15. Sharples J. W., Collison D. The coordination chemistry and magnetism of some 3d-4f and 4f amino-polyalcohol compounds. In: Coord. Chem. Rev., 2014, vol. 260(100), p. 1–20.
- Liu K., Shi W., Cheng P. Towards heterometallic single-molecule magnets: Synthetic strategy, structures and properties of 3d-4f discrete complexes. In: Coord. Chem. Rev., 2015, vol. 289-290, p. 74–122.
- Schray D. et al. Combined magnetic susceptibility measurements and ⁵⁷Fe mössbauer spectroscopy on a ferromagnetic {Fe^{III}₄Dy₄} ring. In: Angew. Chem., Int. Ed., 2010, vol. 49, p. 5185–5188.
- 18. Li H. et al. Remarkable Ln^{III}₃Fe^{III}₂ clusters with magnetocaloric effect and slow magnetic relaxation. In: Dalton Trans., 2015, vol. 44, p. 468-471.
- 19. Ferbinteanu M. et al. Binuclear Fe^{III} -Dy(III) single molecule magnet. Quantum effects and models. In: J. Am. Chem. Soc., 2006, vol. 128, p. 9008-9009.

- 20. Pointillart F. et al. Effects of 3d–4f magnetic exchange interactions on the dynamics of the magnetization of Dy^{III}-M^{II}-Dy^{III} trinuclear clusters. Chem. Eur. J., 2007, vol. 13(5), p. 1602-1609.
- 21. Xu G.-F. et al. $M^{III}Dy^{III}_{3}$ (M = Fe^{III}, Co^{III}) complexes: three-blade propellers exhibiting slow relaxation of magnetization. In: Inorg. Chem., 2012, vol. 51 (10), p. 5693–5698.
- 22. Bag P. et al. Synthesis, magnetism and Mössbauer studies of tetranuclear heterometallic ${Fe^{III}_2Ln_2}$ (Ln = Gd, Dy, Tb) complexes: evidence of slow relaxation of magnetization in the terbium analogue. In: Dalton Trans., 2014, vol. 43, p. 16366–16376.
- Zhang Y. et al. Tuning the origin of magnetic relaxation by substituting the 3d or rare-earth ions into three isostructural cyano-bridged 3d–4f heterodinuclear compounds. In: Inorg. Chem., 2015, vol. 54 (21), p. 10316–10322.
- Sharma K. V. K. Crystal engineering-where do we go from here? In: Cryst. Growth Des., 2002, 2 (6), p. 465–474.
- 25. Bragg W. H. The structure of organic crystals. In: Proc. Phys. Soc. (London) 34, 1921, p. 33-50.
- Robertson J. M. The measurement of bond lengths in conjugated molecules of carbon centres. In: Proc. R. Soc. London Ser. A, 1951, A207, p. 101-110.
- 27. Robertson J. M. Organic Crystals and Molecules. In: Acta Cryst., 1954, vol. 7, p. 523-524.
- Pepinsky R. Crystal engineering a new concept in crystallography. In: Phys. Rev., 1955, vol. 100, p. 971-971.
- 29. Schmidt G. M. J. Photodimerization in the solid state. In: Pure. Appl. chem., 1971, vol. 27, p. 647-678.
- 30. Cohen M. D. Solid-state photochemical reactions. In: Tetrahedron, 1987, vol. 43(7), p. 1211-1224.
- 31. Herbstein F. H. Crystalline molecular complexes and compounds. In: Oxford University Press, 2005, 606 p.
- Addadi L., Lahav M. Photopolymerization of chiral crystals. 1. The planning and execution of a topochemical solid-state asymmetric synthesis with quantitative asymmetric induction. In: J. Am. Chem. Soc., 1978, vol. 100, p. 2838-2844.
- Leiserowitz L. Molecular packing modes. Carboxylic acids. In: Acta Crystallogr. Sect. B 32, 1976, p. 127-128.
- 34. Thomas J. M., Williams J. O. Dislocations and the reactivity of organic solids. In: Prog. in Solid State Chemistry, 1971, vol. 6, p. 119-154.
- 35. Wegner G. et. al. Energy transfer in the solid state photopolymerisation of diacetylenes. In: Reactivity of solids, 1997, p. 487-492.
- Paul I. C., Curtin D. Y. Thermally induced organic reactions in the solid state. In: Acc. Chem. Res., 1973, vol. 6, p. 217-225.
- Curtin D. Y., Paul I. C. Chemical consequences of the polar axis in organic solid-state chemistry. In: Chem. Rev. 1981, vol. 81, p. 525-541.
- Paul I. C., Curtin D. Y. Reactions of organic crystals with gases. In: Science, 1975, vol. 187, p. 19-26.
- 39. Ermer O. Five-fold diamond structure of adamantane-1,3,5,7-tetracarboxylic acid. In: J. Am.

Chem. Soc., 1988, vol. 110(12), p. 3747-3754.

- 40. Desiraju G. R., Gavezzotti A. From molecular to crystal structure; polynuclear aromatic hydrocarbons. In: J. Chem. Soc., Chem. Commun., 1989, p. 621-623.
- 41. Dunitz J. D. Phase transitions in molecular crystals from a chemical viewpoint. In: Pure Appl. Chem., 1991, vol. 63, p. 177-185.
- 42. Dunitz J. D. In Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity; G. R. Desiraju, Ed.; Wiley: Chichester, 1996. 326 p.
- 43. Lehn J.-M. Cryptates: inclusion complexes of macropolycyclic receptor molecules. In: Pure Appl. Chem., 1978, vol. 50, p. 871-892.
- 44. Lehn J. M. Supramolecular chemistry: concepts and perspectives. In: Weinheim: VCH, 1995. 281 p.
- 45. https://www.nobelprize.org/nobel_prizes/chemistry/laureates/1987/
- Desiraju G. R. Crystal Engineering. The design of organic solids. In: Amsterdam, Elsevier, 1989, 312 p.
- 47. Desiraju G. R. Supramolecular synthons in crystal engineering-a new organic synthesis. In: Angew. Chem., Int. Ed. Engl., 1995, vol. 34, p. 2311-2327.
- 48. Etter M. C. J. Hydrogen bonds as design elements in organic chemistry. In: Phys. Chem., 1991, vol. 95, p. 4601-4610.
- 49. Maddox J. Crystals from first principles. In: Nature, 1988, vol. 335, p. 201-201.
- 50. Feynman R. There's plenty of room at the bottom. In: Eng. Sci., 1960, p. 22-36.
- 51. Wells A. F. Three-dimensional nets and polyhedral. In: Wiley: New York, 1977. 268 p.
- 52. Wells A. F. Further studies of threedimensional nets. In: ACA Monograph, Washington: DC, 1979. 73 p.
- Abrahams B. F., Hoskins B. F., Robson R. A new type of infinite 3D polymeric network containing 4-connected, peripherally-linked metalloporphyrin building blocks. In: J. Am. Chem. Soc., 1991, vol. 113, p. 3606-3607.
- 54. Abrahams B. F. et. al. The archetype for a new class of simple extended 3D honeycomb frameworks. The synthesis and x-ray crystal structures of $Cd(CN)_{5/3}(OH)_{1/3}\cdot 1/3(C_6H_{12}N_4)$, $Cd(CN)_2\cdot 1/3(C_6H_{12}N_4)$, and $Cd(Cn)_2\cdot 2/3H_2O\cdot tBuOH$ ($C_6H_{12}N_4$ = hexamethylenetetramine) revealing two topologically equivalent but geometrically different frameworksIn: J. Am. Chem. Soc., 1991, vol. 113, p. 3045-3051.
- 55. Batten S. R., Hoskins B. F., Robson R. 3D Knitting patterns. Two independent, interpenetrating rutile-related infinite frameworks in the structure of Zn[C(CN)₃]₂. In: Chem. Commun., 1991, p. 445-447.
- 56. Gable R. W., Hoskins B. F., Robson R. Synthesis and structure of [NMe₄][CuPt(CN)₄]: an infinite three-dimensional framework related to PtS which generates intersecting hexagonal channels of large cross section. In: Chem. Commun., 1990, p. 762-763.
- 57. Hoskins B. F., Robson R. J. Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related

frameworks $[N(CH_3)_4][Cu^IZn^{II}(CN)_4]$ and $Cu^I[4,4',4'',4'''-$ tetracyanotetraphenylmethane]BF₄·xC₆H₅NO₂. In: Am. Chem. Soc., 1990, vol. 112, p. 1546-1554.

- 58. Abrahams B. F., Hoskins B. F., Robson R. A honeycomb form of cadmium cyanide. A new type of 3D arrangement of interconnected rods generating infinite linear channels of large hexagonal cross-section. In: Chem. Commun., 1990, p. 60-61.
- 59. Hoskins B. F., Robson R. Infinite polymeric frameworks consisting of three dimensionally linked rod-like segments. In: J. Am. Chem. Soc., 1989, vol. 111 (15), p. 5962–5964.
- 60. MacGillivray L. R., Atwood J. L. A chiral spherical molecular assembly held together by 60 hydrogen bonds. Nature, 1997, vol. 389, p. 469-472.
- 61. Stein A., Keller S. W., Mallouk T. E. Turning down the heat: design and mechanism in solid-state synthesis. In: Science, 1993, vol. 259, 1558-1564.
- 62. Bowes C. L., Ozin G. A. Self-assembling frameworks: beyond micro- porous oxides. In: Adv. Mater., 1996, vol. 8, p. 13-28.
- 63. Cheetham A. K., Ferey G., Loiseau T. Open-framework inorganic materials. In: Angew. Chem., Int. Ed., 1999, vol. 38, p. 3268-3292.
- Yaghi O. M. et. al. Reticular synthesis and the design of new materials. In: Nature, 2003, vol. 423, p. 705-714.
- 65. Seo J. S. et. al. A homochiral metal-organic porous material for enantioselective separation and catalysis. In: Nature, 2000, vol. 404, p. 982-986.
- 66. Desiraju G. R. Chemistry beyond the molecule. In: Nature, 2001, vol. 412, p. 397-400.
- 67. Moulton B., Zaworotko M. J. From molecules to crystal engineering: supramolecular isomerism and polymorphism in network solids. In: Chem. Rev., 2001, vol. 101, p. 1629-1658.
- Eddaoudi M. et. al. Modular chemistry: secondary building units as a basis for design of highly porous and robust metal-organic carboxylate frameworks. In: Acc. Chem. Res., 2001, vol. 34, p. 319-330.
- Cairns A. J. et. al. Supermolecular building blocks (SBBs) and crystal design: 12-connected open frameworks based on a molecular cubohemioctahedron. In: J. Am. Chem. Soc., 2008, vol. 130 (5), p. 1560-1561.
- 70. Nouar F. et. al. Supermolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks. In: J. Am. Chem. Soc., 2008, vol. 130 (6), p. 1833–1835.
- Sheldrick G. M. A short history of SHELX. In: Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, vol. 64, p. 112.
- 72. Macrae C. F. et. al. Mercury: Visualization and Analysis of Crystal Structures. In: J. Appl. Cryst., 2006, vol. 39, p. 453-457.
- 73. Groom C. R. et. al. The cambridge structural database. In: Acta Crystallogr., Sect. B 72, 2016, p. 171-179.
- 74. Khan O. Competing spin interactions and degenerate frustration for discrete molecular spec. In: Chem. Phys. Lett., 1997, vol. 265, p.109-114.
- 75. Wernsdorfer W. et al. Nonadiabatic landau-zener tunneling in Fe8 molecular nanomagnets. In: Europh. Lett., 2000, vol. 50(4), p. 552–558.

- Lippard S. J. Oxo-Bridged Polyiron Centers in Biology and Chemistry. In: Angew. Chem., Int. Ed. Engl. 1988, vol. 27(3), p. 344-361.
- Murray K. S. Binuclear oxo-bridged iron(III) complexes. In: Coord. Chem. Rev., 1974, vol. 12, p. 1–35.
- Lynch J. B. et al. Mössbauer and EPR studies of the binuclear iron center in ribonucleotide reductase from Eswcherichia coli. A new iron-to-protein stoichiometry. In: J. Biol. Chem., 1989, vol. 264, p. 8091-8096.
- 79. Pferiffer P., Breith E., Tsumaki T. Tricyclische orthokondensierte Nebenvalenzringe. In: Liebos Ann. Chem., 1933, vol. 503, p. 84-128.
- 80. Jarenmark M. et al. A monocarboxylate-bridged diiron(III) l-oxido complex that catalyzes alkane oxidation by hydrogen peroxide. In: New J. Chem., 2010, 34, p. 2118–2121.
- Qian J. et al. Two novel dinuclear iron(III) complexes containing μ-oxo-di-μ-carboxylato motif. In: Transition Metal chemistry, 2007, vol. 32(7), p. 847–850.
- 82. Ghattas W. et al. Synthesis and characterization of a binuclear iron(III) complex bridged by 1aminocyclopropane-1-carboxylic acid. Ethylene production in the presence of Hydrogen Peroxide. In: J. Inorg. Chem., 2009, vol. 48(9), p. 3910-3912.
- 83. Wang J. et al. Syntheses, crystal structures, and properties of unsymmetrical (μ-oxo)diiron(III) complexes containing polyimidazole ligands. In: Inorg. Chem. 1996, vol. 35, p. 6642-6643.
- 84. Mimmi M. C. et al. Dinuclear iron complexes of the tridentate ligand N,N-bis(2-ethyl-5-methylimidazol-4-ylmethyl)aminopropane (biap). In: Inorg. Chim. Acta, 2002, vol. 340, p. 197-200.
- Wang S. et al. Synthesis, crystal structures and physical properties of μ-oxo-μ-carboxylato-di iron (111) complexes with tripodal polybenzimidazole ligands containing distinct iron sites. In: Chem. Soc. Dalton Trans., 1995, p. 2045-2055.
- Li J. et al. Synthesis, Crystal structure and magnetic properties of oxo-bridged binuclear iron(III) complex [Fe(phen)₂PhCOO]₂OCl₂·7HzO. In: Polyhedron, 1995, vol. 14, p. 3519-3523.
- 87. Adams H. et al. Manganese(II) and iron(III) complexes of the tridentate ligands bis(benzimidazol-2-ylmethyl)-amine (L¹) and -methylamine (L²). Crystal structures of $[MnL^1(CH_3CO_2)_2]$, $[FeL^2Cl_3]$, and $[Fe_2L^1_2(\mu-O){\mu-(CH_3)_3CCO_2}_2][ClO_4]_2$. In: J. Chem. Soc., Dalton Trans., 1990, p. 1727-1735.
- Ookubo T. et al. cis-μ-1,2-peroxo diiron complex: structure and reversible oxygenation. In: J. Am. Chem. Soc., 1996, vol. 118, p. 701-702.
- Yamashita M. et al. Regioselective arene hydroxylation mediated by a (μ-peroxo)diiron(III) complex: a functional model for toluene monooxygenase. In: J. Am. Chem. Soc., 2007, vol. 129, p. 2-3.
- 90. Do L. H., Lippard S. J. Toward functional carboxylate-bridged diiron protein mimics: achieving structural stability and conformational flexibility using a macrocylic ligand framework. In: J. Am. Chem. Soc., 2011, vol. 133, p. 10568-10581.
- Mikuriya M. et al. Synthesis and structural characterization of di-μ-Phenoxo-bridged dinuclear iron(III) complexes with ferromagnetic or weak antiferromagnetic coupling. In: Bull. Chem. Soc. Jpn., 2001, vol. 74, p. 1425-1434.

- 92. Georgopoulou A. N. et al. Mössbauer spectra of two extended series of basic iron(III) carboxylates [Fe₃O(O₂CR)₆(H₂O)₆]A (A⁻ = ClO⁴⁻, NO³⁻). In: Hyperfine Interact (Springer), 2010, vol. 198(1), p. 229-241.
- 93. Duttaa A. K., Majia S. K., Duttab S. A symmetric oxo-centered trinuclear chloroacetato bridged iron(III) complex: Structural, spectroscopic and electrochemical studies. In: Journal of Molecular Structure, 2012, vol. 1027, p. 87-91.
- 94. Boudalis A. K. et al. A trinuclear cluster containing the $\{Fe_3(\mu_3-O)\}^{7+}$ core: Structural, magnetic and spectroscopic (IR, Mössbauer, EPR) studies. In: Polyhedron, 2005, vol. 24, p. 1540–1548.
- 95. Anson C. E. et al. Crystal structures of the isomorphous prototypic oxo-centered trinuclear complexes [Cr₃O(OOCCH₃)₆(H₂O)₃]Cl·6H₂O and [Fe₃O(OOCCH₃)₆(H2O)₃] Cl·6H₂O. In: Inorg. Chem., 1997, vol. 36, p. 1265-1267.
- 96. Abdulwahab K. et al. Synthesis of monodispersed magnetite nanoparticles from iron pivalate clusters. In: Dalton Trans., 2013, vol. 42, p. 196-206.
- 97. Sowrey F. E. et al. Spin frustration and concealed asymmetry: structure and magnetic spectrum of [Fe₃O(O₂CPh)₆(py)₃]ClO₄·py. In: J. Chem. Soc., Dalton Trans., 2001, p. 862–866.
- Çelenligil-Çetin R., Staples R. J., Stavropoulos P. Synthesis, characterization, and reactivity of ferrous and ferric oxo/peroxo pivalate complexes in relation to gif-type oxygenation of substrates. In: Inorg. Chem., 2000, vol. 39, p. 5838-5846.
- 99. Apfela U.-P. et al. Investigation of amino acid containing [FeFe] hydrogenase models concerning pendant base effects. In: J. of Inorg. Biochem., 2009, vol. 103(9), p. 1236–1244.
- Prodius D. et al. Catalytic "triangles": binding of iron in task-specific ionic liquids. In: Chem. Commun., 2013, vol. 49, p. 1915-1917.
- Supriya S., Das S. K. Reversible single crystal to single crystal transformation through Fe-O(H)Me/Fe-OH2 bond formation/bond breaking in a gas-solid reaction at an ambient condition. In: J. Am. Chem. Soc., 2007, vol. 129, p. 3464-3465.
- 102. Thundathil R. V. et. al. Preparation and properties of iron(III)-amino acid complexes. 2. The crystal and molecular structure of monoclinic tri-µ₃-oxo-triaquohexakis(glycine)triiron(III) perchlorate. In: J. Am. Chem. Soc., 1977, vol. 99 (6), p. 1818–1823.
- 103. Holt E. M. et. al. Preparation and properties of iron(III)-amino acid complexes. Iron(III)-alanine, a possible ferritin analog. In: J. Am. Chem. Soc., 1974, vol. 96 (8), p. 2621–2623.
- 104. Blake A. B., Fraser L. R.. Crystal structure and mass spectrum of μ₃-oxo-hexakis(μ-trimethylacetato)-trismethanoltri-iron(III) chloride, a trinuclear basic iron(III) carboxylate. In: J. Chem. Soc., Dalton Trans., 1975, vol. 0, p. 193-197.
- 105. Gorinchoy V. et al. Homotrinuclear $Fe_3^{III} \mu$ oxo salycilate cluster. Synthesis, structure and properties. In: Chem. J. Mold., 2013, vol. 8(2), p. 83-89.
- 106. Shova S. et. al. Mixed-ligands μ_3 -oxo trinuclear carboxylates [Fe₃O(CH₂BrCOO)_{1.5}(CH₂ClCOO)_{4.5}(H₂O)₃] Br_{0.75} Cl_{0.25} 5H₂O and [Fe₃O(BrCH₂COO)₆ (H₂O)₃] NO₃·2.63(H₂O). In: Chem. J. M., 2008, vol. 3, p. 86-94.
- 107. Melnic S. et. al. Biotechnological application of homo- and heterotrinuclear iron(III) furoates for cultivation of iron-enriched *Spirulina*. In: Inorg. Chim. Acta, 2011, vol. 373 (1), p. 167-172.

- 108. Cadelnic I. et. al. Crystal and molecular structure of [Fe₃O(C₆H₅COO)₆(H₂O)3].₃-Cl-PyH.(CH₃C₆H₄SO₃)_{2.2}H₂O. In: Pol. J. Chem., 1997, vol. 71, p. 501-508.
- 109. Пономарев В. И. и др. Кристаллическая структура трифторацетатного трехъядерного комплекса железа смешанной валентности [Fe₃O(O₂CCF₃)₆(H₂O)₃] ·3.5(H₂O). В: Доклад. АН СССР, 1982, т. 262, 2, стр. 346-350.
- Novitchi Gh. Et. al. Mechanism of pyridine–ligand exchanges at the different labile sites of 3d heterometallic and mixed valence μ₃-oxo trinuclear clusters. In: Inorg. Chem., 2008, vol. 47 (22), p. 10587–10599.
- 111. Högbom M., Nordlund P. A protein carboxylate coordinated oxo-centered tri-nuclear iron complex with possible implications for ferritin mineralization. In: FEBS Lett., 2004, vol. 567, p. 179-182.
- 112. Mitrikas G. et al. Electron spin-lattice and spin-spin relaxation study of a trinuclear iron(III) complex and its relevance in quantum computing. In: Phys. Chem. Chem. Phys., 2008, vol. 10, p. 743-748.
- Saalfrank R. W. et al. Trinuclear oxo-centered iron and Iron/Nickel Clusters Ligand-Controlled Homo/Hetero Valency. In: Eur. J. Inorg. Chem., 2005, p. 1383–1387.
- 114. Raptopoulou C. P. et al. Salicylaldoxime (H₂salox) in iron(III) carboxylate chemistry: Synthesis, X-ray crystal structure, spectroscopic characterization and magnetic behavior of trinuclear oxocentered complexes. In: Polyhedron, 2005, vol. 24(5), p. 711–721.
- Georgopoulou A. N., Sanakis Y., Boudalis A. K. Magnetic relaxation in basic iron(III) carboxylate [Fe₃O(O₂CPh)₆(H₂O)₃]ClO₄·py. In: Dalt. Trans., 2011, vol. 40, p. 6371–6374.
- 116. Boskovic C. et al. Synthesis and characterization of a new family of bi-, tri-, tetra-, and pentanuclear ferric complexes. In: Inorg. Chem. 2004, vol. 43, p. 5053–5068.
- Alborés P., Rentschler E. A T-shaped µ₃-oxido trinuclear iron cluster with high easy-plane anisotropy: structural and magnetic characterization. In: Eur. J. Inorg. Chem., 2008, vol. 25, p. 4004–4011.
- 118. Bagai R. et al. Diversity of new structural types in polynuclear iron chemistry with a tridentate N,N,O ligand. In: Inorg. Chem., 2007, vol. 46(11), p. 4535-4547.
- 119. Yana B., Chen Z.-D. A novel tetranuclear iron complex [Fe₄O₂(O₂CC2H₅)₇(bipy)₂]PF₆·2H₂O (bipy=2,2'-bipyridine): crystal structure and magnetic property. In: Inorg. Chem. Comm., 2001, vol. 4, p. 138-141.
- 120. Arizaga L. et al. Synthesis, crystal structures, electrochemical and magnetic properties of polynuclear {Fe₄} and {Fe₈Na₄} carboxylate/picolinate clusters. In: Inorg. Chim. Acta, 2011, vol. 370, p. 427-434.
- 121. Boudalis A. K. et al. Novel rectangular $[Fe_4(\mu_4-OHO)(\mu-OH)_2]^{7+}$ versus "Butterfly" $[Fe_4(\mu_3-O)_2]^{8+}$ core topology in the Fe^{III}/RCO₂⁻/phen reaction systems (R= Me, Ph; phen= 1,10-Phenanthroline): preparation and properties of $[Fe_4(OHO)(OH)_2(O_2CMe)_4(phen)_4](ClO_4)_3$, $[Fe_4O_2(O_2CPh)_7(phen)_2](ClO_4)$, and $[Fe_4O_2(O_2CPh)_8(phen)_2]$. In: Inorg. Chem., 2002, vol. 41, p. 6474-6487.
- 122. Dutta A. K. et al. Synthesis, structural and magnetic properties of oxo-, chloroacetato-bridged

tetra-nuclear iron(III) complex. In: J. Molec. Struct., 2012, vol. 1029, p. 68-74.

- 123. Dutta A. K. et al. Syntheses, crystal structure, spectroscopic, redox and magnetic properties of oxo- and carboxylato-bridged polynuclear iron(III) complexes with phenolate- and pyridine-substituted benzimidazole ligands. In: Polyhedron, 2012, vol. 44, p. 34-43.
- 124. Chaudhuri P. et al. Synthesis, structure and magnetism of a tetranuclear Fe(III) complex containing an $[Fe_4(\mu_3-O)_2]^{8+}$ core. In: Inorg. Chim. Acta, 1993, vol. 212, p. 241-249.
- 125. Dendrinou-Samara C. et al. Interaction of Fe(III) with herbicide-carboxylato ligands di-, tri- and tetra-nuclear compounds: Structure and magnetic behaviour. In: Polyhedron, 2007, vol. 26, p. 763-772.
- 126. Chaudhuri P. et al. Ground spin state variation in carboxylate-bridged tetranuclear [Fe₂Mn₂O₂]⁸⁺ cores and a comparison with their [Fe₄O₂]⁸⁺ and [Mn₄O₂]⁸⁺. In: Congeners. Eur. J. Inorg. Chem., 2003, p. 541-555.
- 127. Bacsa J., Zhao H., Dunbar K. R. Two new soluble iron-oxo complexes: Fe₂(-O)(- $O_2CCF_3)_2(O_2CCF_3)_2(C_{10}H_8N_2)_2$ and Fe₄(3-O)₂(- $O_2CCF_3)_6(O_2CCF_3)_2(C_{10}H_8N_2)_2$ ·CF₃CO₂H. In: Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2003, vol. 59(12), m561-m564.
- 128. Armstrong W. H., Roth M. E., Lippard S. J. Tetranuclear iron-oxo complexes. Synthesis, structure, and properties of species containing the nonplanar {Fe₄O₂}⁸⁺ core and seven bridging carboxylate ligands. In: J. Am. Chem. Soc., 1987, vol. 109 (21), p. 6318-6326.
- 129. Cortes P. et al. Two oxo complexes with tetranuclear $Fe_4(\mu-O)^{28+}$ and trinuclear $Fe_3(\mu-O)^{7+}$ units. In: Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2006, vol. 62(7), m297-m302.
- Dimitrakopoulou A. et al. Interaction of Fe(III) with herbicide-carboxylato ligands. Di-, tri- and tetra-nuclear compounds: Structure, antimicrobial study and DNA interaction. In: Inorg. Chim. Acta, 2007, vol. 360, p. 546-556.
- 131. Overgaard J. et al. Experimental and theoretical electron density distribution and magnetic properties of the butterfly-like complex [Fe₄O₂(O₂CCMe₃)₈(NC₅H₄Me)₂]·2CH₃CN. In: Inorg. Chem., 2003, vol. 42, p. 7593-7601.
- Celenligil-Cetin R., Staples R. J., Stavropoulos P. Synthesis, characterization, and reactivity of ferrous and ferric oxo/peroxo pivalate complexes in relation to Gif-type oxygenation of substrates. In: Inorg. Chem., 2000, vol. 39, p. 5838-5846.
- 133. Gkioni C. et al. 2-Pyridyl ketone oximes in iron(III) carboxylate chemistry: Synthesis, structural and physical studies of tetranuclear clusters containing the $[Fe_4(\mu_3-O)_2]^{8+}$ 'butterfly' core. In: Polyhedron, 2009, vol. 28, p. 3221-3226.
- 134. Wemple M. W. et al. New tetranuclear metal carboxylate clusters with the $[M_4(\mu_3-O)_2]^{8+}$ (M=Mn^{III} or Fe^{III}) cores: crystal structures and properties of $[Mn_4O_2Cl_2(O_2CC_6H_3F_2-3,5)_6(py)_4]$, $[Fe_4O_2Cl_2(O_2CMe)_6(bpy)_2]$ and $[NBu^n_4][Fe_4O_2(O_2CMe)_7(pic)_2]$. In: J. Chem. Soc., Dalton Trans., 1998, p. 719-726.
- 135. Boudalis A. K. et al. A new example of a tetranuclear iron(III) cluster containingthe [Fe₄O₂]⁸⁺ core: preparation, X-ray crystal structure, magnetochemistry and Mössbauer study of [Fe₄O₂(O₂CMe)₆(N₃)₂(phen)₂]. In: Inorg. Chim. Acta, 2004, vol. 357, p. 1345-1354.
- 136. Stamatatos T. C. et al. Reactivity and structural and physical studies of tetranuclear iron(III)

clusters containing the $[Fe_4(\mu_3-O)_2]^{8+}$ "butterfly" core: an Fe^{III}_4 cluster with an S=1 Ground State. In: Inorg. Chem., 2006, vol. 45, p. 7372-7381.

- Dutta S. K. et al. Formation of oxo-bridged tetrairon(III) complexes mediated by oxygen activation. Structure, spectroscopy, magnetism and electrochemistry. In: New J. Chem., 2007, vol. 31, p. 93-101.
- 138. Tanase T. et al. Tetranuclear iron(III) complexes with a planar $(\mu 0x0)(\mu hydroxo)bis(\mu alkoxo)bis(\mu carboxylato)tetrairon core derived from hydrolysis of carboxylic acid amides by diiron(III) center. In: Inorg. Chim. Acta, 2000, vol. 297, p. 18-26.$
- 139. Pires B. M. et al. Synthesis, characterization and catalase-like activity of the tetranuclear iron(III) complex involving a (μ-oxo)(μ-hydroxo)bis(μ-alkoxo)tetra(μ-carboxylato) tetrairon core. In: Inorg. Chim. Acta, 2013, vol. 407, p. 69-81.
- 140. Horn A. et al. Crystal structure and magnetic properties of a new tetranuclear iron (III) complex with asymmetric iron coordination as a model for polynuclear iron proteins. In: Inorg. Chem. Comm., vol. 4(4), 2001, p. 173-176.
- 141. Yao H.-C. et al. Synthesis, structure and magnetic properties of tetra- and heptanuclear iron(III) clusters incorporating phosphonte ligands. In: Inorg. Chim. Acta, 2005, vol. 358, p. 2523-252.
- 142. Mikuriya M., Hashimoto Y., Nakashima S. A novel pentanuclear iron(III) complex with a defective double-cubane core. In: Chem. Commun., 1996, p. 295-296.
- 143. Kizas C. M. et al. Pentanuclear complexes with unusual structural topologies from the initial use of two aliphatic amino-alcohol ligands in Fe chemistry. In: Dalton Trans., 2012, vol. 41, p. 1544-1552.
- 144. Bagai R. et al. Unusual structural types in polynuclear iron chemistry from the use of N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine (edteH₄): Fe₅, Fe₆, and Fe₁₂ Clusters. In: Inorg. Chem., 2008, vol. 47, p. 3318-3327.
- 145. Jones L. F. et al. The role of diisopropanolamine (dipaH₃) in cluster dimerisation and polymerisation: from spin frustrated S=5 Fe^{III}₆ clusters to the novel 1-D covalent polymer of mixed valence [Co^{II}₃Co^{III}] tetramers. Dalton Trans., 2005, p. 3344-3352.
- 146. Jiang G. et al. Synthesis, structure and characterization of Fe₆ molecular clusters with peripheral sulfur atom-capped silver nanoparticles. In: CrystEngComm, 2014, vol. 16, p. 472-478.
- 147. Cooper P. et al. Synthesis, structural, magnetic and high frequency EPR studies on a hexametallic Fe(III) complex with a highly rhombic S = 5 ground state. In: Inorg. Chim. Acta, vol. 361, 2008, p. 3663–3668.
- 148. Cañada-Vilalta C. et al. Two new hexanuclear iron(III) complexes with S = 5 ground states. In: J. Chem. Soc., Dalton Trans., 2002, p. 4005-4010.
- 149. Tahir A. A. et al. Nanostructured r-Fe₂O₃ thin films for photoelectrochemical hydrogen generation. In: Chem. Mater., 2009, vol. 21, p. 3763-3772.
- 150. Smith A. A. et al. High-temperature synthesis of polynuclear iron oxo-hydroxy complexes. In: Polyh., 2004, vol. 23, p. 1557-1565.
- 151. Papatriantafyllopoulou C. et al. Hexanuclear complexes from the use of a series of amino-alcohol ligands in Fe chemistry. In: Polyhedron, 2013, vol. 64, p. 218-230.

- 152. Murugesu M., Abboud K. A., Christou G. New hexanuclear and dodecanuclear Fe(III) clusters with carboxylate and alkoxide-based ligands from cluster aggregation reactions. In: Polyhedron, 2004, vol. 23, p. 2779-2788.
- 153. Micklitz W. et al. Characterization of a novel p,-peroxide tetrairon unit of possible relevance to intermediates in metal-catalyzed oxidations of water to dioxygen. J. Am. Chem. Soc., 1989, vol. 111(1), p. 372-374.
- 154. Houton E. et al. Bulking up: Hexanuclear oximato Fe(III) complexes surrounded by sterically demanding co-ligands. In: Inorg.Chim. Acta, 2014, 421, p. 416–422.
- 155. Canaj A. B. et al. Employment of 2-pyrrole aldoxime in iron cluster chemistry: Trinuclear and hexanuclear clusters In: Polyh., 2013, vol. 52, p. 1411-1415.
- 156. Mason K. et al. Building Fe(III) clusters with derivatised salicylaldoximes. In: Dalton Trans., 2010, vol. 39, p. 2727-2734.
- 157. Raptopoulou C. P. et al. Hexanuclear iron(III) salicylaldoximato complexes presenting the $[Fe_6(\mu_3-O)_2(\mu_2-OR)_2]^{12+}$ core: syntheses, crystal structures, and spectroscopic and magnetic characterization. In: Inorg. Chem., 2006, 45, p. 2317–2326.
- Seddon E. J., Huffman J. C., Christou G. A new core topology in hexanuclear iron(III) carboxylate chemistry: [Fe₆O₃(O₂CMe)₉(OEt)₂(bpy)₂](ClO₄). In: J. Chem. Soc., Dalton Trans., 2000, p. 4446-4452.
- Brechin E. K. et al. New hexanuclear and octanuclear iron(III) oxide clusters: octahedral [Fe₆O₂]¹⁴⁺ species and core isomerism in [Fe₈O₄]¹⁶⁺ complexes. In: Inorg. Chim. Acta, 2000, vol. 297, p. 389-399.
- Cañada-Vilalta C. et al. Methanolysis and phenolysis routes to Fe₆, Fe₈, and Fe₁₀ complexes and their magnetic properties: a new type of Fe₈ ferric wheel. In: Inorg. Chem., 2003, vol. 42, p. 7819-7829.
- 161. Trettenhahn G. et al. A hexanuclear iron(III) carboxylate with an $[Fe_6(\mu_3-O)_3(\mu_2-OH)]^{11+}$ core as an efficient catalyst for cycloalkane oxidation. In: Angew. Chem. Int. Ed., 2006, vol. 45, p. 2794-2798.
- 162. Milunovic M. N. et al. Hexanuclear and undecanuclear iron(III) carboxylates as catalyst precursors for cyclohexane oxidation. In: Dalton Trans., 2013, vol. 42(40), p.14388-14401.
- 163. Ako A. M. et al. Odd-numbered Fe^{III} complexes: synthesis, molecular structure, reactivity and magnetic properties. In: Inorg. Chem., 2007, vol. 46, p. 756–766.
- 164. Mondal K. C. et al. A strongly spin-frustrated Fe^{III}₇ complex with a canted intermediate spin ground state of S=7/2 or 9/2. In: Chem. Eur. J., 2015, vol. 21, p. 10835–10842.
- 165. Kizas C. M. et al. Synthesis, magnetic and spectroscopic characterization of a new Fe₇ cluster with a six-pointed star topology. In: Polyhedron, 2013, vol. 64, p. 280-288.
- 166. Datta S. et al. EPR characterization of half-integer-spin iron molecule-based magnets. In: Polyhedron, 2007, vol. 26, p. 2243-2246.
- 167. Jones L. F. et al. Heptanuclear iron(III) triethanolamine clusters exhibiting 'millennium dome'-like topologies and an octanuclear analogue with ground spin states of S = 5/2 and 0, respectively. In: J. Mater. Chem., 2006, vol. 16, p. 2690-2697.

- Xiong G. et al. C A new octanuclear Fe₈ cluster with antiferromagnetic coupling. In: Inorg. Chem. Comm., 2013, vol. 35, p. 89-91.
- 169. Gass I. A. et al. Polymetallic clusters of iron(III) with derivatised salicylaldoximes. In: Dalton Trans., 2008, p. 2043-2053.
- 170. Murugesu M., Abboud K. A., Christou G. Preparation and properties of new Fe₆ and Fe₈ clusters of iron(III) with tripodal ligands. In: Dalton Trans., 2003, p. 4552-4556.
- 171. Tolis E. I. et al. Synthesis and characterization of iron(III) phosphonate cage complexes. In: Angew. Chem. Int. Ed., 2003, vol. 42, p. 3804–3808.
- 172. Khanra S. et al. Synthesis, structural and magnetochemical studies of iron phosphonate cages based on {Fe₃O}⁷⁺ core. In: Inorg. Chem., 2009, vol. 48, p. 5338–5349.
- 173. Ferguson A., Thomas L. H., Murrie M. Coordinative flexibility of the 2-amino-2-(hydroxymethyl)propane-1,3-diol ligand in the synthesis of polynuclear Fe(III) complexes. In: Polyhedron, 2013, vol. 52, p. 227-233.
- 174 Ammala P. et al. An octanuclear Fe^{III} compound featuring a new type of double butterfly iron–oxo core. Angew. Chem. Int. Ed., 2000, vol. 39, issue 9, p. 1688-1690.
- 175. Khanra S. et al. Synthesis, structural characterisation and magnetic studies of polymetallic iron phosphonate cages. In: Dalton Trans., 2009, p. 6166-6174.
- 176. Cañada-Vilalta C., Pinka M., Christou G. A phenolysis route to a new type of octanuclear iron(III) wheel: [Fe₈(OH)₄(OPh)₈(O₂CBut)₁₂]. In: Chem. Commun., 2003, p. 1240–1241.
- 177. Jones L. F. et al. Octametallic and hexadecametallic ferric wheels. In: Angew. Chem. Int. Ed., 2002, vol. 41, No.22, p. 4318-4321.
- 178. Jones L. F. et al. Fe(III) clusters built with tripodal alcohol ligands. In: Polyhedron, 2006, vol. 25(2), p. 325–333.
- 179. Y. Z. Zeng., Winpenny R. E. P. Solvothermal preparation of iron phosphonate cages. In: Sci China Chem., 2012, vol. 55(6), p. 910-913.
- 180. Goura J, Liu J., Goddard P., Chandrasekhar V. A direct three-component reaction for the isolation of a nonanuclear iron(III) phosphonate. In: Eur. J. Inorg. Chem., 2014, p. 4342–4348.
- Mitkina T. V. et al. Cleavage of P–S bonds and oxygenation by a trinuclear iron carboxylate: Synthesis and structures of iron clusters containing group 15/16 anions. In: Dalton Trans., 2008, p. 1136–1139.
- 182. Konar S., Bhuvanesh N., Clearfield A. Oxo-, hydroxo-, and peroxo-bridged Fe(III) phosphonate cages. In: J. Am. Chem. Soc., 2006, vol. 128, p. 9604-9605.
- Tolis E. I. et al. Studies of an Fe₉ tridiminished icosahedron. In: Chem. Eur. J., 2006, vol. 12, p. 8961–8968.
- Bagai R. et al. Exchange-biased dimers of single-molecule magnets in off and onn states. In: J. Am. Chem. Soc., 2007, vol. 129, p. 12918-12919.
- 185. Benelli C. et al. Template-mediated selfassembly of six- and eight-membered iron coronates. In: Angew. Chem., Int. Ed. Engl., 1996, vol. 35, p. 1825-1828.
- 186. Kooijman H. et al. cyclo-Decakis(μ-2,2-diphenylacetato-*O*,*O*)-dodecakis(μ-methoxo) decairon(III)) mixed solvate. In: Acta Crystallogr., Sect. E, 2002, vol. 58, m93-m95.

- Taft K. L., Lippard S. J. Synthesis and structure of [Fe(OMe)₂(O₂CCH₂CI)] to, a molecular ferric wheel. In: J. Am. Chem. Soc., 1990, vol. 112, p. 9629-9630.
- 188. Taft K. L. et al. [Fe(OMe)₂(O₂CCH₂Cl)]₁₀, a Molecular Ferric Wheel. In: J. Am. Chem. Soc., 1994, vol. 116 (3), p. 823–832.
- Jiang G. et al. A supramolecular assembly of {Fe₁₀} molecular wheels with tubular structures. In: CrystEngComm., 2006, vol. 8, p. 384-387.
- 190. Stamatatos T. C. et al. High-yield syntheses and reactivity studies of Fe10 "ferric wheels": structural, magnetic, and computational characterization of a star-shaped Fe8 complex. In: Inorg. Chem., 2008, vol. 47(19), p. 9021-9034.
- 191. Frey M. et al. Modeling surface engineering: use of polymetallic iron cages and computer graphics to understand the mode of action of a corrosion inhibitor. In: Angew. Chem., Int. Ed., 1998, vol. 37, p. 3246-3248.
- 192. Raptopoulou C. P., Tangoulis V., Devlin E. [{Fe(OMe)₂[O₂CC(OH)Ph₂]}₁₂]: Synthesis and characterization of a new member in the family of molecular ferric wheels with the carboxylatobis(alkoxo) bridging unit. In: Angew. Chem. Int. Ed., 2002, vol. 41(13), p. 2386-2389.
- Konar S., Clearfield A. Synthesis and characterization of high nuclearity iron(III) phosphonate molecular clusters. In: Inorg. Chem., 2008, vol. 47, p. 5573-5579.
- 194. Watton S. P. et al. A cyclic octadecairon(III) complex, the molecular 18-Wheeler. In: Angew. Chem. Int. Ed. Engl., 1997, 36(24), p. 2774-2776.
- 195. Zhang Z.-M. et al. Enantiomerically pure chiral {Fe₂₈} wheels. In: Angew. Chem., Int. Ed., 2009, vol. 48, p. 1581–1584.
- 196. Koumousi E. S. et al. 2-Pyrrolyloximes in high-nuclearity transition-metal cluster chemistry: Fe₁₀ and Fe₁₂. In: Inorg Chem., 2013, vol. 52(3), p. 1176-1178.
- 197. Ako A. M. et al. An undecanuclear Fe^{III} single-molecule magnet. In: Inorg. Chem., 2010, vol. 49, p. 1–3.
- 198. Tong J.-P. et al. Microwave-assisted synthesis of a ferrimagnetic dodecanuclear iron(III) complex with a Fe₄(OH)₄ cubane core. In: Inorg. Chem., 2011, vol. 50, p. 2067–2069.
- 199. Taguchi T. et al. Unusual Fe₉ and Fe₁₈ structural types from the use of 2,6-pyridinedimethanol in Fe^{III} cluster chemistry. In: Dalton Trans., 2010, vol. 39, p. 9131–9139.
- 200. Ferguson A. et al. Access to new magnetic cores in Fe(III) and Fe(III)/Cu(II) spin clusters. In: Dalton Trans., 2009, p. 9395–9397.
- 201. Rafizadeh M., Amani V. Synthesis, characterization, and crystal structure of new macromolecule iron(III) complex containing dimethyl phosphate, acetate, and dimethyl sulfoxide. In: Z. Anorg. Allg. Chem., 2007, vol. 633, p. 2738-2741.
- 202. Bagai R. et. al. A discrete Fe₁₈ 'molecular chain'. In: Chem. Commun., 2007, p. 3359–3361.
- 203. Foguet-Albiol D., Abboud K. A., Christou G. High-nuclearity homometallic iron and nickel clusters: Fe₂₂ and Ni₂₄ complexes from the use of N-methyldiethanolamine. In: ChemComm. (Camb.), 2005, p. 4282-4284.
- 204. Casson I. et al. An {Fe₁₆} barrel: Synthesis, structural and magnetic characterisation of an {Fe₈} ring and its dimer. In: Polyhedron, 2013, vol. 64, p. 59-62.

- 205. Baca S. G. et al. {Fe₆O₂}-based assembly of a tetradecanuclear iron nanocluster. In: Materials, 2011, vol. 4, p. 300-310.
- 206. Baca S. G. et al. Undecametallic and hexadecametallic ferric oxo-hydroxo/ethoxo pivalate clusters. In: Dalton Trans., 2015, vol. 44, p. 7777-7780.
- 207. Gu Z.-G. et al. A Fe₁₇ cluster with S = 35/2 ground state: Synthesis, structure, and magnetic properties. In: Inorg. Chem. Comm., 2011, vol. 14 (6), p. 839-842.
- 208. Liu T. et al. A 64-nuclear cubic cage incorporating propeller-like Fe(III)₈ apices and HCOO⁻ edges. In: J. Am. Chem. Soc., 2008, vol. 130, p. 10500-10501.
- 209. Kitagawa, S., Kitaura, R., Noro, S. Functional porous coordination polymers. In: Angew. Chem. Int. Ed., 2004, vol. 43, p. 2334-2375.
- 210. Li J.-R., Sculley J., Zhou H.-C. Metal–organic frameworks for separations. In: Chem. Rev., vol. 112, 869-932 (2012).
- 211. Yoon M., Srirambalaji R., Kim K. Homochiral metal–organic frameworks for asymmetric heterogeneous catalysis. In: Chem. Rev., vol. 112, 1196-1231 (2012).
- 212. Dinca M. et al. Hydrogen storage in a microporous metal–organic framework with exposed Mn²⁺ coordination sites. In: J. Am. Chem. Soc., 2006, vol. 128, p. 16876-16883.
- 213. Surble S.et al. A new isoreticular class of metal-organic-frameworks with the MIL-88 topology. In: Chem. Commun., 2006, vol. 3, p. 284-286.
- 214. Farha O. K. et al. De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities. In: Nat. Chem., 2010, vol. 2, p. 944-948.
- 215. Herm Z. R. et al. Separation of hexane isomers in a metal-organic framework with triangular channels. In: Science, 2013, vol. 340, p. 960-964.
- 216. Cavka J. H. et al. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. In: J. Am. Chem. Soc., 2008, vol. 130, p. 13850-13851.
- 217. Deng H. et al. Large-pore apertures in a series of metal-organic frameworks. In: Science 2012, vol. 336, p. 1021-1023.
- 218. Albores P., Rentschler E. Structural and magnetic characterization of a μ-1,5-dicyanamide bridged iron basic carboxylate [Fe₃O(O₂C(CH₃)₃)₆] 1D Chain. In: Inorg. Chem., 2008, vol. 47, p. 7960-7962.
- 219. Baca S. G. et al. Avoiding magnetochemical overparametrization, exemplified by onedimensional chains of hexanuclear iron(III) pivalate clusters. In: Inorg. Chem., 2013, vol. 52 (8), p. 4154-4156.
- 220. Turner D. R. et al. A sheet of clusters: self-assembly of a (4,4) network of Fe^{III}₁₀ clusters. In: Dalton Trans., 2008, p. 6877-6879.
- 221. Wei Y.-S. et al. Synthesis and stabilization of a hypothetical porous framework based on a classic flexible metal carboxylate cluster. In: J. Name., 2013, vol. 00, p. 1-3.
- 222. Winpenny R. E. P. Serendipitous assembly of polynuclear cage compounds. In: J. Chem. Soc., Dalton Trans., 2002, vol. 0, p. 1-10.
- 223. Murugesu M. et al. Mixed 3d/4d and 3d/4f metal clusters: tetranuclear $\text{Fe}^{III}_2 M^{III}_2 (M^{III} = \text{Ln}, \text{ Y})$ and $\text{Mn}^{IV}_2 M^{III}_2 (M = \text{Yb}, \text{ Y})$ complexes, and the first Fe/4f single-molecule magnets. In: Polyhedron,

2006, vol. 25, p. 613-625.

- 224. Mukherjee S. et al. A variety of new tri- and tetranuclear Mn–Ln and Fe–Ln (Ln = lanthanide) complexes. In: Polyhedron, 2010, vol. 29, p. 54–65.
- 225. Baniodeh A. et al. Para versus meta ligand substituents as a means of directing magnetic anisotropy in Fe₂Dy₂ coordination clusters. In: Chem. Comm., 2013, vol. 49, p. 9666-9668.
- 226. Peng G. et al. Body-wing swapping in butterfly {Fe^{III}₂Ln^{III}₂} coordination clusters with triethylene glycol as ligand. In: Dalton Trans., 2013, vol. 42, p. 46-49.
- 227. Peng G. et al. Enhancement of spin relaxation in an FeDy₂Fe coordination cluster by magnetic fields. In: Chem. Eur. J., 2014, vol. 20, p. 12381-12384.
- 228. Abbas G. et al. Magnetic and ⁵⁷Fe mössbauer study of the single molecule magnet behavior of a Dy₃Fe₇ coordination cluster. In: Inorg. Chem., 2009, vol. 48, p. 9345-9355.
- 229. Abbas G. et al. Synthesis, magnetism, and 57 Fe mössbauer spectroscopic study of a family of [Ln₃Fe₇] coordination clusters (Ln = Gd, Tb, and Er). In: Inorg. Chem., 2013, vol. 52, p. 11767-11777.
- 230. Chen S. et al. Developing a "highway code" to steer the structural and electronic properties of Fe^{III}/Dy^{III} coordination clusters. In: Inorg. Chem., 2015, vol. 54(7), p. 3218-3227.
- 231. Chen S. et al. A single molecule magnet to single molecule magnet transformation via a solvothermal process: $Fe_4Dy_2 \rightarrow Fe_6Dy_3$. In: Dalt. Trans., 2016, vol. 45, p. 98-106.
- 232. Akhtar M. N. et al. Probing lanthanide anisotropy in Fe-Ln aggregates by using magnetic susceptibility measurements and ⁵⁷Fe mössbauer spectroscopy. In: Chem. Eur. J., 2009, vol. 15(30), p. 7278-7282.
- 233. Ako A. M. et al. High-nuclearity 3d–4f [Fe^{III}₅Ln^{III}₈] complexes: synthesis, structure and magnetic properties. In: Dalton Trans., 2007, p. 5245-5247.
- 234. Mereacre V. et al. Antiferromagnetically coupled iron ions in a polynuclear Fe^{III}–Dy complex: confirmation by variable-field ⁵⁷Fe Mössbauer Spectroscopy. In: Chem. Eur. J., 2011, vol. 17, p. 123-128.
- 235. Pham L. et al. Synthesis, structure and magnetic properties of $[Fe^{III}_4Ln^{III}_2]$ (Ln = Gd, Tb, Dy, Ho) and $[Fe^{III}_4Y^{III}_2]$ clusters. In: Polyhedron, 2013, vol. 66, p. 205-211.
- 236. Nayak S. et al. An S-shaped [Fe₄Dy₂] complex exhibiting slow relaxation of magnetization: synthesis, magnetism, and crystal structures of a family of [Fe₄Ln₂][Ln] coordination compounds (Ln = Nd, Gd, Tb, Dy, and Ho). In: Inorg. Chem., 2010, vol. 49(1), p. 216-221.
- 237. Mereacre V. et al. The synthesis, structural characterization, magnetochemistry and mössbauer spectroscopy of [Fe₃LnO₂(CCl₃COO)₈H₂O(THF)₃] (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Lu and Y). In: Polyhedron, 2009, vol. 28(14), p. 3017-3025.
- Zeng Y.-F. et al. Single-molecule-magnet behavior in a Fe₁₂Sm₄ cluster. In: Inorg. Chem., 2010, vol. 49 (1), p. 9734-9736.
- 239. Polyzou Ch. D. et al. Squashed {Fe2^{III}M4^{III}} octahedra (M =Y, Gd, Dy) from the first use of the cyanoacetate ligand in 3d/4f coordination chemistry. In: Royal Soc. of Chem. Adv., 2015, vol. 5, p. 10763-10767.
- 240. Han S.-D. et al. Synthesis and magnetic properties of a series of octanuclear [Fe₆Ln₂]

nanoclusters. In: Cryst.Grow.Design, 2015, vol. 15(5), p. 2253-2259.

- 241. Schmidt S. et al. Ferromagnetic heteronuclear {Fe₄(Er,Lu)₂} cyclic coordination clusters based on ferric wheels. In: Chem. Commun., 2012, vol. 48, p. 9825–9827.
- 242. Baniodeh A. et al. Heterometallic 20-membered{ $Fe_{16}Ln_4$ }(Ln = Sm, Eu, Gd, Tb, Dy, Ho) metalloring aggregates. In: Dalt. Trans., 2011, vol. 40, p. 4080-4086.
- 243. Baniodeh A., Ansona C. E., Powell A. K. Ringing the changes in Fe^{III}/Yb^{III} cyclic coordination clusters. In: Chem. Sci., 2013, vol. 4, p. 4354-4361.
- 244. Kühne I. A. et al. Nine members of a family of nine-membered cyclic coordination clusters; Fe_6Ln_3 wheels (Ln = Gd to Lu and Y). In: J. Name., 2013, vol. 00, p. 1-3.
- 245. Bergerhoff G., Berndt M., Brandenburg K. Evaluation of crystallographic data with the program DIAMOND. In: Journal of research of the NIST, 2006, vol.101(3), p. 221-225.
- 246. Gerbeleu N. V. et al. Dokl. Akad. Nauk SSSR, 1987, vol. 293, p. 364.
- 247. Gerbeleu N. V. et al. Synthesis and structure of tri- and hexanuclear μ₃-oxo pivalates of iron(III).
 Dokl. Akad. Nauk SSSR (Russ.) 1987, vol. 293, p. 364-367.
- 248. Baca S G. et al. {Fe₆O₂}-based assembly of a tetradecanuclear iron nanocluster. In: Materials, 2011, vol. 4, p. 300-310.
- 249. Baca S. G. et al. Iron(III)-pivalate-based complexes with tetranuclear $\{Fe_4(\mu_3-O)_2\}^{8+}$ cores and N-donor ligands: formation of cluster and polymeric architectures. In: Eur. J. Inorg. Chem., 2011, p. 356–367.
- 250. Botezat O. et. al. Tuning the condensation degree of {Fe^{III}_n} oxo clusters via ligand metathesis, temperature, and solvents. In: Inorg. Chem., 2018, vol. 57 (13), p. 7904–7913.
- 251. Baca S. G. et. al. A Heptanuclear iron(III) oxo-carboxylate cluster. In: Z. Anorg. Allg. Chem., 2011, p. 821–823.
- 252. Botezat O. et. al. Iron(III) carboxylate/aminoalcohol coordination clusters with propeller-shaped Fe₈ cores: approaching reasonable exchange energies. In: Dalt. Trans., 2015, vol. 44, p. 20753-20762.
- 253. Botezat O. et. al. Interpenetrated (8,3)-c and (10,3)-b metal-organic frameworks based on $\{Fe^{III}_3\}$ and $\{Fe^{III}_2Co^{II}\}$ pivalate spin clusters. In: Cryst. Growth Des., 2014, vol. 14(9), p. 4721-4728.
- 254. Smolin E. M., Rapoport L. s-Triazines and Derivatives. In: London: INTERSCIENCE PUBLISHERS INC, 1959, 644 p.
- 255. Speldrich M. et al. A computational framework for magnetic polyoxometalates and molecular spin structures: CONDON 2.0. Isr. J. Chem., 2011, vol. 51, p. 215-227.
- Botezat O. Iron-lanthanide single molecule magnet compound. In: Mold. J. Phys. Sc., vol. 16, N 3-4, 2017, p. 191-210.
- 257. Botezat O. et. al. Ultralarge 3d/4f coordination wheels: from carboxylate/amino alcohol-supported {Fe₄Ln₂} to {Fe₁₈Ln₆} rings. In: Inorg. Chem., 2017, vol. 56 (4), p. 1814–1822.
- 258. Lueken H. Magnetochemie In: Stuttgart: Teubner Studienbücher, 1999, 507 p.
- 259. Cole K. S., Cole, R. H. Dispersion and absorption in dielectrics I. Alternating current characteristics. In: J. Chem. Phys., 1941, vol. 9, p. 341–351.

ANNEXES

| Annexe 1. Selected bond distances for compounds 1–35, 37–42 | 2 |
|---|---|
| Table A1.1. Selected bond distances (Å) for 1-35, 37-42 | 2 |

| Compound 1 | | | | | | | |
|---------------|-----------|---------------|----------|------------------------|----------|--|--|
| Fe(1) - O(1) | 1.899(1) | Fe(2)–O(1) | 1.899(2) | Fe(3)–O(1) | 1.899(2) | | |
| Fe(1)-O(2) | 1.993(1) | Fe(2)–O(3) | 1.996(2) | Fe(3)–O(7) | 2.004(2) | | |
| Fe(1)–O(4) | 2.026(2) | Fe(2)–O(5) | 2.033(2) | Fe(3)–O(9) | 2.040(2) | | |
| Fe(1)–O(11) | 2.043(2) | Fe(2)–O(6) | 2.015(2) | Fe(3)–O(10) | 2.004(2) | | |
| Fe(1)–O(13) | 2.006(1) | Fe(2)–O(8) | 2.032(2) | Fe(3)–O(12) | 2.015(1) | | |
| Fe(1)–O(14) | 2.066(1) | Fe(2)–O(15) | 2.065(2) | Fe(3)–O(16) | 2.048(2) | | |
| | | Compoun | d 2 | | | | |
| Fe(1)–O(4) | 1.7746(9) | Fe(1)–O(1) | 2.164(2) | Fe(1)–N(5) | 2.321(3) | | |
| Fe(1)-O(3) | 2.108(3) | Fe(1)–N(2) | 2.193(3) | Fe(1)–N(1) | 2.323(3) | | |
| Fe(1)–O(2) | 2.162(2) | | | | | | |
| | | Compoun | d 3 | | | | |
| Fe(1)-O(1) | 1.830(3) | Fe(2)-O(81) | 2.082(2) | Fe(4)–O(42) | 2.035(3) | | |
| Fe(1)-O(82) | 2.005(2) | Fe(2)–Fe3 | 2.853(8) | Fe(4)-N(102) | 2.153(5) | | |
| Fe(1)-O(22) | 2.021(3) | Fe(3)–O(2) | 1.921(3) | Fe(4)–N(101) | 2.164(4) | | |
| Fe(1)-O(31) | 2.031(3) | Fe(3)-O(1) | 1.942(3) | $Fe(1)\cdots Fe(3)$ | 2.909(1) | | |
| Fe(1) - N(3) | 2.147(3) | Fe(3)-O(21) | 2.013(3) | $Fe(1)\cdots Fe(2)$ | 3.360(1) | | |
| Fe(1) - N(1) | 2.149(3) | Fe(3)–O(62) | 2.016(3) | $Fe(1)\cdots Fe(4)$ | 3.376(1) | | |
| Fe(2)-O(1) | 1.915(2) | Fe(3)–O(72) | 2.037(3) | $Fe(2)\cdots Fe(3)$ | 3.273(1) | | |
| Fe(2)–O(2) | 1.938(3) | Fe(3)–O(52) | 2.071(3) | $Fe(3)\cdots Fe(4)$ | 3.264(1) | | |
| Fe(2)–O(32) | 2.007(3) | Fe(4) - O(2) | 1.828(2) | $Fe(2)\cdots Fe(4)$ | 5.950(1) | | |
| Fe(2) - O(41) | 2.022(3) | Fe(4)–O(61) | 2.025(4) | | | | |
| Fe(2)-O(71) | 2.056(3) | Fe(4)-O(51) | 2.025(4) | | | | |
| | 1.001(1) | Compoun | d 4 | | | | |
| Fe(1)-O(1) | 1.931(1) | Fe(2)–N(4) | 2.184(2) | Fe(4)–O(11) | 2.034(2) | | |
| Fe(1)-O(2) | 1.963(1) | Fe(2)-N(1) | 2.213(2) | Fe(4) - O(10) | 2.038(2) | | |
| Fe(1) - O(12) | 1.990(2) | Fe(3) - O(2) | 1.932(2) | Fe(4) - O(17) | 2.077(2) | | |
| Fe(1)–O(13) | 2.017(2) | Fe(3)–O(1) | 1.962(2) | Fe(4)–O(18) | 2.174(2) | | |
| Fe(1)–O(16) | 2.081(2) | Fe(3)–O(7) | 2.021(2) | $Fe(1)\cdots Fe(3)$ | 2.909(1) | | |
| Fe(1) - O(15) | 2.101(2) | Fe(3) - O(4) | 2.018(2) | $Fe(1)\cdots Fe(2)$ | 3.360(1) | | |
| Fe(2)–O(1) | 1.829(1) | Fe(3)–O(9) | 2.030(2) | $Fe(1)\cdots Fe(4)$ | 3.376(1) | | |
| Fe(2)–O(5) | 1.976(2) | Fe(3)–O(6) | 2.036(2) | $Fe(2)\cdots Fe(3)$ | 3.273(1) | | |
| Fe(2)–O(3) | 2.031(2) | Fe(4)–O(2) | 1.834(1) | $Fe(3)\cdots Fe(4)$ | 3.264(1) | | |
| Fe(2)–O(14) | 2.052(1) | Fe(4)–O(8) | 2.031(2) | $Fe(2)\cdots Fe(4)$ | 5.950(1) | | |
| | | Compoun | d 5 | • | | | |
| Fe(1A)-O(1A) | 1.956(6) | Fe(4A)-O(15A) | 2.019(9) | Fe(3B)-O(14B) | 2.046(7) | | |
| Fe(1A)-O(2A) | 1.905(7) | Fe(4A)-O(10A) | 2.049(9) | Fe(3B)–O(6B) | 2.064(7) | | |
| Fe(1A)-O(9A) | 2.001(8) | Fe(4A)-O(18A) | 2.055(8) | Fe(4B)–O(2B) | 1.850(7) | | |
| Fe(1A)-O(4A) | 2.036(8) | Fe(4A)-O(17A) | 2.136(8) | Fe(4B)-O(12B) | 1.956(8) | | |
| Fe(1A)-O(13A) | 2.047(8) | Fe(1B)-O(1B) | 1.945(7) | Fe(4B)-O(15B) | 2.004(8) | | |
| Fe(1A)-O(11A) | 2.052(8) | Fe(1B)-O(2B) | 1.913(7) | Fe(4B)-O(10B) | 2.029(8) | | |
| Fe(2A)–O(1A) | 1.803(6) | Fe(1B)-O(9B) | 1.975(8) | Fe(4B)–O(18B) | 2.057(8) | | |
| Fe(2A)–O(5A) | 1.966(8) | Fe(1B)-O(4B) | 1.996(8) | Fe(4B)-O(17B) | 2.148(9) | | |
| Fe(2A)–O(7A) | 2.008(7) | Fe(1B)-O(13B) | 2.042(7) | $Fe(2B)\cdots Fe(4B)$ | 5.471(2) | | |
| Fe(2A)-O(3A) | 2.016(8) | Fe(2B)–O(1B) | 1.800(7) | $Fe(1A) \cdots Fe(3A)$ | 2.867(2) | | |

| $F_{e}(2\Delta) = N(2\Delta)$ | 2 155(1) | $F_{e}(2R) = O(3R)$ | 1.980(7) | $Fe(1A)\cdots Fe(2A)$ | 3443(2) | | |
|-------------------------------|-----------------------------|---------------------|-----------------------------|------------------------|----------------------|--|--|
| Fe(2A)-N(1A) | 2.233(1) | Fe(2B) - O(5B) | 1.983(8) | $Fe(1A \cdots Fe(4A))$ | 3.279(2) | | |
| Fe(3A) = O(2A) | 1.944(7) | Fe(2B) = O(7B) | 2.023(7) | $Fe(3A)\cdots Fe(2A)$ | 3.292(2) | | |
| Fe(3A) - O(1A) | 1.950(7) | Fe(2B) = O(11B) | 2.054(8) | $Fe(3A)\cdots Fe(4A)$ | 3.408(2) | | |
| Fe(3A) = O(16A) | 1.975(9) | Fe(2B) - N(1B) | 2.162(1) | $Fe(2A)\cdots Fe(4A)$ | 5.588(2) | | |
| Fe(3A) - O(14A) | 1.996(1) | Fe(2B) - N(2B) | 2.179(1) | $Fe(1B)\cdots Fe(3B)$ | 2.866(2) | | |
| Fe(3A) = O(8A) | 1.997(7) | Fe(3B)-O(2B) | 1.937(7) | $Fe(1B)\cdots Fe(2B)$ | 3.400(2) | | |
| Fe(3A) - O(6A) | 2.069(8) | Fe(3B) - O(1B) | 1.949(8) | $Fe(1B)\cdots Fe(4B)$ | 3.274(2) | | |
| Fe(4A)-O(2A) | 1.833(7) | Fe(3B)-O(16B) | 1.985(9) | $Fe(3B)\cdots Fe(2B)$ | 3.289(2) | | |
| Fe(4A) - O(12A) | 1.973(7) | Fe(3B)-O(8B) | 2.015(7) | $Fe(3B)\cdots Fe(4B)$ | 3.406(2) | | |
| | | Compoun | d 6 | | | | |
| $Fe(1) - O(2)^{\#1}$ | 1.870(3) | Fe(2) - O(1) | 1.961(3) | Fe(3) - O(15) | 1.991(4) | | |
| Fe(1) = O(1) | $\frac{1.070(3)}{1.984(3)}$ | Fe(2) = O(13) | $\frac{1.931(3)}{1.978(3)}$ | Fe(3) - O(13) | 1.991(3) | | |
| Fe(1) = O(12) | 2.038(4) | Fe(2) = O(4) | 2.032(3) | Fe(3) = O(10) | 2.003(3) | | |
| Fe(1) = O(11) | 2.030(1) 2.039(4) | Fe(2) = O(6) | 2.052(3) | Fe(3) = O(9) | 2.003(3) 2.051(3) | | |
| Fe(1) = O(11) | 2.037(4) 2.041(4) | Fe(2) = O(0) | 2.050(3) | Fe(3)=O(9) | 2.051(3) 2.067(4) | | |
| $F_{0}(1) - O(3)$ | 2.041(4) 2 100(2) | $F_{2}(2) = O(7)$ | $\frac{2.003(4)}{1.008(2)}$ | $F_{0}(2) = O(0)$ | 2.007(4) | | |
| Fe(1) = O(3) | 2.100(3) | Fe(3) = O(2) | 1.908(3) | re(2)re(3) | 2.9183(10) | | |
| Fe(2) = O(2) | 1.939(3) | | | | | | |
| #1 - x + 2, -y, -z + 2 | | 0 | 1. | | | | |
| F (1) Q(2) | 1.07((2)) | Compoun | <u>d 7</u> | | 1.927(2) | | |
| Fe(1) = O(2) | $\frac{1.870(2)}{1.060(2)}$ | Fe(4) - O(4) | $\frac{1.820(2)}{1.022(2)}$ | Fe(7) = O(1) | 1.827(2) | | |
| Fe(1) - O(3) | 1.960(2) | Fe(4)-O(5) | 1.922(2) | Fe(7) - O(20) | 1.980(3) | | |
| Fe(1)–O(4) | 2.012(2) | Fe(4)–O(16) | 2.035(3) | Fe(7)–O(22) | 2.16/(3) | | |
| Fe(1)–O(9) | 2.105(2) | Fe(4)–O(19) | 2.037(3) | Fe(7)–O(23) | 2.083(4) | | |
| Fe(1) - O(15) | 2.064(2) | Fe(4) - N(5) | 2.218(3) | Fe(7)–O(25) | 2.002(3) | | |
| Fe(1)–O(18) | 2.086(2) | Fe(4)-N(7) | 2.242(3) | Fe(7)–O(27) | 2.025(4) | | |
| Fe(2) - O(3) | 1.944(2) | Fe(5) - O(1) | 1.918(2) | $Fe(1)\cdots Fe(2)$ | 2.930(1) | | |
| Fe(2) - O(4) | 1.935(2) | Fe(5)-O(1W) | 2.151(3) | $Fe(5)\cdots Fe(7)$ | 3.449(1) | | |
| Fe(2)-O(5A) | 1.983(2) | Fe(5) - O(2) | 1.933(2) | $Fe(1)\cdots Fe(3)$ | 3.434(1) | | |
| Fe(2)–O(10) | 2.047(3) | Fe(5) - O(6) | 2.032(3) | $Fe(5)\cdots Fe(6)$ | 2.849(1) | | |
| Fe(2) - O(12) | 2.084(3) | Fe(5)–O(14) | 2.003(2) | $Fe(1)\cdots Fe(4)$ | 3.401(1) | | |
| Fe(2)–O(17) | 2.035(3) | Fe(5)–O(24) | 2.011(3) | $Fe(5)\cdots Fe(1)$ | 3.521(1) | | |
| Fe(3) - O(3) | 1.817(2) | Fe(6) - O(1) | 1.967(2) | $Fe(1)\cdots Fe(6)$ | 3.444(1) | | |
| Fe(3) - O(8) | 1.995(3) | Fe(6) - O(2) | 1.949(2) | $Fe(6)\cdots Fe(1)$ | 3.444(1) | | |
| Fe(3) - O(11) | 2.021(3) | Fe(6) - O(5) | 2.035(2) | $Fe(2)\cdots Fe(6)$ | 3.589(1) | | |
| Fe(3)–O(13) | 2.024(3) | Fe(6)–O(5A) | 1.990(2) | $Fe(6)\cdots Fe(4)$ | 3.438(1) | | |
| Fe(3) - N(1) | 2.170(3) | Fe(6)–O(7) | 2.075(3) | $Fe(2)\cdots Fe(4)$ | 3.302(1) | | |
| Fe(3) - N(3) | 2.205(3) | Fe(6)–O(26) | 2.018(3) | $Fe(6)\cdots Fe(7)$ | 3.458(1) | | |
| | | Compoun | d 8 | | | | |
| $Fe(1)-O(7)^{\#1}$ | 1.978(7) | Fe(2)–O(3) | 1.991(8) | Fe(3)–O(1) | 2.264(1) | | |
| Fe(1) - O(3) | 1.989(8) | $Fe(2)-O(3)^{\#1}$ | 1.991(8) | Fe(3)-Cl(3) | 2.266(5) | | |
| Fe(1)–O(2) | 1.990(8) | Fe(2) - O(1) | 2.250(11) | Fe(4)–O(7) | 1.983(8) | | |
| Fe(1)–O(5) | 1.991(8) | Fe(2)–Cl(2) | 2.279(5) | Fe(4)–O(2) | 1.990(8) | | |
| Fe(1)–O(1) | 2.254(2) | $Fe(3)-O(6)^{\#1}$ | 1.985(7) | $Fe(4) - O(4)^{\#1}$ | 1.996(7) | | |
| Fe(1)–Cl(1) | 2.282(3) | Fe(3)–O(6) | 1.985(7) | $Fe(4) - O(6)^{\#1}$ | 2.005(8) | | |
| $Fe(2) - O(4)^{\#1}$ | 1.985(7) | $Fe(3)-O(5)^{\#1}$ | 1.995(8) | Fe(4)–O(1) | 2.223(1) | | |
| Fe(2)–O(4) | 1.985(7) | Fe(3)–O(5) | 1.995(8) | Fe(4)–Cl(4) | 2.292(3) | | |
| #1 x+0, -y+3/2, -z- | +9/4 | | | | | | |
| Compound 9 | | | | | | | |

| Fe(1)–O(28) | 1.934(4) | Fe(3)–O(11) | 2.035(5) | Fe(6)–O(26) | 1.990(4) |
|---|---|---|--|--|---|
| Fe(1)–O(25) | 1.935(4) | Fe(3)–O(13) | 2.062(5) | Fe(6)–O(7) | 2.006(5) |
| Fe(1)–O(22) | 1.945(4) | Fe(4)–O(3) | 1.934(4) | Fe(6)–O(5) | 2.043(4) |
| Fe(1)–O(1) | 2.049(4) | Fe(4)–O(28) | 1.978(4) | Fe(6)–N(2) | 2.295(5) |
| Fe(1)-O(2) | 2.055(4) | Fe(4)–O(29) | 1.979(4) | Fe(7)–O(8) | 1.960(4) |
| Fe(1)–O(3) | 2.116(4) | Fe(4)–O(18) | 2.002(5) | Fe(7)–O(32) | 1.970(4) |
| Fe(2)-O(32) | 1.930(4) | Fe(4)–O(16) | 2.044(5) | Fe(7)–O(23) | 1.977(5) |
| Fe(2)–O(31) | 1.937(4) | Fe(4)–N(3) | 2.292(5) | Fe(7)–O(1) | 1.996(4) |
| Fe(2)–O(33) | 1.939(4) | Fe(5)–O(20) | 1.959(5) | Fe(7)–O(4) | 2.049(5) |
| Fe(2)-O(3) | 2.182(4) | Fe(5)–O(31) | 1.969(4) | Fe(7)–O(6) | 2.058(5) |
| Fe(2)–O(2) | 2.210(4) | Fe(5)–O(26) | 1.987(4) | Fe(8)–O(2) | 1.954(4) |
| Fe(2)–O(1) | 2.234(4) | Fe(5)–O(3) | 1.998(4) | Fe(8)–O(22) | 1.967(4) |
| Fe(3)–O(33) | 1.961(4) | Fe(5)–O(17) | 2.043(5) | Fe(8)–O(23) | 1.978(5) |
| Fe(3)–O(2) | 1.976(4) | Fe(5)–O(19) | 2.096(4) | Fe(8)–O(12) | 1.986(5) |
| Fe(3)–O(14) | 1.977(4) | Fe(6)–O(1) | 1.940(4) | Fe(8)–O(10) | 2.054(5) |
| Fe(3)–O(29) | 1.987(4) | Fe(6)–O(25) | 1.971(4) | Fe(8)–N(1) | 2.285(5) |
| | | Compour | nd 10 | | |
| $Fe(1) - O(6)^{\#1}$ | 1.937(2) | $Fe(2) - O(8)^{#2}$ | 1.945(2) | Fe(3)–O(4) | 2.049(2) |
| $Fe(1) - O(6)^{#2}$ | 1.937(2) | $Fe(2) - O(1)^{\#1}$ | 2.075(2) | Fe(3) - N(2) | 2.273(3) |
| Fe(1) = O(6) | 1.937(2) | Fe(2)=O(1) | 2.075(2) | Fe(4) = O(6) | 1.984(2) |
| $Fe(1) = O(1)^{\#1}$ | 2 198(2) | $Fe(2) = O(1)^{\#2}$ | 2.075(2) | $Fe(4) = O(7)^{#2}$ | 1.992(2) |
| $Fe(1)=O(1)^{\#2}$ | $\frac{2.198(2)}{2.198(2)}$ | Fe(3) = O(1) | $\frac{2.073(2)}{1.943(2)}$ | Fe(4) = O(1) | $\frac{1.992(2)}{2.007(2)}$ |
| Fe(1) = O(1) | $\frac{2.198(2)}{2.108(2)}$ | Fe(3)=O(1) | $\frac{1.943(2)}{1.085(2)}$ | Fe(4) = O(1) | $\frac{2.007(2)}{2.030(2)}$ |
| Fe(1)=O(1) | $\frac{2.198(2)}{1.045(2)}$ | Fe(3)=O(2) | 1.983(2) | Fe(4) = O(3) | 2.030(2) |
| Fe(2) = O(8) | 1.943(2) | Fe(3) = O(8) | $\frac{1.992(2)}{2.007(2)}$ | Fe(4) = N(3) | 2.030(3) |
| He(2) = O(8) | 1.945(2) | Fe(3) = O(7) | 2.007(2) | Fe(4) - O(3) | 2.106(2) |
| $\mu_1 = \mu_2$ | | | < / < | - () - (-) | |
| #1 y, z, x,#2z, x, y | | | . J 11 | | |
| $\frac{\#1}{\#1} y, z, x, \#2z, x, y$ | 1.012(4) | | nd 11 | | 1.047(4) |
| Fe(1)-O(26) Fe(2)-O(26) | 1.912(4) 1.085(4) | Compour Fe(1)-O(2) Fe(2) N(4) | $\frac{11}{2.122(4)}$ | Fe(2)-O(25) | 1.947(4) |
| $\frac{\#1}{\#1} \frac{y}{y} \frac{z}{z} \frac{x}{x} \frac{\#2z}{x} \frac{x}{y} \frac{y}{z} \frac{x}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} \frac{x}{z} \frac{y}{z} \frac{x}{z} $ | 1.912(4) 1.985(4) | Compour Fe(1)-O(2) Fe(3)-N(4) Fe(5)-O(0) | nd 11 2.122(4) 2.026(6) 2.025(4) | Fe(2)-O(25) Fe(4)-O(6) Fe(5)-O(20) Fe(4)-O(6) Fe(5)-O(20) Fe(5)-O(20) Fe(5)-O(20) Fe(5)-O(20) Fe(5)-O(25) Fe(5) | $\frac{1.947(4)}{2.001(5)}$ |
| $\begin{array}{c} Fe(1) = O(2) \\ \#1 \ y, \ z, \ x, \#2z, \ x, \ y \\ \hline Fe(1) = O(26) \\ Fe(3) = O(18) \\ Fe(5) = O(25) \\ Fa(7) = O(2) \\ \hline \end{array}$ | 1.912(4) 1.985(4) 1.995(4) 1.924(4) | Compound Fe(1)-O(2) Fe(3)-N(4) Fe(5)-O(9) Fe(7)_O(11) | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fa(8) O(14) \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \end{array} $ |
| $\begin{array}{c} Fe(1) = O(2) \\ \#1 \ y, \ z, \ x, \#2z, \ x, \ y \\ \hline Fe(1) = O(26) \\ Fe(3) = O(18) \\ Fe(5) = O(25) \\ Fe(7) = O(3) \\ \hline Fe(7) = O(3) \\ \hline Fe(1) = O(10) \\ \hline Fe(1) \\ \hline Fe(1) \\ \hline Fe(1) = O(10) $ | $ \begin{array}{r} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \end{array} $ | Compound Fe(1)-O(2) Fe(3)-N(4) Fe(5)-O(9) Fe(7)-O(11) Fe(1)-O(2) | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.120(4) | Fe(2)-O(25) Fe(4)-O(6) Fe(6)-O(20) Fe(8)-O(14) Fe(2) O(2) Fe(3)-O(2) F | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y \\ \hline \\ Fe(1)-O(26) \\ Fe(3)-O(18) \\ \hline \\ Fe(5)-O(25) \\ \hline \\ Fe(7)-O(3) \\ \hline \\ Fe(1)-O(19) \\ \hline \\ Fe(2) \\ O(24) \end{array}$ | $ \begin{array}{r} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \end{array} $ | $\begin{array}{c} \hline Compour \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(10) \\ Fe(2)-O(2) \\ Fe(4)-O(10) $ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \end{array} $ |
| $\begin{array}{c} Fe(1) = O(26) \\ \#1 \ y, \ z, \ x, \#2z, \ x, \ y \\ \hline Fe(1) = O(26) \\ Fe(3) = O(18) \\ Fe(5) = O(25) \\ Fe(7) = O(25) \\ Fe(1) = O(19) \\ Fe(3) = O(24) \\ Fe(5) = O(20) \\ \hline Fe(5) = O(20) \\ \hline \end{array}$ | $ \begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \end{array} $ | $\begin{array}{c} \hline Compour \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5) O(7) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6) O(10) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \end{array} $ |
| $\begin{array}{c} Fe(1) = O(2) \\ \#1 \ y, \ z, \ x, \#2z, \ x, \ y \\ \hline Fe(1) = O(26) \\ Fe(3) = O(18) \\ Fe(5) = O(25) \\ Fe(7) = O(25) \\ \hline Fe(7) = O(2) \\ Fe(3) = O(24) \\ \hline Fe(5) = O(20) \\ \hline Fe(5) = O(20) \\ \hline Fe(7) = O(23) \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \end{array}$ | $\begin{array}{c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(7) N(3) \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) | Fe(2)-O(25) $Fe(4)-O(6)$ $Fe(6)-O(20)$ $Fe(8)-O(14)$ $Fe(2)-O(2)$ $Fe(4)-O(19)$ $Fe(6)-O(10)$ $Fe(8) N(10)$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \\ 2.038(6) \\ \end{array} $ |
| $\begin{array}{c} \#1 \ y, \ z, \ x, \#2z, \ x, \ y\\ \hline \\ Fe(1)-O(26)\\ Fe(3)-O(18)\\ \hline \\ Fe(5)-O(25)\\ \hline \\ Fe(7)-O(3)\\ \hline \\ Fe(1)-O(19)\\ \hline \\ Fe(3)-O(24)\\ \hline \\ Fe(5)-O(20)\\ \hline \\ Fe(7)-O(23)\\ \hline \\ Fe(1)-O(21)\\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \end{array}$ | $\begin{array}{c} \hline Compour \\ \hline Compour \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(7)-N(3) \\ \hline Fe(2)-O(24) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.000(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(8)-N(10) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(3)-O(1) \\ Fe(3)$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \end{array} $ |
| $\begin{array}{c} \#1 \ y, \ z, \ x, \#2z, \ x, \ y\\ \hline \\ Fe(1)-O(26)\\ Fe(3)-O(18)\\ \hline \\ Fe(5)-O(25)\\ \hline \\ Fe(7)-O(3)\\ \hline \\ Fe(1)-O(19)\\ \hline \\ Fe(3)-O(24)\\ \hline \\ Fe(5)-O(20)\\ \hline \\ Fe(7)-O(23)\\ \hline \\ Fe(1)-O(21)\\ \hline \\ Fe(3)-O(1)\\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ \hline 1.985(4) \\ \hline 1.995(4) \\ \hline 1.924(4) \\ \hline 1.920(4) \\ \hline 2.013(4) \\ \hline 2.005(4) \\ \hline 1.978(4) \\ \hline 1.944(4) \\ \hline 2.018(4) \end{array}$ | $\begin{array}{c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(7)-N(3) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-N(10) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ \end{array} $ |
| $\begin{array}{c} Fe(2) = O(3) \\ \#1 \ y, \ z, \ x, \#2z, \ x, \ y \\ \hline Fe(1) - O(26) \\ Fe(3) - O(18) \\ Fe(5) - O(25) \\ \hline Fe(7) - O(3) \\ \hline Fe(1) - O(19) \\ \hline Fe(3) - O(24) \\ \hline Fe(5) - O(20) \\ \hline Fe(7) - O(23) \\ \hline Fe(1) - O(21) \\ \hline Fe(3) - O(1) \\ \hline Fe(3) - O(1) \\ \hline Fe(5) = N(7) \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \end{array}$ | $\begin{array}{c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(7)-N(3) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(8)-N(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y \\ \hline \#1 \ y, z, x, \#2z, x, y \\ \hline Fe(1)-O(26) \\ \hline Fe(3)-O(18) \\ \hline Fe(5)-O(25) \\ \hline Fe(7)-O(3) \\ \hline Fe(1)-O(19) \\ \hline Fe(3)-O(24) \\ \hline Fe(5)-O(20) \\ \hline Fe(7)-O(23) \\ \hline Fe(1)-O(21) \\ \hline Fe(3)-O(1) \\ \hline Fe(5)-N(7) \\ \hline Fe(7)-O(22) \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \end{array}$ | $\begin{array}{c} \hline Compour \\ \hline Compour \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(7)-N(3) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.988(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(8)-N(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \\ 2.040(4) \\ \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y \\ \hline \#1 \ y, z, x, \#2z, x, y \\ \hline Fe(1)-O(26) \\ \hline Fe(3)-O(18) \\ \hline Fe(5)-O(25) \\ \hline Fe(7)-O(3) \\ \hline Fe(1)-O(19) \\ \hline Fe(3)-O(24) \\ \hline Fe(5)-O(20) \\ \hline Fe(7)-O(23) \\ \hline Fe(7)-O(23) \\ \hline Fe(1)-O(21) \\ \hline Fe(3)-O(1) \\ \hline Fe(5)-N(7) \\ \hline Fe(7)-O(22) \\ \hline Fe(1)-O(1) \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.059(4) \end{array}$ | $\begin{array}{c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.988(4) 1.943(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ Fe(2)-O(3) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.004(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \\ 2.040(4) \\ 2.124(4) \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y \\ \hline \#1 \ y, z, x, \#2z, x, y \\ \hline Fe(1)-O(26) \\ \hline Fe(3)-O(18) \\ \hline Fe(5)-O(25) \\ \hline Fe(7)-O(3) \\ \hline Fe(1)-O(19) \\ \hline Fe(3)-O(24) \\ \hline Fe(5)-O(20) \\ \hline Fe(7)-O(23) \\ \hline Fe(1)-O(21) \\ \hline Fe(3)-O(1) \\ \hline Fe(3)-O(1) \\ \hline Fe(5)-N(7) \\ \hline Fe(7)-O(22) \\ \hline Fe(1)-O(1) \\ \hline Fe(3)-O(17) \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.059(4) \\ 2.020(5) \end{array}$ | $\begin{array}{c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline Fe(4)-O(18) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.033(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.988(4) 1.943(4) 1.986(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ Fe(2)-O(3) \\ Fe(4)-N(1) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \\ 2.040(4) \\ 2.124(4) \\ 2.23(5) \end{array} $ |
| $\begin{array}{c} \#1 \ y, \ z, \ x, \#2z, \ x, \ y\\ \hline\\ Fe(1)-O(26)\\ Fe(3)-O(18)\\ \hline\\ Fe(5)-O(25)\\ \hline\\ Fe(7)-O(3)\\ \hline\\ Fe(7)-O(2)\\ \hline\\ Fe(5)-O(20)\\ \hline\\ Fe(7)-O(23)\\ \hline\\ Fe(7)-O(23)\\ \hline\\ Fe(1)-O(21)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(5)-N(7)\\ \hline\\ Fe(5)-N(7)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(17)\\ \hline\\ Fe(5)-O(2)\\ \hline\end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.985(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.059(4) \\ 2.020(5) \\ 2.023(4) \end{array}$ | $\begin{array}{c c} \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline Fe(4)-O(18) \\ \hline Fe(6)-O(21) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.988(4) 1.988(4) 1.988(4) 1.988(4) 1.978(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(8)-N(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(1) \\ Fe(2)-O(3) \\ Fe(4)-N(1) \\ Fe(6)-N(2) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \\ 2.040(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y\\ \hline\\ \#1 \ y, z, x, \#2z, x, y\\ \hline\\ Fe(1)-O(26)\\ \hline\\ Fe(3)-O(18)\\ \hline\\ Fe(5)-O(25)\\ \hline\\ Fe(7)-O(3)\\ \hline\\ Fe(1)-O(19)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(20)\\ \hline\\ Fe(7)-O(23)\\ \hline\\ Fe(1)-O(21)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(17)\\ \hline\\ Fe(5)-O(2)\\ \hline\\ Fe(7)-O(23)\\ \hline\\ Fe(7$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.029(4) \\ 2.029(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \end{array}$ | $\begin{array}{c} \hline \textbf{Compour} \\ \hline \textbf{Fe}(1) - O(2) \\ \hline \textbf{Fe}(3) - N(4) \\ \hline \textbf{Fe}(5) - O(9) \\ \hline \textbf{Fe}(5) - O(9) \\ \hline \textbf{Fe}(7) - O(11) \\ \hline \textbf{Fe}(1) - O(3) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(7) - N(3) \\ \hline \textbf{Fe}(2) - O(24) \\ \hline \textbf{Fe}(4) - O(2) \\ \hline \textbf{Fe}(4) - O(2) \\ \hline \textbf{Fe}(6) - O(3) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(2) - O(22) \\ \hline \textbf{Fe}(4) - O(18) \\ \hline \textbf{Fe}(6) - O(21) \\ \hline \textbf{Fe}(8) - O(23) \\ \hline \end{array}$ | $\begin{array}{c} \textbf{nd 11} \\ \hline 2.122(4) \\ \hline 2.026(6) \\ \hline 2.036(4) \\ \hline 2.056(5) \\ \hline 2.129(4) \\ \hline 2.057(5) \\ \hline 2.205(5) \\ \hline 1.900(4) \\ \hline 1.926(4) \\ \hline 1.916(4) \\ \hline 1.943(4) \\ \hline 1.943(4) \\ \hline 1.978(4) \\ \hline 2.005(4) \\ \hline \end{array}$ | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ Fe(2)-O(3) \\ Fe(4)-N(1) \\ Fe(6)-N(2) \\ Fe(8)-O(16) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.040(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ 2.052(4) \\ \end{array} $ |
| $\begin{array}{c} \#1 \ y, \ z, \ x, \#2z, \ x, \ y\\ \hline\\ Fe(1)-O(26)\\ \hline\\ Fe(3)-O(18)\\ \hline\\ Fe(5)-O(25)\\ \hline\\ Fe(7)-O(3)\\ \hline\\ Fe(1)-O(19)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(5)-O(20)\\ \hline\\ Fe(1)-O(21)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(5)-O(2)\\ \hline\\ Fe(7)-O(13)\\ \hline\end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \end{array}$ | $\begin{tabular}{ c c c c c c } \hline Compound \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(7)-N(3) \\ \hline Fe(2)-O(24) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline Fe(4)-O(18) \\ \hline Fe(6)-O(21) \\ \hline Fe(8)-O(23) \\ \hline $ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.926(4) 1.943(4) 1.988(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(1) \\ Fe$ | $\begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.041(4) \\ 2.050(4) \\ 2.124(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ 2.052(4) \end{array}$ |
| $\begin{array}{c} \texttt{Fe(1)} = \texttt{O(2)} \\ \texttt{#1 y, z, x, \texttt{#2z, x, y}} \\ \texttt{Fe(1)} = \texttt{O(26)} \\ \texttt{Fe(3)} = \texttt{O(18)} \\ \texttt{Fe(3)} = \texttt{O(25)} \\ \texttt{Fe(7)} = \texttt{O(25)} \\ \texttt{Fe(7)} = \texttt{O(25)} \\ \texttt{Fe(7)} = \texttt{O(26)} \\ \texttt{Fe(7)} = \texttt{O(26)} \\ \texttt{Fe(3)} = \texttt{O(24)} \\ \texttt{Fe(5)} = \texttt{O(20)} \\ \texttt{Fe(7)} = \texttt{O(20)} \\ \texttt{Fe(7)} = \texttt{O(20)} \\ \texttt{Fe(1)} = \texttt{O(1)} \\ \texttt{Fe(3)} = \texttt{O(2)} \\ \texttt{Fe(1)} = \texttt{O(1)} \\ \texttt{Fe(1)} = \texttt{O(1)} \\ \end{bmatrix}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.985(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.978(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \end{array}$ | $\begin{tabular}{ c c c c c c } \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(2)-O(24) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline Fe(4)-O(18) \\ \hline Fe(6)-O(21) \\ \hline Fe(8)-O(23) \\ \hline \hline Compoun \\ \hline Fe(3)-O(1) \\ \hline \end{tabular}$ | $\begin{array}{r} \textbf{nd 11} \\ \hline 2.122(4) \\ \hline 2.026(6) \\ \hline 2.036(4) \\ \hline 2.056(5) \\ \hline 2.129(4) \\ \hline 2.057(5) \\ \hline 2.205(5) \\ \hline 1.900(4) \\ \hline 1.926(4) \\ \hline 1.916(4) \\ \hline 1.988(4) \\ \hline 1.988(4) \\ \hline 1.978(4) \\ \hline 2.005(4) \\ \textbf{nd 12} \\ \hline 1.988(4) \\ \hline 1.988(4) \\ \hline 1.988(4) \\ \hline 1.988(4) \\ \hline 1.978(4) \\ \hline 2.005(4) \\ \textbf{nd 12} \\ \hline 1.988(4) \\ \hline 1.$ | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(1) \\ F$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.050(4) \\ 2.040(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ 2.052(4) \\ \hline 2.015(4) \\ \end{array} $ |
| $\begin{array}{c} \texttt{Fe(1)} = \texttt{O(2)} \\ \texttt{#1 y, z, x, \texttt{#2z, x, y}} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(3)} = \texttt{O(18)} \\ \hline \texttt{Fe(5)} = \texttt{O(25)} \\ \hline \texttt{Fe(7)} = \texttt{O(25)} \\ \hline \texttt{Fe(7)} = \texttt{O(25)} \\ \hline \texttt{Fe(7)} = \texttt{O(26)} \\ \hline \texttt{Fe(3)} = \texttt{O(24)} \\ \hline \texttt{Fe(3)} = \texttt{O(24)} \\ \hline \texttt{Fe(5)} = \texttt{O(20)} \\ \hline \texttt{Fe(7)} = \texttt{O(21)} \\ \hline \texttt{Fe(3)} = \texttt{O(1)} \\ \hline \texttt{Fe(1)} = \texttt{O(1)} \\ \hline \hline \texttt{Fe(1)} = \texttt{O(1)} \\ \hline \texttt{Fe(1)} = \texttt{O(16)} \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline 1.868(4) \\ 1.975(4) \end{array}$ | $\begin{array}{c} \hline \textbf{Compout} \\ \hline \textbf{Fe}(1) - O(2) \\ \hline \textbf{Fe}(3) - N(4) \\ \hline \textbf{Fe}(5) - O(9) \\ \hline \textbf{Fe}(5) - O(9) \\ \hline \textbf{Fe}(7) - O(11) \\ \hline \textbf{Fe}(1) - O(3) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(7) - N(3) \\ \hline \textbf{Fe}(7) - O(24) \\ \hline \textbf{Fe}(7) - O(24) \\ \hline \textbf{Fe}(8) - O(24) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(8) - O(22) \\ \hline \textbf{Fe}(8) - O(21) \\ \hline \textbf{Fe}(8) - O(23) \\ \hline \textbf{Compout} \\ \hline \textbf{Fe}(3) - O(1) \\ \hline \textbf{Fe}(3) - O(3) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.926(4) 1.943(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1. | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ Fe(6)-O(1) \\ Fe$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.041(4) \\ 2.040(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ 2.052(4) \\ \hline 2.015(4) \\ 2.075(4) \\ 2.075(4) \\ \end{array} $ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y\\ \hline\\ \#1 \ y, z, x, \#2z, x, y\\ \hline\\ Fe(1)-O(26)\\ \hline\\ Fe(3)-O(18)\\ \hline\\ Fe(5)-O(25)\\ \hline\\ Fe(1)-O(19)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(24)\\ \hline\\ Fe(3)-O(20)\\ \hline\\ Fe(1)-O(21)\\ \hline\\ Fe(3)-O(21)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(3)-O(1)\\ \hline\\ Fe(1)-O(1)\\ \hline\\ Fe(1)-O(1)\\ \hline\\ Fe(1)-O(1)\\ \hline\\ Fe(1)-O(17)\\ \hline\end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline \\ 1.868(4) \\ 1.975(4) \\ 2.004(4) \\ \hline \end{array}$ | $\begin{array}{c} \hline \textbf{Compout} \\ \hline \textbf{Fe}(1) - O(2) \\ \hline Fe(3) - N(4) \\ \hline Fe(5) - O(9) \\ \hline Fe(5) - O(9) \\ \hline Fe(7) - O(11) \\ \hline Fe(1) - O(3) \\ \hline Fe(3) - O(15) \\ \hline Fe(3) - O(15) \\ \hline Fe(5) - O(7) \\ \hline Fe(5) - O(7) \\ \hline Fe(5) - O(7) \\ \hline Fe(7) - N(3) \\ \hline Fe(2) - O(24) \\ \hline Fe(2) - O(24) \\ \hline Fe(2) - O(24) \\ \hline Fe(4) - O(2) \\ \hline Fe(6) - O(3) \\ \hline Fe(6) - O(2) \\ \hline Fe(8) - O(26) \\ \hline Fe(2) - O(22) \\ \hline Fe(8) - O(26) \\ \hline Fe(6) - O(21) \\ \hline Fe(8) - O(21) \\ \hline Fe(8) - O(23) \\ \hline \hline \textbf{Compout} \\ \hline Fe(3) - O(1) \\ \hline Fe(3) - O(1) \\ \hline Fe(3) - O(18) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.943(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1.988(4) 1.988(4) 1.988(4) 1.992(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(2)-O(1) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(5)-O(5)^{\#1} \\ Fe(5)-O(17) \\ Fe(5)-O(12) \\ Fe(5)-O(12$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.038(6) \\ 2.078(4) \\ 2.041(4) \\ 2.041(4) \\ 2.040(4) \\ 2.124(4) \\ 2.223(5) \\ 2.212(5) \\ 2.052(4) \\ \hline 2.015(4) \\ 2.075(4) \\ 2.148(4) \\ \end{array} $ |
| $\begin{array}{c} \texttt{Fe(1)} = \texttt{O(2)} \\ \texttt{#1 y, z, x, \texttt{#2z, x, y}} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(3)} = \texttt{O(18)} \\ \hline \texttt{Fe(3)} = \texttt{O(25)} \\ \hline \texttt{Fe(7)} = \texttt{O(25)} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(3)} = \texttt{O(24)} \\ \hline \texttt{Fe(3)} = \texttt{O(26)} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(1)} = \texttt{O(26)} \\ \hline \texttt{Fe(1)} = \texttt{O(17)} \\ \hline \texttt{Fe(3)} = \texttt{O(17)} \\ \hline \texttt{Fe(1)} = \texttt{O(16)} \\ \hline \texttt{Fe(1)} = \texttt{O(16)} \\ \hline \texttt{Fe(1)} = \texttt{O(17)} \\ \hline \texttt{Fe(1)} = \texttt{O(17)} \\ \hline \texttt{Fe(1)} = \texttt{O(17)} \\ \hline \texttt{Fe(1)} = \texttt{O(18)} \\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline \\ 1.868(4) \\ 1.975(4) \\ 2.026(4) \\ \hline \end{array}$ | $\begin{array}{c} \hline \textbf{Compout} \\ \hline \textbf{Fe}(1) - O(2) \\ \hline \textbf{Fe}(3) - N(4) \\ \hline \textbf{Fe}(5) - O(9) \\ \hline \textbf{Fe}(7) - O(11) \\ \hline \textbf{Fe}(7) - O(11) \\ \hline \textbf{Fe}(1) - O(3) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(3) - O(15) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(5) - O(7) \\ \hline \textbf{Fe}(7) - N(3) \\ \hline \textbf{Fe}(7) - N(3) \\ \hline \textbf{Fe}(2) - O(24) \\ \hline \textbf{Fe}(2) - O(24) \\ \hline \textbf{Fe}(4) - O(2) \\ \hline \textbf{Fe}(4) - O(2) \\ \hline \textbf{Fe}(6) - O(3) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(8) - O(26) \\ \hline \textbf{Fe}(4) - O(18) \\ \hline \textbf{Fe}(6) - O(21) \\ \hline \textbf{Fe}(8) - O(23) \\ \hline \hline \textbf{Compout} \\ \hline \textbf{Fe}(3) - O(1) \\ \hline \textbf{Fe}(3) - O(18) \\ \hline \textbf{Fe}(3) - O(18) \\ \hline \textbf{Fe}(3) - O(20) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.988(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1.988(4) 1.988(4) 1.992(4) 2.013(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(5)-O(5)^{\#1} \\ Fe(5)-O(17) \\ Fe(5)-O(12) \\ Fe(5)-O(12) \\ Fe(5)-O(15) \\ \end{array}$ | $ \begin{array}{r} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.0018(4) \\ 2.0019(4) \\ 2.010(4) \\ 2.010(4) \\ 2.0010(4) \\ 2.010(4) \\ 2.0010(4) \\ 2.0010(4) \\ 2.0010(4) \\ 2.0010(4) \\ 2.0010(4$ |
| $\begin{array}{c} \#1 \ y, \ z, \ x, \#2z, \ x, \ y\\ \hline \\ \hline \\ Fe(1)-O(26)\\ \hline \\ Fe(3)-O(18)\\ \hline \\ Fe(5)-O(25)\\ \hline \\ Fe(7)-O(3)\\ \hline \\ Fe(1)-O(19)\\ \hline \\ Fe(3)-O(24)\\ \hline \\ Fe(5)-O(20)\\ \hline \\ Fe(7)-O(23)\\ \hline \\ Fe(7)-O(23)\\ \hline \\ Fe(7)-O(23)\\ \hline \\ Fe(3)-O(1)\\ \hline \\ Fe(1)-O(1)\\ \hline \\ Fe(1)-O(16)\\ \hline \\ Fe(1)-O(6)\\ \hline \\ Fe(1)-O(6)\\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.978(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline \\ 1.868(4) \\ 1.975(4) \\ 2.004(4) \\ 2.026(4) \\ 2.066(4) \\ \hline \end{array}$ | $\begin{array}{c c} \hline Compoun \\ \hline Compoun \\ \hline Fe(1)-O(2) \\ \hline Fe(3)-N(4) \\ \hline Fe(5)-O(9) \\ \hline Fe(7)-O(11) \\ \hline Fe(1)-O(3) \\ \hline Fe(1)-O(3) \\ \hline Fe(3)-O(15) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(5)-O(7) \\ \hline Fe(2)-O(24) \\ \hline Fe(2)-O(24) \\ \hline Fe(4)-O(2) \\ \hline Fe(6)-O(3) \\ \hline Fe(6)-O(3) \\ \hline Fe(6)-O(2) \\ \hline Fe(8)-O(26) \\ \hline Fe(2)-O(22) \\ \hline Fe(4)-O(18) \\ \hline Fe(6)-O(21) \\ \hline Fe(6)-O(21) \\ \hline Fe(3)-O(1) \\ \hline Fe(3)-O(1) \\ \hline Fe(3)-O(1) \\ \hline Fe(3)-O(18) \\ \hline Fe(3)-O(20) \\ \hline Fe(3)-O(16) \\ \hline \end{array}$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.943(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1.992(4) 2.013(4) 2.038(4) 1.992(4) 2.038(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(2)-O(1) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(8)-O(1) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(5)-O(17) \\ Fe(5)-O(17) \\ Fe(5)-O(15) \\ Fe(6)-O(3) \\ \end{array}$ | $\begin{array}{c} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.00$ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y\\ \hline \#1 \ y, z, x, \#2z, x, y\\ \hline Fe(1)-O(26)\\ \hline Fe(3)-O(18)\\ \hline Fe(5)-O(25)\\ \hline Fe(7)-O(3)\\ \hline Fe(1)-O(19)\\ \hline Fe(3)-O(24)\\ \hline Fe(5)-O(20)\\ \hline Fe(7)-O(23)\\ \hline Fe(7)-O(23)\\ \hline Fe(7)-O(23)\\ \hline Fe(7)-O(21)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(1)-O(16)\\ \hline Fe(1)-O(17)\\ \hline Fe(1)-O(8)\\ \hline Fe(1)-O(6)\\ \hline Fe(1)-N(1)\\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.023(4) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline \\ 1.868(4) \\ 1.975(4) \\ 2.004(4) \\ 2.026(4) \\ 2.026(4) \\ 2.035(5) \\ \hline \end{array}$ | Compoun $Fe(1)-O(2)$ $Fe(3)-N(4)$ $Fe(5)-O(9)$ $Fe(7)-O(11)$ $Fe(1)-O(3)$ $Fe(3)-O(15)$ $Fe(5)-O(7)$ $Fe(7)-N(3)$ $Fe(2)-O(24)$ $Fe(4)-O(2)$ $Fe(6)-O(3)$ $Fe(6)-O(21)$ $Fe(6)-O(21)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(16)$ $Fe(4)-O(2)$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.943(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1.992(4) 2.013(4) 2.038(4) 1.905(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(2)-O(1) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-N(2) \\ Fe(6)-N(2) \\ Fe(5)-O(15) \\ Fe(5)-O(15) \\ Fe(6)-O(2) \\ F$ | $\begin{array}{c} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.015(4) \\ 2.0015(4)$ |
| $\begin{array}{c} \#1 \ y, z, x, \#2z, x, y\\ \hline \#1 \ y, z, x, \#2z, x, y\\ \hline Fe(1)-O(26)\\ \hline Fe(3)-O(18)\\ \hline Fe(5)-O(25)\\ \hline Fe(7)-O(3)\\ \hline Fe(1)-O(19)\\ \hline Fe(3)-O(24)\\ \hline Fe(5)-O(20)\\ \hline Fe(7)-O(23)\\ \hline Fe(1)-O(21)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(3)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(1)-O(1)\\ \hline Fe(1)-O(16)\\ \hline Fe(1)-O(6)\\ \hline Fe(1)-O(1)\\ \hline Fe(2)-O(1)\\ \hline Fe(2)-O(1)\\ \hline \end{array}$ | $\begin{array}{c} 1.912(4) \\ 1.985(4) \\ 1.995(4) \\ 1.995(4) \\ 1.924(4) \\ 1.920(4) \\ 2.013(4) \\ 2.005(4) \\ 1.978(4) \\ 1.978(4) \\ 1.944(4) \\ 2.018(4) \\ 2.021(6) \\ 1.992(4) \\ 2.020(5) \\ 2.020(5) \\ 2.023(4) \\ 2.010(4) \\ \hline \\ 1.868(4) \\ 1.975(4) \\ 2.004(4) \\ 2.026(4) \\ 2.026(4) \\ 2.025(5) \\ 1.882(4) \\ \hline \end{array}$ | Compoun $Fe(1)-O(2)$ $Fe(3)-N(4)$ $Fe(5)-O(9)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(11)$ $Fe(7)-O(15)$ $Fe(7)-N(3)$ $Fe(2)-O(24)$ $Fe(4)-O(2)$ $Fe(6)-O(2)$ $Fe(6)-O(2)$ $Fe(6)-O(21)$ $Fe(6)-O(21)$ $Fe(6)-O(21)$ $Fe(6)-O(21)$ $Fe(3)-O(18)$ $Fe(3)-O(1)$ $Fe(3)-O(1)$ $Fe(3)-O(16)$ $Fe(4)-O(2)$ $Fe(4)-O(2)$ $Fe(4)-O(2)$ $Fe(4)-O(2)$ $Fe(4)-O(2)$ | nd 11 2.122(4) 2.026(6) 2.036(4) 2.056(5) 2.129(4) 2.057(5) 2.205(5) 1.900(4) 1.926(4) 1.916(4) 1.943(4) 1.943(4) 1.988(4) 1.978(4) 2.005(4) nd 12 1.988(4) 1.988(4) 1.988(4) 1.992(4) 2.013(4) 2.038(4) 1.905(4) 1.936(4) | $\begin{array}{c} Fe(2)-O(25) \\ Fe(4)-O(6) \\ Fe(6)-O(20) \\ Fe(8)-O(14) \\ Fe(2)-O(2) \\ Fe(4)-O(19) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(6)-O(10) \\ Fe(2)-O(1) \\ Fe(4)-O(8) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(6)-O(12) \\ Fe(5)-O(5)^{\#1} \\ Fe(5)-O(15) \\ Fe(5)-O(15) \\ Fe(6)-O(20) \\ Fe(6)-O(21) \\ \end{array}$ | $\begin{array}{c} 1.947(4) \\ 2.001(5) \\ 1.996(4) \\ 2.017(5) \\ 2.070(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.008(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.009(4) \\ 2.009(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0015(4) \\ 2.0000(4) \\ 2.000(4) \\ 2.000(4) \\ 2.000(4) \\ 2.000(4) \\ 2.000(4) \\ 2$ |

| Fe(2)-O(21) | 1.991(4) | Fe(4) - O(18) | 1.969(4) | Fe(6) - O(13) | 2.044(4) |
|-----------------------|-----------|--------------------------|-------------------------------|----------------------|------------------------|
| Fe(2) - O(10) | 2.045(4) | Fe(4) - O(19) | 2.198(4) | Fe(6)-N(3) | 2.274(5) |
| Fe(2) - O(7) | 2.089(4) | Fe(4) - N(2) | 2.318(5) | $Fe(1)\cdots Fe(3)$ | 2.9411(1) |
| Fe(2)-O(9) | 2.142(4) | $Fe(5)-O(3)^{\#1}$ | 1.876(4) | $Fe(3)\cdots Fe(4)$ | 2.9490(16) |
| Fe(3)–O(2) | 1.971(4) | Fe(5) - O(2) | 1.880(4) | Fe(3)Fe(6) | 2.9560(19) |
| #1 -x+1,-y+2,-z | | | | | |
| | | Compound | 1 13 | | |
| Fe(1)-O(1) | 1.913(15) | Fe(5) - O(17) | 2.018(16) | Fe(9)-O(13) | 1.937(16) |
| Fe(1)-O(4) | 1.947(15) | Fe(5) - O(12) | 2.046(16) | Fe(9)-O(3) | 2.024(16) |
| Fe(1)-O(18) | 1.962(15) | Fe(5)-O(3) | 2.049(16) | Fe(9)-O(14) | 2.107(15) |
| Fe(1)-O(5) | 1.969(15) | Fe(5)-O(15) | 2.094(15) | Fe(9)-O(11) | 2.261(16) |
| Fe(1)-O(23) | 2.049(15) | Fe(6)-O(17) | 1.960(15) | Fe(9)-N(3) | 2.280(19) |
| Fe(1)-O(19) | 2.142(14) | Fe(6)-O(16) | 1.996(18) | Fe(9)-N(4) | 2.30(2) |
| Fe(2)-O(23) | 2.000(15) | Fe(6)-O(4) | 2.061(15) | Fe(10)-O(14) | 1.961(15) |
| Fe(2) - N(9) | 2.007(19) | Fe(6)-O(18) | 2.086(15) | Fe(10)–O(4) | 1.964(16) |
| Fe(2)-O(10) | 2.016(16) | Fe(6)-N(6) | 2.25(2) | Fe(10)-O6 | 1.982(15) |
| Fe(3)-O(10) | 1.951(16) | Fe(6)-O(15) | 2.282(16) | Fe(10)–O(3) | 1.993(16) |
| Fe(3)-O(8) | 1.977(15) | Fe(6)-N(5) | 2.31(2) | Fe(10)–O(26) | 2.020(15) |
| Fe(3)-O(2) | 2.049(14) | Fe(7)-O(6) | 1.953(15) | Fe(10)–O(15) | 2.171(17) |
| Fe(3)-O(7) | 2.085(15) | Fe(7)–O(22) | 1.955(14) | Fe(11)-O(21) | 2.016(16) |
| Fe(3) - O(9) | 2.234(14) | Fe(7) - O(2) | 1.980(14) | Fe(11) - O(26) | 2.025(16) |
| Fe(3) = N(1) | 2.278(19) | Fe(7) - O(1) | 2.013(15) | Fe(11) - N(18) | 2.040(19) |
| Fe(3) - N(2) | 2.319(18) | Fe(7) - O(25) | 2.035(15) | Fe(11) = O(16) | 2.049(19) |
| Fe(4) - O(5) | 1 932(15) | Fe(7) - O(9) | 2 123(15) | Fe(11) = O(4) | 2.055(14) |
| Fe(4) = O(2) | 1.932(13) | Fe(8) = O(13) | 1 990(15) | $F_{e}(11) = O(10)$ | 2.033(11) 2.087(15) |
| Fe(4) = O(3) | 1.953(15) | Fe(8) - O(25) | 2 008(16) | $F_{e}(12) = O(21)$ | 1.935(15) |
| Fe(4) = O(7) | 1.965(15) | Fe(8) - O(8) | 2.000(10) 2.044(15) | Fe(12) = O(21) | 1.953(13) 1.963(17) |
| Fe(4) = O(24) | 2 029(16) | Fe(8) - N(12) | 2.011(13) | $F_{e}(12) = O(20)$ | 2.081(15) |
| Fe(4) = O(11) | 2.029(10) | Fe(8) = O(2) | 2.05(2) | Fe(12) = O(22) | 2.001(15) |
| Fe(5) = O(24) | 1.948(16) | Fe(8) = O(11) | 2.03+(10) 2.111(17) | $F_{e}(12) = O(13)$ | 2.272(13) |
| Fe(5) = N(15) | 1.97(2) | Fe(9) = O(12) | $\frac{2.111(17)}{1.922(17)}$ | $F_{e}(12) - N(8)$ | 2.277(19) 2 304(18) |
| | 1.97(2) | | 1.922(17) | 10(12)-11(0) | 2.504(10) |
| Fe(1) = O(9) | 1 937(6) | Fe(3) = O(5) | 2,000(7) | $Fe(5) = O(7)^{\#1}$ | 1 958(7) |
| Fe(1) = O(3) | 1.941(6) | Fe(3) = O(7) | 2.084(7) | Fe(5) = O(4) | 1.980(4) |
| Fe(1) - O(2) | 1.960(6) | Fe(3) - O(2) | 2.107(7) | $Fe(5) - O(2)^{\#1}$ | 1.986(7) |
| Fe(1) - O(1) | 1.984(4) | Fe(3) - O(6) | 2.151(7) | Fe(5) - O(12) | 2.151(6) |
| Fe(1)-O(6) | 2.062(7) | Fe(3) - N(2) | 2.305(8) | Fe(5)-Cl(2) | 2.444(3) |
| Fe(1)-Cl(1) | 2.566(3) | Fe(3) - N(1) | 2.309(9) | Fe(6)-O(11) | 1.957(7) |
| $Fe(2) - O(10)^{\#1}$ | 1.983(7) | Fe(4)-O(8) | 2.010(7) | Fe(6)-O(10) | 1.964(7) |
| Fe(2)-O(5) | 2.004(7) | Fe(4)-O(11) | 2.057(7) | Fe(6)-O(3) | 2.038(6) |
| Fe(2)–O(2) | 2.017(6) | Fe(4)-O(3) | 2.191(7) | Fe(6)-O(9) | 2.083(6) |
| $Fe(2) - O(12)^{\#1}$ | 2.073(7) | Fe(4)-O(6) | 2.289(7) | Fe(6) - N(3) | 2.272(8) |
| Fe(2)-Cl(3) | 2.337(3) | $Fe(4)-Cl(\overline{4})$ | 2.432(3) | Fe(6)-O(12) | 2.304(7) |
| Fe(2)-Cl(1) | 2.459(3) | Fe(4)-Cl(2) | 2.603(3) | Fe(6)–N(4) | 2.348(8) |
| Fe(3)-O(8) | 1.936(6) | Fe(5)-O(3) | 1.908(7) | | |
| #1 - x, y, -z + 1/2 | | | | | |
| | 1.000/5 | Compound | 115 | | |
| Fe(1)=O(1) | 1.838(5) | Fe(5) = O(2) | 1.906(6) | Fe(8) = O(35) | 2.087(6) |
| Fe(1) = O(6) | 1.957(5) | Fe(5)=O(3) | 1.918(5) | Fe(9) = O(35) | 1.916(6) |
| Fe(1)=O(8) | 1.964(6) | Fe(5)=O(1) | 1.924(5) | Fe(9) = O(29) | 1.991(6) |
| re(1) = O(23) | 2.018(6) | re(3)=O(3) | 2.095(5) | Fe(9) = O(30) | 1.997(6) |

| Fe(1) - O(33) | 2.089(6) | Fe(5) - O(35) | 2.140(5) | Fe(9) - O(25) | 2.033(7) |
|--------------------------------|-----------------------------|-------------------------------|-----------------------------|------------------------------|-----------------------------|
| Fe(2)-O(2) | 1.910(5) | Fe(5)-O(4) | 2.143(5) | Fe(9)-O(18) | 2.047(7) |
| Fe(2) - O(9) | 2.007(6) | Fe(6) - O(4) | 1.935(5) | Fe(9) - N(2) | 2.223(8) |
| Fe(2) = O(34) | 2.014(6) | Fe(6) - O(28) | 1.967(6) | Fe(10) - O(5) | 1.911(5) |
| Fe(2) = O(7) | 2.034(5) | Fe(6) = O(27) | 1 997(6) | Fe(10) - O(31) | 1.987(5) |
| Fe(2) = O(8) | 2.055(5) | Fe(6) = O(14) | 2 010(6) | Fe(10) = O(32) | 1 990(6) |
| Fe(2) = O(6) | 2.033(6) | Fe(6) = O(16) | 2.013(6) | Fe(10) = O(22) | 2 019(6) |
| Fe(3) = O(3) | 1.852(5) | Fe(6) = N(1) | 2.013(0) 2.241(7) | Fe(10) = O(20) | 2.019(0) 2.048(6) |
| $Fe(3) = O(34)^{\#1}$ | 1.052(5) | Fe(7) = O(3) | 1.910(5) | Fe(10) = N(3) | 2.040(0) |
| Fe(3) = O(6) | 1.955(0) | Fe(7) = O(4) | 1.956(5) | Fe(10) = R(3) | 1.906(6) |
| $Fe(3) = O(6)^{\#1}$ | 2 011(5) | Fe(7) = O(32) | 1.991(6) | Fe(11) = O(29) | 1.970(6) |
| Fe(3) = O(11) | 2.011(5) | Fe(7) = O(15) | 2.043(6) | Fe(11) = O(5) | 2,005(5) |
| Fe(3) = O(7) | 2.113(5) | Fe(7) = O(12) | 2.043(6) | Fe(11) = O(19) | 2.003(5) 2.047(6) |
| Fe(4) = O(2) | 1 906(5) | Fe(7) = O(12) | 2.045(6) | Fe(11) = O(24) | 2.077(0) |
| Fe(4) = O(25) | 1.984(6) | Fe(8) = O(30) | 1.913(6) | Fe(11) = O(24) | 2.030(0) 2.070(6) |
| $F_{e}(4) = O(27)$ | 1.007(6) | $F_{e}(8) = O(28)$ | 1.913(6) | Fe(11) = O(21) | 2.070(0) 2.0378(18) |
| Fe(4) = O(27) | $\frac{1.992(0)}{2.023(6)}$ | $F_{0}(8) = O(21)$ | 1.916(0) 1.026(6) | $Fe(4)\cdots Fe(3)$ | 2.9378(18) 2.9530(17) |
| Fe(4) = O(10) Fe(4) = O(17) | 2.023(0) 2.070(6) | $F_{0}(8) = O(4)$ | $\frac{1.920(0)}{2.070(6)}$ | $Fe(5) \cdots Fe(7)$ | 2.9330(17) |
| Fe(4) = O(17) | 2.070(0) | $F_{c}(8) = O(5)$ | 2.079(0) | Fe(5) = Fe(11) | 2.8330(17) |
| Fe(4)=O(20) | 2.090(0) | $re(\delta) = O(3)$ | 2.080(3) | re(3)re(11) | 2.9004(18) |
| #1 - X + 1, -y + 1, -2 + 1 | | Compound | 116 | | |
| $E_{2}(1) = O(6)$ | 1 967(7) | $E_{2}(5) = O(6)$ | 1.802(7) | $E_{2}(8) = O(2)$ | 2.110(8) |
| Fe(1) = O(0) | $\frac{1.007(7)}{1.026(7)}$ | Fe(3)=O(0) | $\frac{1.092(7)}{1.001(7)}$ | Fe(0) = O(3) | 2.110(6) 1.022(7) |
| Fe(1)=O(4) Fe(1)=O(8) | 1.930(7) 1.084(7) | Fe(3)=O(3) $F_2(5)=O(31)$ | 1.991(7) | Fe(9)=O(3) $F_2(0)=O(17)$ | 1.923(7) 1.094(9) |
| Fe(1) = O(8) | 1.964(7) | Fe(3)=O(31) $F_2(5)=O(18)$ | 1.991(8) | Fe(9)=O(17) | 1.964(6) |
| Fe(1) = O(10) Fe(1) = O(25) | 2.000(8) | Fe(3)=O(16) $F_2(5)=O(11)$ | 2.020(8) | Fe(9)=O(28) | 1.963(6) |
| Fe(1) = O(53) | $\frac{2.113(7)}{1.000(7)}$ | Fe(3)=O(11) Fa(5)=O(16) | 2.039(8) | Fe(9)=O(29) | 2.029(8) |
| Fe(2)=O(3) | 1.000(7) | Fe(3)=O(10) | $\frac{2.117(8)}{1.009(8)}$ | Fe(9)=O(19) | 2.070(8) |
| Fe(2)=O(34) | 1.982(7) | Fe(0)=O(3) | 1.908(8) | Fe(9) = N(1) | 2.233(10) |
| Fe(2)=O(4) | 2.003(7) | Fe(6)=O(29) | 1.989(8) | Fe(10)=O(1) | 1.929(8) |
| Fe(2)=O(4) | 2.018(7) | Fe(0)=O(1) | 1.989(8) | Fe(10) = O(33) | 1.989(8) |
| Fe(2)=O(12) | 2.090(8) | Fe(0)=O(20) | 2.054(8) | Fe(10)=O(32) | 2.003(8) |
| Fe(2)=O(9) | $\frac{2.131(7)}{1.014(7)}$ | Fe(6)=O(13) | 2.056(8) | Fe(10) = O(23) | 2.022(8) |
| Fe(3)=O(7) | 1.914(7) | Fe(6)=O(22) | $\frac{2.147(9)}{1.002(7)}$ | Fe(10) = O(21) | 2.027(8) |
| Fe(3)=O(34) | 2.017(7) | Fe(7)=O(7) | 1.903(7) | Fe(10) = N(3) | 2.214(10) |
| Fe(3)=O(14) | 2.025(8) | Fe(7)=O(2) | $\frac{1.9/3(7)}{1.007(0)}$ | Fe(11)=O(2) | 1.934(7) |
| Fe(3)=O(9) | 2.040(7) | Fe(7)=O(32) | $\frac{1.997(9)}{2.022(7)}$ | Fe(11)=O(31) | $\frac{2.007(8)}{2.012(8)}$ |
| Fe(3)=O(8) | 2.042(8) | Fe(7)=O(15) | 2.033(7) | Fe(11)=O(27) | 2.013(8) |
| Fe(3)=O(4) | 2.088(7) | Fe(7)=O(24) | 2.048(7) | Fe(11) = O(25) | 2.050(8) |
| Fe(4)=O(5) | 1.90/(7) | Fe(7)=O(26) | 2.112(8) | Fe(11)=N(2) | 2.200(10) |
| Fe(4) = O(6) | 1.918(7) | Fe(8) = O(30) | 1.932(7) | Fe(8) - Fe(10) | 2.976(2) |
| Fe(4) = O(7) | 1.918(7) | Fe(8) = O(28) | 1.933(7) | $Fe(4)\cdots Fe(8)$ | 2.849(2) |
| Fe(4) = O(3) | 2.084(7) | Fe(8) = O(33) | 1.944(8) | $Fe(4)\cdots Fe(7)$ | 2.943(2) |
| Fe(4) = O(1) | 2.129(8) | Fe(8) = O(1) | 2.075(7) | $Fe(4) \cdots Fe(6)$ | 2.950(2) |
| Fe(4) = O(2) | 2.143(7) | Fe(8) = O(2) | 2.080(7) | $Fe(4)\cdots Fe(5)$ | 2.970(2) |
| #1 -x+2,-y+2,-z | | a | | | |
| E (1) 0(12) | 1.00.4/2 | | 1.002/2 | F (2) O(12) | 1.051(4) |
| Fe(1)=O(13) | 1.894(3) | Fe(2)=O(13) | 1.883(3) | Fe(3)=O(13) | 1.951(4) |
| Fe(1) = O(7) | 1.988(5) | Fe(2) = O(6) | 2.000(4) | Fe(3) = O(4) | 2.010(4) |
| Fe(1)=O(3) | 1.999(4) | Fe(2) = O(10) | 2.013(4) | Fe(3) = O(15) | 2.014(5) |
| Fe(1)=O(1) | 2.003(5) | Fe(2) = O(11) | 2.015(4) | Fe(3) = O(8) | 2.015(5) |
| Fe(1) = O(12) | 2.022(5) | Fe(2)=O(2) | 2.022(4) | Fe(3) = O(5) | 2.024(4) |
| Fe(1) = N(1) | 2.207(5) | $Fe(2)=N(2)^{\#1}$ | 2.190(4) | Fe(3) = O(9) | 2.031(5) |

| #1 -x+3/2, y-1/2, -z+3/ | #1 -x+3/2,y-1/2,-z+3/2 | | | | | | |
|--|------------------------|---------------------------|-----------|-------------------------|------------|--|--|
| Compound 18 | | | | | | | |
| Fe(1)–O(1) | 1.906(4) | $Fe(2)-N(4)^{\#1}$ | 2.350(5) | Fe(4)–O(18) | 2.047(5) | | |
| Fe(1)–O(2) | 1.970(4) | Fe(3)–O(1) | 1.897(4) | Fe(4)–O(17) | 2.162(4) | | |
| Fe(1)–O(4) | 1.979(4) | Fe(3)–O(2) | 1.968(4) | Fe(4)–N(1) | 2.204(6) | | |
| Fe(1)–O(15) | 2.022(5) | Fe(3)–O(6) | 1.979(4) | $Fe(1)\cdots Fe(2)$ | 3.323(1) | | |
| Fe(1)–O(13) | 2.025(4) | Fe(3)–O(9) | 2.025(4) | $Fe(1)\cdots Fe(3)$ | 2.855(2) | | |
| Fe(2)–O(1) | 1.803(4) | Fe(3)–O(11) | 2.050(5) | $Fe(1)\cdots Fe(4)$ | 3.402(2) | | |
| Fe(2)–O(12) | 2.028(4) | Fe(3)–O(16) | 2.053(5) | $Fe(2)\cdots Fe(3)$ | 3.311(1) | | |
| Fe(2)–O(14) | 2.038(4) | Fe(4)–O(2) | 1.821(4) | $Fe(3)\cdots Fe(4)$ | 3.440(1) | | |
| Fe(2)–O(8) | 2.047(5) | Fe(4)–O(3) | 2.040(5) | $Fe(2)\cdots Fe(4)$ | 6.015(2) | | |
| Fe(2)–O(10) | 2.058(4) | Fe(4)–O(5) | 2.044(5) | | | | |
| $\#1 x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{3}{2}$ | 1/2 | • · · · · · · | | | | | |
| | | Compoun | d 19 | | | | |
| Fe(1)-O(1) | 1.898(5) | Fe(2)-O(1) | 1.866(9) | Fe(3)-O(9) | 2.018(11) | | |
| Fe(1)-O(5) | 1.980(9) | Fe(2)-O(2) | 1.987(10) | Fe(3)-N(3) | 2.142(17) | | |
| Fe(1)-O(3) | 1.982(10) | Fe(2)-O(4) | 1.983(9) | Fe(2)-O _{carb} | 2000 | | |
| Fe(1)-O(6) | 2.023(8) | Fe(2)-N(2) | 2.193(12) | $Fe(1)\cdots Fe(1)$ | 3.282(2) | | |
| Fe(1)-O(7) | 2.010(8) | Fe(2)-O _{carb} | 1.985 | $Fe(1)\cdots Fe(2)$ | 3.263(2) | | |
| Fe(1)-N(1) | 2.138(10) | Fe(3)-O(8) | 1.881(2) | $Fe(3)\cdots Fe(3)$ | 3.259(4) | | |
| Fe(1)-O _{carb} | 1.999 | Fe(3)-O(10) ^{#1} | 1.981(10) | $Fe(2)\cdots Fe(3)$ | 11.380(3) | | |
| #1 - y + 1, x - y + 1, - | -Z | | | | | | |
| | | Compoun | d 20 | | | | |
| Dy(1)-O(22) | 2.274(6) | Dy(3)-N(5) | 2.658(8) | Fe(4)-O(33) | 1.971(6) | | |
| Dy(1)-O(20) | 2.299(5) | Dy(3)–N(6) | 2.676(8) | Fe(4)-O(34) | 2.007(8) | | |
| Dy(1)-O(19) | 2.320(6) | Fe(1)-O(20) | 1.949(6) | Fe(4)-O(11) | 2.035(7) | | |
| Dy(1)-O(21) | 2.326(6) | Fe(1)-O(21) | 1.960(6) | Fe(4)-O(10) | 2.070(7) | | |
| Dy(1)-O(1) | 2.338(7) | Fe(1)-O(32) | 1.981(5) | Fe(5)-O(28) | 1.954(7) | | |
| Dy(1)-O(18) | 2.348(6) | Fe(1)-O(31) | 1.994(6) | Fe(5)-O(35) | 1.955(6) | | |
| Dy(1)-N(1) | 2.660(7) | Fe(1)-O(2) | 2.041(6) | Fe(5)-O(30) | 1.960(7) | | |
| Dy(1)-N(2) | 2.673(7) | Fe(1) - O(3) | 2.056(6) | Fe(5)-O(36) | 2.004(7) | | |
| Dy(2)-O(26) | 2.278(6) | Fe(2)–O(23) | 1.938(6) | Fe(5)-O(14) | 2.040(7) | | |
| Dy(2)-O(23) | 2.294(6) | Fe(2)–O(25) | 1.966(6) | Fe(5)-O(15) | 2.071(8) | | |
| Dy(2)–O(6) | 2.330(7) | Fe(2)–O(32) | 1.988(6) | Fe(6)-O(19) | 1.944(6) | | |
| Dy(2)-O(24) | 2.341(6) | Fe(2)-O(31) | 1.994(6) | Fe(6)-O(22) | 1.966(7) | | |
| Dy(2)-O(7) | 2.348(6) | Fe(2)-O(4) | 2.049(7) | Fe(6)-O(35) | 1.972(6) | | |
| Dy(2)-O(25) | 2.352(6) | Fe(2) - O(5) | 2.050(7) | Fe(6)-O(36) | 2.004(7) | | |
| Dy(2)-N(4) | 2.660(8) | Fe(3)–O(24) | 1.949(6) | Fe(6)-O(17) | 2.054(7) | | |
| Dy(2)-N(3) | 2.685(7) | Fe(3)–O(26) | 1.956(6) | Fe(6)-O(16) | 2.070(8) | | |
| Dy(3)–O(27) | 2.291(7) | Fe(3)-O(33) | 1.977(7) | $Dy(1)\cdots Fe(6)$ | 3.3603(17) | | |
| Dy(3)-O(30) | 2.297(6) | Fe(3)-O(34) | 1.994(7) | $Dy(1)\cdots Fe(1)$ | 3.3697(14) | | |
| Dy(3)-O(29) | 2.311(7) | Fe(3)–O(9) | 2.047(7) | $Dy(2)\cdots Fe(3)$ | 3.3536(16) | | |
| Dy(3)-O(28) | 2.326(7) | Fe(3)-O(8) | 2.067(9) | $Dy(2)\cdots Fe(2)$ | 3.3744(14) | | |
| Dy(3)-O(13) | 2.340(7) | Fe(4)-O(27) | 1.946(8) | $Dy(3)\cdots Fe(5)$ | 3.3718(17) | | |
| Dy(3)-O(12) | 2.351(7) | Fe(4)-O(29) | 1.956(6) | $Dy(3)\cdots Fe(4)$ | 3.3733(17) | | |
| | | Compoun | d 21 | | | | |
| Dy(1)-O(19) | 2.305(9) | Dy(4)-O(30) | 2.338(7) | Fe(4)-O(31) | 1.987(8) | | |
| Dy(1)-O(17) | 2.312(8) | Dy(4)-O(32) | 2.344(8) | Fe(4)–O(29) | 1.991(8) | | |
| Dy(1)-O(18) | 2.324(8) | Dy(4)-O(15) | 2.377(7) | Fe(4)-O(12) | 2.041(8) | | |
| Dy(1)-O(36) | 2.327(8) | Dy(4)-O(13) | 2.391(7) | Fe(4)-N(7) | 2.270(9) | | |
| Dy(1)-O(3) | 2.341(8) | Dy(4)–O(14) | 2.468(8) | Fe(5)-O(32) | 1.943(8) | | |
| Dy(1)-O(1) | 2.371(11) | Dy(4)–N(8) | 2.689(10) | Fe(5)-O(33) | 1.956(7) | | |

| Dy(1)-O(2) | 2.455(9) | Fe(1)-O(18) | 1.942(8) | Fe(5)-O(35) | 1.961(7) |
|-------------------------------|-----------------------------|-----------------------|------------------------------|--------------------------------------|--------------------------|
| Dy(1)-N(1) | 2.663(10) | Fe(1)-O(21) | 1.973(8) | Fe(5)-O(34) | 2.011(7) |
| Dy(2)-O(23) | 2.291(7) | Fe(1)-O(20) | 1.978(8) | Fe(5)-O(16) | 2.039(7) |
| Dy(2) - O(21) | 2.291(9) | Fe(1)–O(19) | 2.000(8) | Fe(5)-N(9) | 2.235(10) |
| Dv(2) - O(20) | 2.354(8) | Fe(1) - O(4) | 2.043(9) | Fe(6) - O(17) | 1.957(8) |
| Dv(2) - O(5) | 2.358(9) | Fe(1) - N(2) | 2.266(10) | Fe(6)-O(36) | 1.979(8) |
| Dv(2) - O(22) | 2.375(8) | Fe(2) - O(22) | 1.937(8) | Fe(6) - N(14) | 1.988(11) |
| Dy(2) = O(7) | 2.388(9) | Fe(2) = O(23) | 1.965(8) | Fe(6) = O(34) | 1.988(8) |
| Dy(2) - O(6) | 2.452(8) | Fe(2) - O(25) | 1.982(8) | Fe(6)-O(35) | 2.067(7) |
| Dv(2)-N(3) | 2.644(9) | Fe(2) - O(8) | 2.004(9) | Fe(6) - N(10) | 2.271(10) |
| Dy(3)–O(28) | 2.315(7) | Fe(2) - O(24) | 2.006(8) | $Dy(1)\cdots Fe(1)$ | 3.3881(19) |
| Dv(3) - O(27) | 2.321(8) | Fe(2) - N(4) | 2.243(9) | $Dv(1)\cdots Fe(6)$ | 3.4879(16) |
| Dy(3) = O(29) | 2.326(7) | Fe(3) = O(27) | 1.940(9) | $Dv(2)\cdots Fe(2)$ | 3.3683(17) |
| Dy(3) = O(26) | 2.327(8) | Fe(3) = O(26) | $\frac{1.910(9)}{1.981(7)}$ | $Dy(2)\cdots Fe(1)$ | 3 4672(19) |
| Dy(3) = O(11) | 2.363(8) | Fe(3) = O(24) | $\frac{1.981(7)}{1.984(8)}$ | $Dy(3)\cdots Fe(4)$ | 3 3950(16) |
| Dy(3) = O(9) | 2.305(0) | Fe(3) = N(11) | 2.002(10) | Dy(3) + Fe(3) | 3.4776(18) |
| Dy(3) = O(10) | 2.420(0) | Fe(3) = O(25) | $\frac{2.002(10)}{2.035(9)}$ | Dy(3) = Fe(3) $Dy(4) \dots Fe(5)$ | 3 3686(16) |
| Dy(3) = N(6) | 2.400(0) | Fe(3) = N(5) | $\frac{2.033(7)}{2.291(10)}$ | $Dy(4) \cdots Fe(4)$ | 3.3000(10) 3.4541(16) |
| Dy(3) = N(0) Dy(4) = O(33) | 2.009(10) | Fe(4) = O(28) | $\frac{2.291(10)}{1.030(7)}$ | Dy(4)10(4) | 3.4341(10) |
| Dy(4) = O(33) | $\frac{2.202(7)}{2.311(7)}$ | Fe(4) = O(20) | $\frac{1.939(7)}{1.981(7)}$ | | |
| Dy(4) 0(31) | 2.311(7) | $\frac{10(4)}{0(30)}$ | 1.901(7) | | |
| Gd(1) = O(36) | 2301(4) | Gd(4)=O(31) | $\frac{1122}{2359(4)}$ | $E_{0}(4) = O(27)$ | 1.084(4) |
| Gd(1) = O(18) | $\frac{2.301(4)}{2.325(4)}$ | Gd(4) = O(31) | $\frac{2.339(4)}{2.363(4)}$ | $F_{0}(4) = O(27)$ | 1.984(4) 1.084(4) |
| Gd(1) = O(10) | 2.323(4) | Gd(4) = O(33) | 2.303(4) | Fe(4) = O(30) | 1.904(4) 1.001(4) |
| Gu(1)=O(19) | 2.303(4) | Gu(4)=O(12) | 2.380(4) | Fe(4)=O(29) | 1.991(4) |
| Gd(1)=O(17) | $\frac{2.390(4)}{2.412(4)}$ | Gd(4)=O(14) | $\frac{2.422(4)}{2.479(4)}$ | Fe(4)=O(11) | 2.039(4) |
| Gd(1)=O(16) | 2.413(4) | Gd(4) = O(13) | $\frac{2.478(4)}{2.41(5)}$ | Fe(4) = N(7) | 2.257(5) |
| Gd(1) = O(1) | 2.413(4) | Gd(4) = N(8) | 2.641(5) | Fe(5)=O(31) | 1.953(4) |
| Gd(1) = O(2) | 2.500(4) | Fe(1)=O(22) | 1.945(4) | Fe(5)=O(33) | 1.984(4) |
| Gd(1) = N(1) | 2.698(5) | Fe(1)=O(19) | 1.977(4) | Fe(5)=O(35) | 1.990(4) |
| Gd(2)=O(22) | $\frac{2.337(4)}{2.240(4)}$ | Fe(1)=O(18) | 1.987(4) | Fe(5) = N(14) | 2.008(6) |
| Gd(2)=O(21) | 2.340(4) | Fe(1)=O(20) | 1.988(4) | Fe(5)=O(34) | 2.066(4) |
| Gd(2) = O(24) | 2.348(4) | Fe(1) = O(3) | 2.045(4) | Fe(5) = N(9) | 2.279(5) |
| Gd(2)=O(20) | $\frac{2.360(4)}{2.400(4)}$ | Fe(1)=N(2) | $\frac{2.271(5)}{1.046(4)}$ | Fe(6)=O(17) | 1.938(4) |
| Gd(2)=O(4) | 2.400(4) | Fe(2)=O(21) | 1.946(4) | Fe(6) = O(36) | 1.967(4) |
| Gd(2) = O(6) | 2.413(5) | Fe(2) = O(26) | 1.986(4) | Fe(6) = O(34) | 1.96/(4) |
| Gd(2) = O(5) | 2.4/3(4) | Fe(2) = O(24) | 1.986(4) | Fe(6) = O(35) | 2.027(4) |
| Gd(2) - N(3) | 2.605(5) | Fe(2) - N(11) | 1.996(6) | Fe(6) - O(15) | 2.044(4) |
| Gd(3-O(25) | 2.310(4) | Fe(2)–O(23) | 2.042(4) | Fe(6)-N(10) | 2.248(5) |
| Gd(3)–O(27) | 2.333(4) | Fe(2)-N(4) | 2.289(5) | $Gd(1)\cdots Fe(6)$ | 3.4002(10) |
| Gd(3)-O(30) | 2.365(4) | Fe(3)–O(28) | 1.929(4) | $Gd(1)\cdots Fe(1)$ | 3.4708(10) |
| Gd(3)-O(28) | 2.392(4) | Fe(3) - O(25) | 1.966(4) | $Gd(2)\cdots Fe(1)$ | 3.4177(10) |
| Gd(3)-O(9) | 2.422(4) | Fe(3)–O(23) | 1.973(4) | $Gd(2)\cdots Fe(2)$ | 3.5083(10) |
| Gd(3)-O(8) | 2.427(4) | Fe(3)–O(26) | 2.014(4) | $Gd(3)\cdots Fe(3)$ | 3.3941(10) |
| Gd(3)-O(10) | 2.454(4) | Fe(3) - O(7) | 2.030(4) | $Gd(3)\cdots Fe(4)$ | 3.4930(9) |
| Gd(3)-N(6) | 2.658(5) | Fe(3)-N(5) | 2.252(5) | $Gd(4)\cdots Fe(4)$ | 3.4208(9) |
| Gd(4)-O(29) | 2.347(4) | Fe(4)-O(32) | 1.948(4) | $Gd(4)\cdots Fe(5)$ | 3.5212(10) |
| Gd(4)-O(32) | 2.356(4) | | | | |
| | | Compound | d 23 | | |
| Ho(1)-O(19) | 2.270(15) | Ho(4)-O(31) | 2.297(12) | Fe(4) - O(30) | 1.940(13) |
| Ho(1)-O(18) | 2.286(17) | Ho(4)-O(32) | 2.307(14) | Fe(4) - O(31) | 1.982(13) |
| Ho(1)-O(36) | 2.302(13) | Ho(4)-O(30) | 2.315(13) | Fe(4)-O(29) | 1.990(12) |
| Ho(1)-O(1) | 2.310(13) | Ho(4) - O(15) | 2.357(12) | Fe(4) - O(12) | 2.033(13) |

| Ho(1)-O(17) | 2.310(12) | Ho(4)-O(13) | 2.376(12) | Fe(4) - N(7) | 2.251(17) |
|--------------------------------------|-------------------------------|----------------------------------|-------------------------------|--|-------------------------------|
| Ho(1)-O(3) | 2.330(13) | Ho(4)-O(14) | 2.454(13) | Fe(5)-O(33) | 1.924(13) |
| $H_{0}(1) - O(2)$ | 2.431(17) | Ho(4)-N(8) | 2.694(16) | Fe(2) - O(22) | 1.915(14) |
| $H_{0}(1)-N(1)$ | 2.646(17) | Fe(1) - O(21) | 1.960(13) | Fe(5) - O(32) | 1.928(13) |
| $H_0(2) - O(23)$ | 2.270(13) | Fe(1) - O(18) | 1.961(15) | Fe(5) - O(35) | 1.969(13) |
| $H_0(2) - O(21)$ | 2.277(13) | Fe(1) - O(20) | 1.968(14) | Fe(5) = O(34) | 1.993(12) |
| $H_0(2) = O(20)$ | 2.361(12) | Fe(1) = O(19) | $\frac{1.983(14)}{1.983(14)}$ | Fe(5) = O(16) | 2.029(12) |
| $H_0(2) = O(6)$ | 2.367(12) | Fe(1) - O(4) | 2.042(14) | Fe(5) - N(9) | 2.025(12) |
| $H_0(2) = O(22)$ | 2.367(13) | Fe(1) - N(2) | 2.012(11) 2.238(18) | Fe(6) = O(17) | 1.957(12) |
| $H_0(2) = O(7)$ | 2.307(13) 2 371(14) | Fe(2) = O(22) | 1.915(14) | Fe(6) = O(36) | 1.937(12) 1.973(13) |
| $H_0(2) = O(5)$ | 2.371(11) 2 416(13) | Fe(2) = O(22) | 1.913(11) 1.948(13) | Fe(6) - N(14) | 1.996(17) |
| $H_0(2) = N(3)$ | 2.410(15) | Fe(2) = O(8) | 1.943(15) | Fe(6) - O(34) | 1.999(17) |
| $H_0(3) = O(26)$ | 2.030(10) | Fe(2) = O(25) | 1.984(13) | Fe(6) = O(35) | $\frac{1.999(12)}{2.064(12)}$ |
| $H_0(3) = O(20)$ | $\frac{2.275(13)}{2.311(13)}$ | Fe(2) = O(24) | $\frac{1.964(13)}{1.007(13)}$ | Fe(6) = N(10) | 2.00+(12) 2.296(15) |
| $H_{0}(3) = O(28)$ | $\frac{2.311(13)}{2.321(13)}$ | $F_{2}(2) = N(4)$ | $\frac{1.337(13)}{2.203(18)}$ | $H_0(2) = F_0(2)$ | 2.290(13) |
| $H_{2}(3) - O(27)$ | 2.331(13) | Fe(2) = N(4) $F_2(2) = O(27)$ | $\frac{2.203(16)}{1.022(15)}$ | $H_0(2) = F_0(1)$ | 3.330(3) |
| $H_0(3) = O(27)$ $H_0(2) = O(11)$ | 2.334(10) | Fe(3)=O(27) | $\frac{1.923(13)}{1.080(12)}$ | $Ho(2)\cdots Fe(1)$ | 3.430(3) |
| $H_0(3)=O(11)$ | $\frac{2.368(13)}{2.412(12)}$ | Fe(3)=O(26) | 1.980(13) | $Ho(1)\cdots Fe(1)$ | 3.308(3) |
| $H_0(3) = O(10)$ | $\frac{2.413(13)}{2.442(16)}$ | Fe(3)=O(24) | $\frac{1.995(12)}{2.002(17)}$ | $Ho(3)\cdots Fe(4)$ | 3.378(3) |
| $H_{0}(3) - O(9)$ | 2.443(16) | Fe(3)=N(11) | $\frac{2.002(17)}{2.010(14)}$ | $Ho(3)\cdots Fe(3)$ | 3.469(3) |
| Ho(3) - N(6) | 2.553(19) | Fe(3) = O(25) | 2.019(14) | $Ho(4)\cdots Fe(5)$ | 3.352(3) |
| Ho(1) = O(19) | 2.270(15) | Fe(3) - N(5) | 2.271(16) | $Ho(4)\cdots Fe(4)$ | 3.442(3) |
| Ho(4)-O(33) | 2.275(13) | Fe(4) - O(28) | 1.916(13) | | |
| $\mathbf{V}(1) = \mathbf{O}(17)$ | 2.297(0) | Compound V(4) Q(20) | d 24 | $\mathbf{F}_{\mathbf{r}}(4) = \mathbf{O}(29)$ | 1.072(9) |
| Y(1) = O(17) V(1) = O(25) | $\frac{2.287(9)}{2.207(8)}$ | Y(4) = O(29) V(4) = O(28) | $\frac{2.301(8)}{2.325(8)}$ | Fe(4) = O(28) | 1.972(8) |
| I(1)=O(35) V(1)=O(36) | $\frac{2.307(8)}{2.310(9)}$ | I(4) = O(28) V(4) = O(20) | $\frac{2.323(8)}{2.325(9)}$ | Fe(4)=O(29) Fe(4)=O(27) | 1.970(9) 1.002(8) |
| Y(1) = O(3) | $\frac{2.310(9)}{2.333(9)}$ | Y(4) = O(13) | $\frac{2.323(9)}{2.369(8)}$ | Fe(4) = O(27) | $\frac{1.992(8)}{2.043(8)}$ |
| Y(1) = O(34) | 2.335(7) | Y(4) = O(15) | 2.309(8) | Fe(4) - N(6) | 2.043(0) |
| Y(1) = O(1) | 2.368(12) | Y(4) = O(14) | 2.440(10) | Fe(5) = O(30) | 1.947(8) |
| Y(1) = O(2) | 2.451(10) | Y(4) - N(7) | 2.687(11) | Fe(5) = O(31) | 1.963(9) |
| Y(1) - N(10) | 2.659(11) | Fe(1)-O(36) | 1.936(9) | Fe(5)-O(33) | 1.977(9) |
| Y(2)-O(21) | 2.279(8) | Fe(1)-O(19) | 1.963(9) | Fe(5)-O(32) | 2.002(9) |
| Y(2)-O(19) | 2.288(9) | Fe(1)-O(18) | 1.987(9) | Fe(5)-O(16) | 2.044(8) |
| Y(2)-O(5) | 2.350(9) | Fe(1)-O(17) | 1.994(9) | Fe(5)–N(8) | 2.240(11) |
| Y(2)-O(18) | 2.351(9) | Fe(1)-O(4) | 2.037(9) | Fe(6)-O(35) | 1.947(9) |
| Y(2)-O(20) | 2.358(9) | Fe(1) - N(1) | 2.258(11) | Fe(6)–O(34) | 1.973(9) |
| Y(2)-O(7) | 2.372(10) | Fe(2)–O(20) | 1.936(8) | Fe(6) - N(14) | 1.994(11) |
| Y(2)-O(6) | 2.449(9) | Fe(2)–O(21) | 1.963(8) | Fe(6)-O(32) | 2.000(9) |
| Y(2)-N(2) | 2.644(10) | Fe(2) - O(23) | 1.985(8) | Fe(6)-O(33) | 2.048(8) |
| Y(3) - O(24) | 2.307(9) | Fe(2) = O(8) | 2.000(10) | Fe(6) - N(9) | 2.274(11) |
| Y(3) = O(27) | 2.322(9) | Fe(2) = O(22) | 2.031(9) | $Y(1) \cdots Fe(1)$ | $\frac{3.3/3(3)}{2.480(2)}$ |
| Y(3) = O(26) Y(2) = O(11) | $\frac{2.329(8)}{2.329(0)}$ | Fe(2)=N(3) | $\frac{2.254(10)}{1.012(10)}$ | $Y(1) \cdots Fe(6)$ | 3.480(2) |
| 1(3)=0(11) V(1)=0(17) | 2.337(9) | Fe(3)=O(23) | 1.912(10) 1.92(8) | $1(2)\cdots \Gamma e(2)$ $V(2)\cdots Fe(1)$ | 3.337(2) |
| Y(3) = O(25) | $\frac{2.207(9)}{2.344(10)}$ | Fe(3) = O(24) | 1.902(0) | Y(3)Fe(4) | 3 385(2) |
| Y(3) - O(9) | 2.3406(9) | Fe(3) = N(11) | 2.002(11) | $Y(3) \cdots Fe(3)$ | 3 474(2) |
| Y(3) - O(10) | 2.446(9) | Fe(3) - O(23) | 2.040(9) | $Y(3) \cdots Fe(4)$ | 3.385(2) |
| Y(3) - N(5) | 2.621(12) | Fe(3) - N(4) | 2.297(11) | $Y(4)\cdots$ Fe(5) | 3.362(2) |
| Y(4)-O(31) | 2.264(8) | Fe(4)-O(26) | 1.930(9) | $Y(4) \cdots Fe(4)$ | 3.455(2) |
| | ~ / | Compoun | d 25 | | |

| Dy(1)-O(6) | 2.310(5) | Fe(1)–O(11) | 1.977(5) | Fe(3) - O(7) | 1.966(5) |
|---------------------------|-------------------------------|--------------------------------|-------------------------------|--|-----------|
| $Dy(1) - O(15)^{\#1}$ | 2.315(5) | Fe(1)-O(9) | 2.026(5) | Fe(3)-O(15) | 1.984(5) |
| $Dy(1) - O(7)^{\#1}$ | 2.320(5) | Fe(1)–O(4) | 2.028(6) | Fe(3)–O(14) | 1.998(5) |
| Dy(1)-O(8) | 2.322(5) | Fe(1) - N(2) | 2.260(7) | Fe(3)-O(12) | 2.020(5) |
| Dy(1)-O(1) | 2.354(6) | Fe(2)–O(13) | 1.899(5) | Fe(3)-N(5) | 2.028(7) |
| Dy(1)-O(3) | 2.383(6) | Fe(2)–O(14) | 1.990(5) | Fe(3)-N(4) | 2.308(6) |
| Dy(1)-O(5) | 2.421(6) | Fe(2)–O(12) | 2.017(5) | $Dy(1) \cdots Fe(1)$ | 3.378(1) |
| Dy(1) - N(1) | 2.602(7) | Fe(2)–O(9) | 2.020(5) | $Fe(1)\cdots Fe(2)$ | 3.160(2) |
| Fe(1) - O(6) | 1.943(5) | Fe(2) - O(11) | 2.030(5) | $Fe(2)\cdots Fe(3)$ | 3.200(2) |
| Fe(1) - O(8) | 1.949(5) | Fe(2)-N(3) | 2.265(7) | $Fe(3)\cdots Dv(1)^{\#2}$ | 3.524(2) |
| #1 y+1/3, -x+y+2/3, -z | +2/3 #2 x-y+ | 1/3, x-1/3, -z+2/3 | | | |
| | - | Compound | 1 26 | | |
| Dy(1)-O(31) | 2.310(9) | Fe(2)-O(31) | 1.936(8) | Fe(7)–O(44) | 1.939(8) |
| Dy(1)-O(33) | 2.312(9) | Fe(2)–O(16) | 1.962(9) | Fe(7)-O(26) | 1.949(8) |
| Dy(1)-O(3) | 2.323(1) | Fe(2)-O(17) | 1.997(7) | Fe(7)-O(40) | 1.954(9) |
| Dy(1)-O(16) | 2.342(7) | Fe(2)–N(13) | 2.010(1) | Fe(7)–O(25) | 2.019(8) |
| Dy(1)-O(2) | 2.346(9) | Fe(2)–O(36) | 2.016(8) | Fe(7)–O(9) | 2.036(8) |
| Dy(1)-O(13) | 2.352(8) | Fe(2) - N(2) | 2.280(1) | Fe(7)-N(5) | 2.285(1) |
| Dy(1)-O(32) | 2.381(1) | Fe(3)–O(35) | 1.897(8) | Fe(8)–O(45) | 1.923(9) |
| Dy(1)-N(7) | 2.681(1) | Fe(3)–O(19) | 1.998(8) | Fe(8)–O(28) | 1.981(8) |
| Dy(2)–O(7) | 2.304(1) | Fe(3)–O(17) | 1.998(7) | Fe(8)–N(19) | 1.992(1) |
| Dy(2)–O(37) | 2.309(9) | Fe(3)-O(36) | 2.022(7) | Fe(8)–O(29) | 1.994(1) |
| Dy(2)-O(39) | 2.323(8) | Fe(3)–O(34) | 2.039(8) | Fe(8)–O(48) | 2.030(8) |
| Dy(2)–O(20) | 2.339(9) | Fe(3)–N(8) | 2.263(1) | Fe(8)-N(6) | 2.298(1) |
| Dy(2)–O(22) | 2.342(8) | Fe(4)-O(39) | 1.942(8) | Fe(9)–O(47) | 1.889(1) |
| Dy(2)-O(6) | 2.364(9) | Fe(4)–O(20) | 1.958(9) | Fe(9)–O(29) | 1.979(9) |
| Dy(2)–O(38) | 2.419(1) | Fe(4)-O(34) | 1.968(8) | Fe(9)–O(14) | 1.989(8) |
| Dy(2)-N(9) | 2.652(1) | Fe(4)–O(19) | 2.025(8) | Fe(9)–O(48) | 2.025(9) |
| Dy(3)–O(44) | 2.321(8) | Fe(4)–O(5) | 2.035(8) | Fe(9)–O(46) | 2.029(9) |
| Dy(3)–O(11) | 2.321(8) | Fe(4) - N(3) | 2.255(1) | Fe(9)–N(12) | 2.251(1) |
| Dy(3)–O(45) | 2.329(8) | Fe(5)–O(37) | 1.934(8) | $Dy(1) \cdots Fe(2)$ | 3.464(2) |
| Dy(3)–O(28) | 2.333(8) | Fe(5)–O(22) | 1.978(8) | $Fe(2)\cdots Fe(3)$ | 3.205(3) |
| Dy(3)–O(26) | 2.346(8) | Fe(5)-O(23) | 1.985(8) | $Fe(3)\cdots Fe(4)$ | 3.165(3) |
| Dy(3)–O(10) | 2.355(8) | Fe(5)–N(16) | 2.002(1) | $Fe(4)\cdots Dy(2)$ | 3.369(2) |
| Dy(3)–O(43) | 2.381(8) | Fe(5)-O(41) | 2.013(8) | $Dy(2)\cdots Fe(5)$ | 3.490(2) |
| Dy(3)–N(11) | 2.654(1) | Fe(5) - N(4) | 2.274(9) | $Fe(5)\cdots Fe(6)$ | 3.197(2) |
| Fe(1)-O(33) | 1.918(9) | Fe(6)-O(42) | 1.884(9) | $Fe(6)\cdots Fe(7)$ | 3.168(2) |
| Fe(1)-O(13) | 1.949(8) | Fe(6)–O(25) | 1.986(8) | $Fe(7)\cdots Dy(3)$ | 3.366(2) |
| $Fe(1) - O(46)^{\#1}$ | 1.971(8) | Fe(6)–O(23) | 1.994(8) | $Dy(3)\cdots Fe(8)$ | 3.488(2) |
| $Fe(1) - O(14)^{\#1}$ | 2.018(8) | Fe(6)–O(41) | 2.026(9) | $Fe(8)\cdots Fe(9)$ | 3.211(2) |
| Fe(1) - O(1) | 2.040(9) | Fe(6) - O(40) | 2.040(8) | $\operatorname{Fe}(9)\cdots\operatorname{Fe}(1)^{\#1}$ | 3.164(2) |
| Fe(1) - N(1) | 2.210(1) | Fe(6) - N(10) | 2.258(1) | | |
| #1 -x+1,-y+2,-z | | ~ | | | |
| | 2.2.40(1.1) | Compound | 1 27 | | 1.005(11) |
| Gd(1)=O(3) | $\frac{2.340(11)}{2.240(11)}$ | Fe(2)=O(20) | 1.880(12) | Fe(7) = O(32) | 1.92/(11) |
| Ga(1) = O(14) | 2.349(11) | $Fe(2)=O(47)^{++}$ | 1.991(11) | Fe(7) = O(34) | 1.9/8(11) |
| Gd(1)=O(16) | $\frac{2.332(11)}{2.255(11)}$ | Fe(2)=O(17) | 2.014(11) | Fe(7) = O(35) | 2.007(9) |
| Ga(1)=O(22) | $\frac{2.333(11)}{2.362(11)}$ | Fe(2)=O(19) | 2.018(10) | Fe(7) = U(37) E ₂ (7) = N(16) | 2.011(10) |
| Gu(1)=O(13) | 2.303(11) | Fe(2)=U(21) $F_{2}(2)=N(2)$ | 2.043(10) | Fe(7) = N(10) E ₂ (7) = N(2) | 2.03(2) |
| Gu(1)=O(2) Gd(1)=O(12) | $\frac{2.403(11)}{2.407(11)}$ | Fe(2)=IN(3) Fo(3)=O(14) | $\frac{2.270(14)}{1.025(10)}$ | $\frac{\Gamma C(I) - N(\delta)}{\Gamma C(20)}$ | 2.201(13) |
| Gu(1) = O(13) | $\frac{2.427(11)}{2.641(14)}$ | Fe(3)=O(14) | 1.923(10) 1.047(11) | FC(0)=O(39) | 1.090(10) |
| Ou(1)-IN(1) | 2.041(14) | 10(3) - 0(10) | 1.74/(11) | 10(0)-0(33) | 1.704(10) |

| Gd(2)-O(34) | 2.356(10) | Fe(3)-O(19) | 1.951(11) | Fe(8)-O(40) | 1.996(10) |
|------------------------|-------------------------------|---------------|-----------|-----------------------|-----------|
| Gd(2)-O(31) | 2.356(11) | Fe(3)-O(17) | 2.014(10) | Fe(8)-O(37) | 2.017(10) |
| Gd(2)–O(7) | 2.364(14) | Fe(3)-O(1) | 2.039(10) | Fe(8)–O(38) | 2.037(10) |
| Gd(2) - O(32) | 2.369(12) | Fe(3) - N(2) | 2.281(14) | Fe(8) - N(9) | 2.281(14) |
| Gd(2) - O(6) | 2.382(12) | Fe(4) = O(15) | 1.939(12) | Fe(9) - O(43) | 1.958(11) |
| Gd(2) - O(29) | 2.393(11) | Fe(4) - O(22) | 1.980(10) | Fe(9)–O(41) | 1.970(10) |
| Gd(2) - O(33) | 2.417(12) | Fe(4) - N(13) | 1.999(17) | Fe(9)-O(38) | 1.974(10) |
| Gd(2) - N(7) | 2.697(15) | Fe(4) - O(23) | 2.022(11) | Fe(9) - O(9) | 2.020(10) |
| Gd(3) = O(11) | 2.299(13) | Fe(4) - O(25) | 2.036(11) | Fe(9) - O(40) | 2.033(10) |
| Gd(3) = O(45) | 2.323(11) | Fe(4) - N(4) | 2.324(15) | Fe(9) = N(10) | 2.266(13) |
| Gd(3) - O(43) | 2.350(10) | Fe(5) - O(26) | 1.915(12) | $Gd(1)\cdots Fe(3)$ | 3.381(2) |
| Gd(3) - O(46) | 2.360(9) | Fe(5) - O(23) | 1.990(11) | $Gd(1)\cdots Fe(4)$ | 3.516(3) |
| Gd(3) - O(41) | 2.374(10) | Fe(5) - O(28) | 1.995(10) | $Fe(4)\cdots Fe(5)$ | 3.222(4) |
| Gd(3) = O(10) | 2.437(11) | Fe(5) = O(27) | 2.024(10) | $Fe(5)\cdots Fe(6)$ | 3.162(3) |
| Gd(3) - O(44) | 2.456(11) | Fe(5) = O(25) | 2.046(11) | $Gd(2)\cdots Fe(6)$ | 3.389(3) |
| Gd(3) = N(11) | 2.692(14) | Fe(5) = N(5) | 2.247(13) | $Gd(2)\cdots Fe(7)$ | 3.494(3) |
| Fe(1) - O(45) | 1.947(11) | Fe(6) = O(31) | 1.881(12) | $Fe(7)\cdots Fe(8)$ | 3.205(4) |
| Fe(1) - O(46) | 1.974(10) | Fe(6) = O(27) | 1.960(10) | $Fe(8)\cdots Fe(9)$ | 3.184(4) |
| Fe(1) - O(47) | 1.986(11) | Fe(6) = O(29) | 2.001(10) | $Gd(3)\cdots Fe(9)$ | 3.412(2) |
| $Fe(1) = O(21)^{\#1}$ | $\frac{2.008(10)}{2.008(10)}$ | Fe(6) = O(5) | 2.048(11) | $Gd(3)\cdots Fe(1)$ | 3.529(2) |
| Fe(1) - N(19) | 2.018(18) | Fe(6) - O(28) | 2.050(11) | $Fe(1)\cdots Fe(2)$ | 3.201(3) |
| Fe(1) - N(12) | 2.275(13) | Fe(6) = N(6) | 2.222(16) | $Fe(2)\cdots Fe(3)$ | 3.178(3) |
| #1 - x + 1 - y + 1 - 7 | 2.275(15) | 10(0) 11(0) | 2.222(10) | 10(2) 10(3) | 5.170(5) |
| | | Compound | 1 28 | | |
| Tb(1) - O(1) | 2.337(6) | Fe(2) = O(20) | 1.905(6) | Fe(7) = O(39) | 1.946(6) |
| Tb(1) - O(14) | 2.338(6) | Fe(2) - O(22) | 1.987(6) | Fe(7) = O(43) | 1.955(5) |
| Tb(1) - O(15) | 2.346(5) | Fe(2) - O(17) | 2.011(6) | Fe(7) - O(40) | 1.962(5) |
| $Tb(1) - O(47)^{\#1}$ | 2.359(6) | Fe(2)–O(21) | 2.022(6) | Fe(7)–O(41) | 2.040(5) |
| Tb(1) - O(3) | 2.364(5) | Fe(2) - O(19) | 2.037(5) | Fe(7) - O(12) | 2.061(5) |
| Tb(1) - O(16) | 2.369(5) | Fe(2) - N(3) | 2.276(8) | Fe(7) - N(10) | 2.231(7) |
| Tb(1)-O(13) | 2.404(5) | Fe(3)-O(25) | 1.952(5) | Fe(8)–O(45) | 1.915(6) |
| Tb(1)-N(1) | 2.669(7) | Fe(3)-O(23) | 1.986(6) | Fe(8)–O(46) | 1.987(6) |
| Tb(2)–O(5) | 2.295(7) | Fe(3)-O(22) | 1.989(6) | Fe(8)–O(41) | 1.993(5) |
| Tb(2)-O(25) | 2.329(6) | Fe(3)-O(21) | 2.012(5) | Fe(8)–O(44) | 2.032(6) |
| Tb(2)–O(27) | 2.345(6) | Fe(3)-N(13) | 2.033(8) | Fe(8)–O(43) | 2.034(5) |
| Tb(2)-O(23) | 2.357(5) | Fe(3)-N(4) | 2.283(7) | Fe(8)–N(11) | 2.260(6) |
| Tb(2)–O(28) | 2.372(5) | Fe(4)–O(27) | 1.946(5) | $Fe(9) - O(14)^{\#1}$ | 1.953(6) |
| Tb(2)–O(7) | 2.399(6) | Fe(4)-O(28) | 1.959(5) | Fe(9)–O(47) | 1.982(6) |
| Tb(2)-O(26) | 2.429(6) | Fe(4)-O(31) | 1.985(6) | Fe(9)-O(46) | 2.005(6) |
| Tb(2)-N(5) | 2.653(7) | Fe(4)–O(8) | 2.034(5) | Fe(9)–O(44) | 2.033(5) |
| Tb(3)-O(9) | 2.331(6) | Fe(4)–O(29) | 2.038(5) | Fe(9)–N(19) | 2.045(8) |
| Tb(3)-O(37) | 2.335(6) | Fe(4)-N(6) | 2.279(7) | Fe(9)–N(12) | 2.300(7) |
| Tb(3)-O(35) | 2.337(5) | Fe(5)-O(32) | 1.897(6) | $Tb(1)\cdots Fe(1)$ | 3.369(1) |
| Tb(3)-O(39) | 2.342(5) | Fe(5)-O(34) | 2.000(5) | $Fe(1)\cdots Fe(2)$ | 3.174(2) |
| Tb(3)–O(11) | 2.360(6) | Fe(5)-O(29) | 2.004(6) | $Fe(2)\cdots Fe(3)$ | 3.199(2) |
| Tb(3)-O(40) | 2.363(5) | Fe(5)-O(33) | 2.037(5) | $Fe(3)\cdots Tb(2)$ | 3.511(1) |
| Tb(3)-O(38) | 2.427(6) | Fe(5)-O(31) | 2.043(6) | $Tb(2)\cdots Fe(4)$ | 3.397(1) |
| Tb(3)-N(9) | 2.687(7) | Fe(5)–N(7) | 2.273(7) | $Fe(4)\cdots Fe(5)$ | 3.186(2) |
| Fe(1)-O(15) | 1.946(5) | Fe(6)–O(37) | 1.934(5) | Fe(5)Fe(6) | 3.209(2) |
| Fe(1)-O(16) | 1.951(5) | Fe(6)-O(35) | 1.980(6) | $Fe(6)\cdots Tb(3)$ | 3.483(1) |
| Fe(1)-O(19) | 1.963(6) | Fe(6)-O(34) | 1.998(5) | $Tb(3)\cdots Fe(7)$ | 3.375(1) |
| Fe(1)-O(17) | 2.021(5) | Fe(6)-O(33) | 2.017(5) | $Fe(7)\cdots Fe(8)$ | 3.164(2) |

| Fe(1)-O(4) | 2.033(6) | Fe(6)-N(16) | 2.058(8) | $Fe(8)\cdots Fe(9)$ | 3.216(2) | | | |
|--|-----------------------------|------------------------------------|----------|--|----------|--|--|--|
| Fe(1)-N(2) | 2.273(7) | Fe(6)–N(8) | 2.269(7) | $Fe(9)\cdots Tb(1)^{\#1}$ | 3.506(1) | | | |
| #1 -x+2,-y+1,-z+1 | | | | | | | | |
| Compound 29 | | | | | | | | |
| $Sm(1) - O1(5)^{\#1}$ | 2.372(5) | Fe(1)-O(11) | 1.992(5) | $Fe(3) - O(6)^{#2}$ | 1.970(5) | | | |
| Sm(1)–O(8) | 2.380(5) | Fe(1)-O(9) | 2.034(5) | Fe(3)-O(15) | 1.992(5) | | | |
| Sm(1)–O(7) | 2.381(5) | Fe(1)–O(2) | 2.035(5) | Fe(3)–O(14) | 1.999(5) | | | |
| Sm(1)–O(6) | 2.392(5) | Fe(1)-N(2) | 2.287(6) | Fe(3)–O(12) | 2.031(5) | | | |
| Sm(1)-O(3) | 2.403(5) | Fe(2)–O(13) | 1.910(5) | Fe(3)–N(5) | 2.035(7) | | | |
| Sm(1)-O(1) | 2.454(6) | Fe(2)–O(14) | 1.992(5) | Fe(3)–N(4) | 2.296(6) | | | |
| Sm(1)–O(5) | 2.469(6) | Fe(2)–O(9) | 2.028(5) | $Sm(1)\cdots Fe(1)$ | 3.431(1) | | | |
| Sm(1)-N(1) | 2.646(6) | Fe(2)–O(12) | 2.031(5) | $Fe(1)\cdots Fe(2)$ | 3.173(2) | | | |
| Fe(1)-O(7) | 1.943(5) | Fe(2)–O(11) | 2.045(5) | $Fe(2)\cdots Fe(3)$ | 3.204(2) | | | |
| Fe(1)-O(8) | 1.956(5) | Fe(2) - N(3) | 2.273(6) | $Fe(3)\cdots Sm(1)$ | 3.574(1) | | | |
| <i>#1 y-1/3,-x+y+1/3,- z+</i> | -1/3 #2 x-y+2 | 2/3, <i>x</i> +1/3,- <i>z</i> +1/3 | | | | | | |
| | | Compound | 1 30 | | | | | |
| Eu(1)-O(22) | 2.354(6) | $Fe(2) = O(14)^{\#1}$ | 1.992(6) | Fe(7)–O(38) | 1.984(6) | | | |
| Eu(1)-O(25) | 2.366(5) | Fe(2)-O(19) | 2.00(5) | Fe(7)–O(37) | 1.986(5) | | | |
| Eu(1)-O(24) | 2.366(6) | Fe(2)–O(17) | 2.026(6) | Fe(7)–N(19) | 2.016(9) | | | |
| Eu(1)-O(3) | 2.380(7) | Fe(2)–O(18) | 2.033(6) | Fe(7)–O(40) | 2.016(5) | | | |
| Eu(1)-O(20) | 2.382(5) | Fe(2) - N(2) | 2.252(7) | Fe(7) - N(9) | 2.266(7) | | | |
| Eu(1)-O(2) | 2.403(6) | Fe(3)–O(22) | 1.931(6) | Fe(8)–O(41) | 1.902(7) | | | |
| Eu(1)-O(23) | 2.418(7) | Fe(3)–O(18) | 1.963(6) | Fe(8)–O(43) | 1.992(6) | | | |
| Eu(1) - N(4) | 2.683(10) | Fe(3)–O(20) | 1.968(5) | Fe(8)–O(38) | 2.001(6) | | | |
| Eu(2)–O(7) | 2.342(6) | Fe(3)-O(19) | 2.032(6) | Fe(8)–O(40) | 2.020(6) | | | |
| Eu(2)-O(36) | 2.38(5) | Fe(3) = O(1) | 2.043(6) | Fe(8)–O(42) | 2.027(6) | | | |
| Eu(2)-O(34) | 2.363(5) | Fe(3) - N(3) | 2.225(7) | Fe(8)–N(10) | 2.270(8) | | | |
| Eu(2)–O(37) | 2.376(5) | Fe(4)–O(24) | 1.943(6) | Fe(9)-O(46) | 1.947(6) | | | |
| Eu(2)-O(32) | 2.394(5) | Fe(4)–O(25) | 1.979(6) | Fe(9)–O(44) | 1.953(5) | | | |
| Eu(2)–O(6) | 2.421(5) | Fe(4)–O(26) | 1.989(5) | Fe(9)–O(42) | 1.965(6) | | | |
| Eu(2)–O(35) | 2.448(6) | Fe(4)–O(29) | 2.011(6) | Fe(9)–O(43) | 2.023(6) | | | |
| Eu(2)–N(8) | 2.670(6) | Fe(4) - N(16) | 2.030(8) | Fe(9)–O(9) | 2.030(5) | | | |
| Eu(3)–O(11) | 2.352(6) | Fe(4) - N(5) | 2.2697 | Fe(9)–N(11) | 2.269(7) | | | |
| Eu(3)–O(46) | 2.361(6) | Fe(5)–O(28) | 1.901(5) | $Eu(1)\cdots Fe(3)$ | 3.391(1) | | | |
| Eu(3)–O(13) | 2.368(5) | Fe(5)–O(26) | 1.995(5) | $Fe(3)\cdots Fe(2)$ | 3.171(2) | | | |
| Eu(3)–O(48) | 2.372(5) | Fe(5) = O(31) | 2.003(5) | $Eu(1)\cdots Fe(4)$ | 3.501(1) | | | |
| Eu(3)–O(44) | 2.381(5) | Fe(5)–O(29) | 2.019(5) | $Eu(2)\cdots Fe(6)$ | 3.412(1) | | | |
| Eu(3)-O(10) | 2.407(5) | Fe(5)-O(30) | 2.035(5) | $Eu(2)\cdots Fe(7)$ | 3.534(1) | | | |
| Eu(3)–O(47) | 2.419(5) | Fe(5)–N(6) | 2.260(7) | $Fe(4)\cdots Fe(5)$ | 3.201(2) | | | |
| Eu(3) - N(12) | 2.680(7) | Fe(6)-O(34) | 1.942(5) | $Fe(5)\cdots Fe(6)$ | 3.176(2) | | | |
| Fe(1)-O(48) | 1.933(6) | Fe(6)-O(32) | 1.956(5) | $Eu(3)\cdots Fe(9)$ | 3.387(1) | | | |
| Fe(1)-O(13) | 1.986(6) | Fe(6)-O(30) | 1.981(5) | $Eu(3)\cdots Fe(1)$ | 3.520(1) | | | |
| Fe(1) - O(14) | 1.994(6) | Fe(6)-O(31) | 2.029(5) | $Fe(7)\cdots Fe(8)$ | 3.198(2) | | | |
| Fe(1) = N(13) | 2.009(10) | Fe(6) - O(5) | 2.035(6) | $Fe(8)\cdots Fe(9)$ | 3.178(2) | | | |
| $Fe(1) = O(17)^{\pi 1}$ | 2.039(6) | Fe(6) = N(7) | 2.261(7) | $\operatorname{Fe}(1)\cdots\operatorname{Fe}(2)^{\pi_1}$ | 3.212(2) | | | |
| $\frac{Fe(1)-N(1)}{F(2)}$ | 2.300(8) | Fe(7) = O(36) | 1.939(5) | | | | | |
| Fe(2)=O(16) | 1.900(7) | | | | | | | |
| #1 - x, -y + 1, -z | | | 1.21 | | | | | |
| $\mathbf{H}_{\mathbf{a}}(1) = \mathbf{O}(1 4)$ | 2 219(7) | Compound | 1.001(0) | $\mathbf{E}_{\mathbf{r}}(7) = \mathbf{O}(20)$ | 1.041(9) | | | |
| HO(1)=O(14) | $\frac{2.318(7)}{2.220(8)}$ | Fe(2) = O(21) | 1.901(9) | Fe(7) = O(39) | 1.941(8) | | | |
| $H_0(1) = U(15)$ | 2.329(8) | Fe(2) = O(22) | 1.989(8) | Fe(7) = O(40) | 1.957(7) | | | |
| H0(1)-O(1) | 2.558(8) | re(2)=O(1/) | 2.011(/) | re(/)=0(43) | 1.95/(8) | | | |

| | 2.339(7) | Fe(2)–O(19) | 2.026(7) | Fe(7)–O(41) | 2.023(7) |
|---|--|--|---|---|---|
| Ho(1)-O(16) | 2.347(7) | Fe(2)–O(20) | 2.027(8) | Fe(7)–O(12) | 2.048(8) |
| Ho(1)-O(3) | 2.358(7) | Fe(2) - N(3) | 2.275(2) | Fe(7)-N(10) | 2.242(1) |
| Ho(1)-O(13) | 2.376(7) | Fe(3)–O(25) | 1.952(7) | Fe(8)–O(44) | 1.916(8) |
| $H_0(1) - N(1)$ | 2.656(2) | Fe(3) - N(13) | 1.967(2) | Fe(8)-O(46) | 1.977(8) |
| Ho(2)–O(5) | 2.275(8) | Fe(3)–O(23) | 1.981(7) | Fe(8)–O(41) | 1.999(7) |
| Ho(2)–O(25) | 2.314(7) | Fe(3)–O(22) | 1.997(8) | Fe(8)–O(43) | 2.039(8) |
| $H_0(2) - O(27)$ | 2.31(7) | Fe(3) - O(20) | 2.015(7) | Fe(8)-O(45) | 2.046(7) |
| Ho(2)–O(23) | 2.337(7) | Fe(3) - N(4) | 2.279(9) | Fe(8)–N(11) | 2.252(9) |
| Ho(2)–O(28) | 2.362(7) | Fe(4)–O(28) | 1.954(7) | $Fe(9) - O(14)^{\#1}$ | 1.944(8) |
| Ho(2)–O(7) | 2.383(8) | Fe(4)-O(27) | 1.956(7) | Fe(9)–O(47) | 1.979(7) |
| Ho(2)–O(26) | 2.409(7) | Fe(4)-O(31) | 1.986(7) | Fe(9)–O(46) | 2.006(8) |
| Ho(2)-N(5) | 2.621(9) | Fe(4)–O(29) | 2.033(7) | Fe(9)-O(45) | 2.021(7) |
| Ho(3)-O(37) | 2.306(8) | Fe(4)–O(8) | 2.040(7) | Fe(9)–N(19) | 2.08(3) |
| Ho(3)-O(39) | 2.310(7) | Fe(4)-N(6) | 2.262(2) | Fe(9)-N(12) | 2.302(2) |
| Ho(3)-O(35) | 2.328(7) | Fe(5)–O(32) | 1.911(8) | $Ho(1)\cdots Fe(1)$ | 3.357(2) |
| Ho(3)-O(9) | 2.333(8) | Fe(5)-O(34) | 2.001(7) | $Fe(1)\cdots Fe(2)$ | 3.177(2) |
| Ho(3)-O(11) | 2.345(7) | Fe(5)–O(29) | 2.011(7) | $Fe(2)\cdots Fe(3)$ | 3.206(2) |
| Ho(3)-O(40) | 2.358(7) | Fe(5)-O(33) | 2.035(8) | $Fe(3)\cdots Ho(2)$ | 3.503(2) |
| Ho(3)-O(38) | 2.393(8) | Fe(5)–O(31) | 2.036(7) | $Ho(2)\cdots Fe(4)$ | 3.381(2) |
| Ho(3)-N(9) | 2.660(2) | Fe(5)-N(7) | 2.270(9) | $Fe(4)\cdots Fe(5)$ | 3.180(3) |
| Fe(1)-O(15) | 1.937(8) | Fe(6)–O(37) | 1.942(7) | $Fe(5)\cdots Fe(6)$ | 3.205(3) |
| Fe(1)-O(16) | 1.952(7) | Fe(6)-O(35) | 1.977(8) | $Fe(6) \cdots Ho(3)$ | 3.470(2) |
| Fe(1)-O(19) | 1.970(7) | Fe(6)-O(34) | 1.95(7) | $Ho(3)\cdots Fe(7)$ | 3.361(2) |
| Fe(1)-O(17) | 2.025(7) | Fe(6)-O(33) | 2.014(7) | $Fe(7)\cdots Fe(8)$ | 3.168(2) |
| Fe(1)-O(4) | 2.044(7) | Fe(6)–N(16) | 2.057(2) | $Fe(8)\cdots Fe(9)$ | 3.215(2) |
| Fe(1)-N(2) | 2.268(9) | Fe(6)-N(8) | 2.280(9) | $\operatorname{Fe}(9)\cdots\operatorname{Ho}(1)^{\#1}$ | 3.485(2) |
| #1 -x+1,-y,-z+1 | | • | | | |
| | | Compound | d 32 | | |
| Y(1)-O(15) | 2 313(5) | Fe(2) - O(20) | 1.887(5) | Fe(7)–O(38) | 1.929(5) |
| | 2.515(5) | | · · · | | |
| Y(1)-O(1) | 2.315(5) | Fe(2) = O(22) | 1.987(5) | Fe(7)–O(40) | 1.948(5) |
| Y(1)-O(1) Y(1)-O(14) | 2.315(5) 2.325(5) | Fe(2)-O(22) Fe(2)-O(17) | 1.987(5) 2.004(5) | Fe(7)-O(40) Fe(7)-O(43) | 1.948(5) 1.957(5) |
| $\begin{array}{c} Y(1) - O(1) \\ Y(1) - O(14) \\ Y(1) - O(47)^{\#1} \end{array}$ | 2.315(5) 2.325(5) 2.325(5) | Fe(2)-O(22) Fe(2)-O(17) Fe(2)-O(21) | 1.987(5) 2.004(5) 2.024(5) | Fe(7)-O(40) Fe(7)-O(43) Fe(7)-O(41) | 1.948(5) 1.957(5) 2.033(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\# 1} \\ Y(1)-O(3) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \end{array}$ | 1.987(5)2.004(5)2.024(5)2.030(5) | Fe(7)-O(40) Fe(7)-O(43) Fe(7)-O(41) Fe(7)-O(12) | 1.948(5)1.957(5)2.033(5)2.046(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \end{array}$ | 1.987(5)2.004(5)2.024(5)2.030(5)2.243(7) | Fe(7)-O(40) Fe(7)-O(43) Fe(7)-O(41) Fe(7)-O(12) Fe(7)-N(10) | 1.948(5)1.957(5)2.033(5)2.046(5)2.201(7) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(21) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) | Fe(7)-O(40) Fe(7)-O(43) Fe(7)-O(41) Fe(7)-O(12) Fe(7)-N(10) Fe(8)-O(45) | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \end{array}$ | 1.948(5)1.957(5)2.033(5)2.046(5)2.201(7)1.904(5)1.987(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(21) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \\ Fe(3) - O(22) \\ Fe(3) - O(23) \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \\ Fe(8)-O(41) \\ \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \\ Fe(3) - O(23) \\ Fe(3) - O(23) \\ Fe(3) - N(13) \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ \end{array}$ | 1.948(5)1.957(5)2.033(5)2.046(5)2.201(7)1.904(5)1.987(5)1.993(5)2.031(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \\ Fe(3) - O(23) \\ Fe(3) - O(23) \\ Fe(3) - O(21) \\ \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ \end{array}$ | 1.948(5)1.957(5)2.033(5)2.046(5)2.201(7)1.904(5)1.987(5)1.993(5)2.031(5)2.048(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(23) \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.337(5) | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(21) \\ Fe(2) - O(17) \\ Fe(2) - O(19) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \\ Fe(3) - O(22) \\ Fe(3) - O(23) \\ Fe(3) - O(21) \\ Fe(3) - O(21) \\ Fe(3) - N(4) \\ \end{array}$ | 1.987(5)2.004(5)2.024(5)2.030(5)2.243(7)1.953(5)1.983(5)1.991(5)1.994(8)2.013(5)2.275(6) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-O(12) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(8)-N(11) \\ \end{array}$ | 1.948(5)1.957(5)2.033(5)2.046(5)2.201(7)1.904(5)1.987(5)1.993(5)2.031(5)2.048(5)2.258(6) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(2)-O(28) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.337(5) 2.343(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(21) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - N(4) \\ \hline Fe(4) - O(27) \\ \end{array}$ | $\begin{array}{r} 1.987(5)\\ \hline 2.004(5)\\ \hline 2.024(5)\\ \hline 2.030(5)\\ \hline 2.243(7)\\ \hline 1.953(5)\\ \hline 1.983(5)\\ \hline 1.991(5)\\ \hline 1.994(8)\\ \hline 2.013(5)\\ \hline 2.275(6)\\ \hline 1.944(5)\\ \end{array}$ | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(8)-N(11) \\ Fe(9)-O(14)^{\#1} \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.936(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(2)-O(28) \\ Y(2)-O(7) \\ \end{array}$ | $\begin{array}{r} 2.315(5)\\ \hline 2.315(5)\\ \hline 2.325(5)\\ \hline 2.325(5)\\ \hline 2.325(5)\\ \hline 2.339(5)\\ \hline 2.348(5)\\ \hline 2.377(5)\\ \hline 2.649(6)\\ \hline 2.259(6)\\ \hline 2.311(5)\\ \hline 2.315(5)\\ \hline 2.337(5)\\ \hline 2.343(5)\\ \hline 2.364(5)\\ \hline \end{array}$ | $\begin{array}{c} Fe(2) - O(22) \\ Fe(2) - O(22) \\ Fe(2) - O(17) \\ Fe(2) - O(21) \\ Fe(2) - O(19) \\ Fe(2) - N(3) \\ Fe(3) - O(25) \\ Fe(3) - O(25) \\ Fe(3) - O(22) \\ Fe(3) - O(23) \\ Fe(3) - O(23) \\ Fe(3) - O(21) \\ Fe(3) - N(13) \\ Fe(3) - N(4) \\ Fe(4) - O(27) \\ Fe(4) - O(28) \\ \end{array}$ | $\begin{array}{r} 1.987(5)\\ \hline 2.004(5)\\ \hline 2.024(5)\\ \hline 2.030(5)\\ \hline 2.243(7)\\ \hline 1.953(5)\\ \hline 1.983(5)\\ \hline 1.991(5)\\ \hline 1.994(8)\\ \hline 2.013(5)\\ \hline 2.275(6)\\ \hline 1.944(5)\\ \hline 1.949(5)\\ \end{array}$ | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-N(11) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ \end{array}$ | $\begin{array}{r} 1.948(5) \\ \hline 1.957(5) \\ \hline 2.033(5) \\ \hline 2.046(5) \\ \hline 2.201(7) \\ \hline 1.904(5) \\ \hline 1.987(5) \\ \hline 1.993(5) \\ \hline 2.031(5) \\ \hline 2.048(5) \\ \hline 2.258(6) \\ \hline 1.936(5) \\ \hline 1.983(5) \end{array}$ |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(2)-O(28) \\ Y(2)-O(7) \\ Y(2)-O(26) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.337(5) 2.343(5) 2.364(5) 2.402(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - N(3) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(31) \\ \hline \end{array}$ | $\begin{array}{r} 1.987(5)\\ \hline 2.004(5)\\ \hline 2.024(5)\\ \hline 2.030(5)\\ \hline 2.243(7)\\ \hline 1.953(5)\\ \hline 1.983(5)\\ \hline 1.991(5)\\ \hline 1.994(8)\\ \hline 2.013(5)\\ \hline 2.275(6)\\ \hline 1.944(5)\\ \hline 1.949(5)\\ \hline 1.987(5)\\ \hline \end{array}$ | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(14) \\ Fe(9)-O(47) \\ \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.983(5) 1.990(5) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(27) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(7) \\ Y(2)-O(26) \\ Y(2)-N(5) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.337(5) 2.343(5) 2.343(5) 2.402(5) 2.639(6) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(21) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(31) \\ \hline Fe(4) - O(29) \\ \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.987(5) 2.037(5) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(47) \\ Fe(9)-O(47) \\ Fe(9)-N(19) \\ \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.936(5) 1.990(5) 2.010(7) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(26) \\ Y(2)-N(5) \\ Y(3)-O(38) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.337(5) 2.343(5) 2.364(5) 2.402(5) 2.639(6) 2.301(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(21) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(8) \\ \hline \end{array}$ | $\begin{array}{r} 1.987(5)\\ \hline 2.004(5)\\ \hline 2.024(5)\\ \hline 2.030(5)\\ \hline 2.243(7)\\ \hline 1.953(5)\\ \hline 1.983(5)\\ \hline 1.991(5)\\ \hline 1.994(8)\\ \hline 2.013(5)\\ \hline 2.275(6)\\ \hline 1.944(5)\\ \hline 1.949(5)\\ \hline 1.949(5)\\ \hline 1.987(5)\\ \hline 2.037(5)\\ \hline 2.041(5)\\ \end{array}$ | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(41) \\ Fe(8)-O(41) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(44) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ Fe(9)-O(47) \\ Fe(9)-O(47) \\ Fe(9)-N(19) \\ Fe(9)-O(44) \\ \end{array}$ | $\begin{array}{r} 1.948(5) \\ \hline 1.957(5) \\ \hline 2.033(5) \\ \hline 2.046(5) \\ \hline 2.201(7) \\ \hline 1.904(5) \\ \hline 1.987(5) \\ \hline 1.993(5) \\ \hline 2.031(5) \\ \hline 2.048(5) \\ \hline 2.258(6) \\ \hline 1.936(5) \\ \hline 1.983(5) \\ \hline 1.983(5) \\ \hline 1.990(5) \\ \hline 2.010(7) \\ \hline 2.040(5) \\ \end{array}$ |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(26) \\ Y(2)-O(26) \\ Y(2)-N(5) \\ Y(3)-O(38) \\ Y(3)-O(35) \\ \end{array}$ | $\begin{array}{r} 2.315(5)\\ 2.315(5)\\ 2.325(5)\\ 2.325(5)\\ 2.339(5)\\ 2.339(5)\\ 2.348(5)\\ 2.377(5)\\ 2.649(6)\\ 2.259(6)\\ 2.311(5)\\ 2.315(5)\\ 2.315(5)\\ 2.337(5)\\ 2.343(5)\\ 2.364(5)\\ 2.402(5)\\ 2.639(6)\\ 2.301(5)\\ 2.324(5)\\ \end{array}$ | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(21) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - N(3) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(8) \\ \hline Fe(4) - O(8) \\ \hline Fe(4) - N(6) \\ \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.987(5) 2.037(5) 2.041(5) 2.276(6) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(46) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ Fe(9)-O(47) \\ Fe(9)-O(47) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-O(42) \\ \end{array}$ | $\begin{array}{r} 1.948(5) \\ \hline 1.957(5) \\ \hline 2.033(5) \\ \hline 2.046(5) \\ \hline 2.201(7) \\ \hline 1.904(5) \\ \hline 1.987(5) \\ \hline 1.987(5) \\ \hline 1.987(5) \\ \hline 2.031(5) \\ \hline 2.031(5) \\ \hline 2.048(5) \\ \hline 2.258(6) \\ \hline 1.936(5) \\ \hline 1.936(5) \\ \hline 1.983(5) \\ \hline 1.990(5) \\ \hline 2.010(7) \\ \hline 2.040(5) \\ \hline 2.300(6) \\ \end{array}$ |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(27) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(28) \\ Y(2)-O(26) \\ Y(2)-O(26) \\ Y(2)-O(26) \\ Y(2)-O(38) \\ Y(3)-O(37) \\ \hline \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.337(5) 2.343(5) 2.364(5) 2.402(5) 2.639(6) 2.301(5) 2.324(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(21) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - N(3) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(23) \\ \hline Fe(4) - O(23) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(8) \\ \hline Fe(4) - N(6) \\ \hline Fe(5) - O(33) \\ \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.987(5) 2.037(5) 2.041(5) 2.276(6) 1.907(5) | $\begin{array}{r} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ Fe(9)-O(47) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-N(12) \\ Y(1)\cdots Fe(1) \\ \hline \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.983(5) 1.990(5) 2.010(7) 2.040(5) 2.300(6) 3.354(1) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(27) \\ Y(2)-O(28) \\ Y(3)-O(38) \\ Y(3)-O(37) \\ Y(3)-O(37) \\ Y(3)-O(9) \\ \hline \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.337(5) 2.343(5) 2.343(5) 2.364(5) 2.402(5) 2.639(6) 2.301(5) 2.324(5) 2.325(5) 2.326(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - O(19) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(8) \\ \hline Fe(4) - O(8) \\ \hline Fe(4) - O(31) \\ \hline Fe(5) - O(33) \\ \hline Fe(5) - O(34) \\ \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.949(5) 1.987(5) 2.037(5) 2.041(5) 2.276(6) 1.997(5) | $\begin{array}{r} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(41) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(44) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ Fe(9)-O(47) \\ Fe(9)-O(47) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-N(12) \\ Y(1)\cdots Fe(1) \\ Fe(1)\cdots Fe(2) \\ \hline\end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.936(5) 1.983(5) 2.010(7) 2.040(5) 2.300(6) 3.354(1) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(2)-O(23) \\ Y(2)-O(28) \\ Y(3)-O(28) \\ Y(3)-O(37) \\ Y(3)-O(37) \\ Y(3)-O(40) \\ Y(3)-O(40)$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.343(5) 2.364(5) 2.364(5) 2.301(5) 2.324(5) 2.326(5) 2.340(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - N(3) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(23) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(33) \\ \hline Fe(5) - O(34) \\ \hline Fe(5) - O(29) \\ \hline \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.947(5) 2.037(5) 2.041(5) 2.276(6) 1.997(5) 2.002(5) | $Fe(7)-O(40)$ $Fe(7)-O(43)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(7)-O(12)$ $Fe(8)-O(45)$ $Fe(8)-O(44)$ $Fe(8)-O(44)$ $Fe(8)-O(43)$ $Fe(8)-O(43)$ $Fe(9)-O(14)^{\#1}$ $Fe(9)-O(46)$ $Fe(9)-O(47)$ $Fe(9)-O(47)$ $Fe(9)-O(44)$ $Fe(9)-O(44)$ $Fe(9)-O(44)$ $Fe(9)-O(12)$ $Y(1)\cdots Fe(1)$ $Fe(1)\cdots Fe(2)$ $Fe(2)\cdots Fe(3)$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.936(5) 1.983(5) 1.990(5) 2.010(7) 2.040(5) 2.300(6) 3.354(1) 3.179(2) 3.205(2) |
| $\begin{array}{c} Y(1)-O(1) \\ Y(1)-O(14) \\ Y(1)-O(47)^{\#1} \\ Y(1)-O(3) \\ Y(1)-O(3) \\ Y(1)-O(16) \\ Y(1)-O(13) \\ Y(1)-N(1) \\ Y(2)-O(5) \\ Y(2)-O(25) \\ Y(2)-O(25) \\ Y(2)-O(25) \\ Y(2)-O(27) \\ Y(2)-O(23) \\ Y(3)-O(23) \\ Y(3)-O(35) \\ Y(3)-O(35) \\ Y(3)-O(37) \\ Y(3)-O(37) \\ Y(3)-O(40) \\ Y(3)-O(11) \\ \end{array}$ | 2.315(5) 2.315(5) 2.325(5) 2.325(5) 2.339(5) 2.348(5) 2.377(5) 2.649(6) 2.259(6) 2.311(5) 2.315(5) 2.337(5) 2.343(5) 2.364(5) 2.402(5) 2.639(6) 2.324(5) 2.325(5) 2.326(5) 2.340(5) 2.343(5) | $\begin{array}{c} Fe(2) - O(22) \\ \hline Fe(2) - O(22) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(17) \\ \hline Fe(2) - O(19) \\ \hline Fe(2) - N(3) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(25) \\ \hline Fe(3) - O(22) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(23) \\ \hline Fe(3) - O(21) \\ \hline Fe(3) - O(23) \\ \hline Fe(4) - O(27) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(28) \\ \hline Fe(4) - O(29) \\ \hline Fe(4) - O(3) \\ \hline Fe(5) - O(34) \\ \hline Fe(5) - O(32) \\ \hline Fe(5) - O(32) \\ \hline \end{array}$ | 1.987(5) 2.004(5) 2.024(5) 2.030(5) 2.243(7) 1.953(5) 1.983(5) 1.991(5) 1.994(8) 2.013(5) 2.275(6) 1.944(5) 1.949(5) 1.987(5) 2.037(5) 2.041(5) 2.276(6) 1.997(5) 2.002(5) 2.035(5) | $\begin{array}{c} Fe(7)-O(40) \\ Fe(7)-O(43) \\ Fe(7)-O(41) \\ Fe(7)-O(12) \\ Fe(7)-N(10) \\ Fe(8)-O(45) \\ Fe(8)-O(45) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(44) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(8)-O(43) \\ Fe(9)-O(44) \\ Fe(9)-O(14)^{\#1} \\ Fe(9)-O(46) \\ Fe(9)-O(47) \\ Fe(9)-O(47) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-O(44) \\ Fe(9)-N(12) \\ Y(1)\cdots Fe(1) \\ Fe(1)\cdots Fe(2) \\ Fe(2)\cdots Fe(3) \\ Y(2)\cdots Fe(3) \\ \end{array}$ | 1.948(5) 1.957(5) 2.033(5) 2.046(5) 2.201(7) 1.904(5) 1.987(5) 1.993(5) 2.031(5) 2.048(5) 2.258(6) 1.936(5) 1.983(5) 1.990(5) 2.040(5) 2.300(6) 3.354(1) 3.205(2) 3.498(1) |

| Y(3)-N(9) | 2.671(6) | Fe(5) - N(7) | 2.262(6) | $Fe(4)\cdots Fe(5)$ | 3.180(2) | | |
|---|-------------------------------|--|-------------------------------|----------------------------------|------------------------------|--|--|
| Fe(1)-O(16) | 1.942(5) | Fe(6)-O(37) | 1.936(5) | $Fe(5)\cdots Fe(6)$ | 3.209(2) | | |
| Fe(1)-O(15) | 1.958(5) | Fe(6)-O(35) | 1.978(5) | $Y(3) \cdots Fe(6)$ | 3.469(2) | | |
| Fe(1)-O(19) | 1.982(5) | Fe(6)-O(34) | 1.986(5) | $Y(3) \cdots Fe(7)$ | 3.357(1) | | |
| Fe(1)-O(4) | 2.027(5) | Fe(6)-O(32) | 2.017(5) | $Fe(7)\cdots Fe(8)$ | 3.164(1) | | |
| Fe(1)-O(17) | 2.028(5) | Fe(6)-N(16) | 2.062(8) | $Fe(8)\cdots Fe(9)$ | 3.218(2) | | |
| Fe(1)-N(2) | 2.273(6) | Fe(6)–N(8) | 2.273(6) | $Y(1) \cdots Fe(9)^{\#1}$ | 3.488(1) | | |
| #1 - <i>x</i> +1,- <i>y</i> +1,- <i>z</i> | | · | | · | | | |
| | | Compound | d 33 | | | | |
| Dy(1)-O(16) | 2.296(11) | Fe(4)-O(8) | 2.022(11) | Fe(4) - N(6) | 2.284(11) | | |
| Dy(1)-O(15) | 2.313(10) | Fe(7)–O(39) | 1.914(10) | Fe(2)–O(21) | 1.991(12) | | |
| Dy(1)-O(46) | 2.320(10) | Fe(7) - O(41) | 1.960(11) | Fe(2)-O(17) | 2.058(13) | | |
| Dy(1)-O(14) | 2.324(10) | Fe(7)-O(45)#1 | 1.967(11) | Fe(2)-N(3) | 2.206(15) | | |
| Dy(1)-O(3) | 2.337(11) | Fe(7)–O(40) | 2.026(11) | Fe(3)-O(25) | 1.926(11) | | |
| Dy(1)=O(1) | 2.344(10) | Fe(7)–O(12) | 2.029(11) | Fe(3)-O(22) | 1.952(12) | | |
| Dy(1)-O(13) | 2.383(9) | Fe(7) - N(10) | 2.287(13) | Fe(3)-O(23) | 1.980(9) | | |
| Dy(1)-N(1) | 2.619(10) | Fe(5)–O(32) | 1.912(10) | Fe(3) - N(13) | 2.01(4) | | |
| Dy(1)-Fe(1) | 3.367(3) | Fe(5)-O(34) | 1.993(10) | Fe(3)-O(21) | 2.008(13) | | |
| Dy(3)-O(37) | 2.305(8) | Fe(5)-O(31) | 2.009(11) | Fe(3)–N(13') | 2.21(4) | | |
| Dy(3)-O(41) | 2.318(11) | Fe(5) - O(33) | 2.026(9) | Fe(3)-N(4) | 2.283(14) | | |
| Dy(3)-O(35) | 2.338(8) | Fe(5) - O(29) | 2.049(8) | Fe(9)-N(19') | 1.81(2) | | |
| Dy(3)-O(11) | 2.356(11) | Fe(5)-N(7) | 2.254(12) | Fe(9)-O(15) | 1.928(10) | | |
| Dy(3)-O(9) | 2.359(11) | Fe(8) - O(43) | 1.897(11) | Fe(9)-O(46) | 1.992(13) | | |
| Dy(3)-O(38) | 2.369(11) | Fe(8) - O(47) | 1.963(11) | Fe(9) - O(44) | 2.019(11) | | |
| Dy(3)-O(39) | 2.387(11) | $Fe(8) = O(40)^{#1}$ | 1.984(11) | Fe(9) - O(47) | 2.034(11) | | |
| Dy(3) - N(9) | 2.648(12) | Fe(8) - O(45) | 2.007(11) | Fe(9) - N(19) | 2.24(2) | | |
| Dy(2)-O(23) | 2.304(10) | Fe(8) - O(44) | 2.052(10) | Fe(9) - N(12) | 2.277(19) | | |
| Dy(2) - O(25) | 2.320(10) | Fe(8) - N(11) | 2.221(12) | Fe(1) = O(14) | 1.937(9) | | |
| Dy(2) - O(27) | 2.324(10) | Fe(6) - O(37) | 1.927(9) | Fe(1) = O(20) | 1.952(18) | | |
| Dy(2) - O(5) | 2.326(11) | Fe(6) = O(35) | 1.989(9) | Fe(1) = O(4) | 1.966(15) | | |
| Dy(2) = O(7) | 2.334(10) | Fe(6) = O(33) | 1.990(11) | Fe(1) = O(16) | 2.003(14) | | |
| Dy(2) = O(28) | 2.357(8) | Fe(6) = O(34) | 1.991(9) | Fe(1) = O(17) | 2.046(11) | | |
| Dy(2) = O(26) | $\frac{2.370(11)}{2.629(11)}$ | Fe(6) = N(16) | $\frac{2.025(13)}{2.020(12)}$ | Fe(1) = N(2') | 2.368(12) | | |
| Dy(2)=N(5) | 2.638(11) | Fe(6)=N(8) | $\frac{2.329(13)}{1.972(10)}$ | Fe(1)=N(2) | $\frac{2.388(11)}{2.412(2)}$ | | |
| Fe(4)=O(28) | 1.940(9) | Fe(2)=O(19) | $\frac{1.8/3(10)}{1.072(12)}$ | $Dy(3)\cdots Fe(7)$ | 3.412(3) | | |
| Fe(4)=O(27) | 1.968(9) | Fe(2)=O(22) | $\frac{1.973(12)}{1.076(14)}$ | $Dy(3) \cdots Fe(6)$ | 3.478(2) | | |
| Fe(4)=O(31) $F_{2}(4)=O(20)$ | 1.964(9) 2.015(0) | re(2)=0(20) | 1.970(14) | $Dy(2)\cdots Fe(4)$ | 5.561(2) | | |
| Compound 24 | | | | | | | |
| Nd(1) = O(8) | 2 382(5) | $E_{e}(1) = O(5)$ | 1.060(5) | $E_{0}(2) = O(14)$ | 2.028(5) | | |
| Nd(1) = O(0) | $\frac{2.362(3)}{2.301(5)}$ | Fe(1) = O(3) $F_2(1) = O(15)^{\#1}$ | 1.909(3) 1.002(5) | Fe(2) = O(14) $F_2(2) = N(2)$ | 2.028(3) | | |
| Nd(1)=O(11) | 2.391(3) | Fe(1)=O(13) | 1.995(3) | Fe(2) = N(3) | 2.330(8) | | |
| Nd(1) = O(5) | 2.407(5) | Fe(1)=O(1) | 2.008(6) | Fe(3)=O(16) | 1.912(5) | | |
| Nd(1) = O(3) | 2.408(5) | Fe(1) - O(6) | 2.012(5) | Fe(3)=O(12) | 1.985(6) | | |
| Nd(1)-O(10) | 2.413(5) | Fe(1)-N(1) | 2.299(6) | Fe(3) = O(14) | 2.011(5) | | |
| Nd(1)-O(9) | 2.461(6) | Fe(2) - O(10) | 1.969(6) | $Fe(3) - O(6)^{\#2}$ | 2.021(5) | | |
| Nd(1)-O(2) | 2.484(6) | Fe(2) - O(11) | 1.981(5) | Fe(3)–O(15) | 2.029(5) | | |
| Nd(1)-N(2) | 2.676(6) | Fe(2)–N(5) | 1.991(8) | Fe(3) - N(4) | 2.273(6) | | |
| Fe(1)–O(8) | 1.966(5) | Fe(2)–O(12) | 1.997(6) | $Nd(1)\cdots Fe(1)$ | 3.4697(12) | | |
| #1 y, -x+y+1, -z #2 x-y+1, x, -z | | | | | | | |
| Compound 35 | | | | | | | |
| Dy(1)-O(7) | 2.294(5) | Dy(2) - O(21) | 2.575(5) | Fe(3) - O(12) | 2.000(5) | | |

| Dy(1)-O(15) | 2.295(4) | Fe(1) - O(15) | 1.964(5) | Fe(3) - N(8) | 2.015(7) |
|--------------------------------|-------------------------------|---|-------------------------------|--|-------------------------------|
| Dy(1) - O(22) | 2.318(5) | Fe(1) - O(16) | 2.002(5) | Fe(3) - O(21) | 2.071(5) |
| Dv(1) - O(3) | 2.350(5) | Fe(1) - N(5) | 2.004(6) | Fe(3) - N(3) | 2.225(6) |
| Dy(1) - O(1) | 2.359(4) | Fe(1) - O(4) | 2.016(5) | Fe(4) - O(2) | 1.943(4) |
| Dv(1) - O(5) | 2.370(4) | Fe(1) - O(17) | 2.069(5) | Fe(4) - O(20) | 1.970(5) |
| Dv(1) - O(2) | 2.421(5) | Fe(1) - N(1) | 2.220(6) | Fe(4) - O(22) | 1.974(5) |
| Dv(1) - O(17) | 2.569(4) | Fe(2) - O(1) | 1.952(4) | Fe(4) - O(6) | 1.981(5) |
| Dv(2) - O(19) | 2.298(5) | Fe(2) - O(16) | 1.970(5) | Fe(4) - O(21) | 2.083(5) |
| Dy(2) - O(18) | 2.302(5) | Fe(2) - O(18) | 1.986(5) | Fe(4) - N(4) | 2.241(6) |
| Dv(2) - O(13) | 2.302(5) | Fe(2) - O(10) | 1.989(5) | $Dv(1)\cdots Fe(4)$ | 3.3867(10) |
| Dy(2)-O(11) | 2.348(5) | Fe(2)-O(17) | 2.085(5) | $Dy(1)\cdots Fe(1)$ | 3.4629(10) |
| Dy(2)-O(9) | 2.372(5) | Fe(2) - N(2) | 2.241(7) | $Dy(1)\cdots Dy(2)$ | 3.8849(5) |
| Dy(2)-O(2) | 2.383(4) | Fe(3)-O(19) | 1.968(5) | $Dy(2)\cdots Fe(2)$ | 3.3904(10) |
| Dy(2)-O(1) | 2.433(5) | Fe(3)-O(20) | 1.999(5) | $Dy(2)\cdots Fe(3)$ | 3.4669(10) |
| #1 -x+1,-y+2,-z+1 | | | | • • | |
| • | | Compound | d 37 | | |
| Tb(1)-O(22) | 2.321(12) | Tb(4)-O(24) | 2.413(11) | Fe(5)-O(26) | 1.989(12) |
| Tb(1)-O(15) | 2.322(12) | Tb(4)-O(41) | 2.581(11) | Fe(5)-O(41) | 2.079(11) |
| Tb(1)-O(13) | 2.324(13) | Fe(1)-O(1) | 1.946(12) | Fe(5)-N(13) | 2.252(15) |
| Tb(1)-O(3) | 2.343(11) | Fe(1)-O(15) | 1.972(12) | Fe(6)-O(39) | 1.960(12) |
| Tb(1)-O(10) | 2.349(14) | Fe(1)-O(17) | 1.979(13) | Fe(6)-O(29) | 1.993(12) |
| Tb(1)-O(1) | 2.409(12) | Fe(1) - O(4) | 1.986(12) | Fe(6)-O(40) | 2.013(11) |
| Tb(1)-O(2) | 2.409(11) | Fe(1)-O(16) | 2.071(12) | Fe(6)-N(16) | 2.034(16) |
| Tb(1)-O(20) | 2.577(11) | Fe(1) - N(1) | 2.233(15) | Fe(6)-O(41) | 2.072(12) |
| Tb(2)–O(11) | 2.278(12) | Fe(2)-O(18) | 1.967(11) | Fe(6)-N(12) | 2.223(15) |
| Tb(2)-O(18) | 2.291(11) | Fe(2)-O(17) | 1.986(13) | Fe(7)–O(24) | 1.954(12) |
| Tb(2)-O(19) | 2.333(11) | Fe(2)-N(5) | 1.995(16) | Fe(7)–O(43) | 1.955(12) |
| Tb(2)-O(6) | 2.356(13) | Fe(2)-O(5) | 2.016(13) | Fe(7)–O(32) | 1.963(12) |
| Tb(2)-O(1) | 2.368(11) | Fe(2)-O(16) | 2.086(12) | Fe(7)–O(45) | 1.968(13) |
| Tb(2)-O(7) | 2.382(12) | Fe(2)-N(2) | 2.225(15) | Fe(7)–O(44) | 2.066(13) |
| Tb(2)-O(2) | 2.408(11) | Fe(3)–O(21) | 1.964(12) | Fe(7) - N(14) | 2.224(15) |
| Tb(2)-O(16) | 2.581(11) | Fe(3)-O(2) | 1.968(11) | Fe(8)–O(46) | 1.952(11) |
| Tb(3)-O(27) | 2.312(13) | Fe(3) - O(19) | 1.969(12) | Fe(8)-O(45) | 1.975(13) |
| Tb(3)-O(46) | 2.314(11) | Fe(3) - O(8) | 1.986(12) | Fe(8) - N(19) | 1.980(16) |
| Tb(3)-O(42) | 2.318(12) | Tb(4)-O(24) | 2.413(11) | Fe(8)-O(35) | 2.015(12) |
| Tb(3) - O(36) | 2.374(13) | Fe(3) - O(20) | 2.075(12) | $\frac{\text{Tb}(1)\cdots\text{Fe}(1)}{\text{Tb}(1)}$ | 3.389(3) |
| Tb(3) = O(25) | 2.392(12) | Fe(3) - N(3) | 2.197(14) | $Tb(1)\cdots Fe(4)$ | 3.461(3) |
| 1b(3) - O(24) | 2.399(11) | Fe(4) = O(22) | 1.952(12) | $Tb(1)\cdots Tb(2)$ | 3.8/58(14) |
| 1b(3)=O(23) | 2.442(11) | Fe(4) = N(8) | 2.008(16) | $1b(2)\cdots Fe(3)$ | 3.385(3) |
| 1b(3)=O(44) | 2.569(11) | Fe(4)=O(21) | 2.013(12) | $1b(2)\cdots Fe(2)$ | 3.458(3) |
| 1b(4) = O(43) | 2.307(13) | Fe(4)=O(9) | 2.030(13) | $1b(3)\cdots Fe(5)$ | 3.407(3) |
| 1b(4) = O(39) | $\frac{2.313(12)}{2.220(12)}$ | Fe(4)=O(20) | 2.061(13) | $\frac{1 \text{ b}(3) \cdots \text{Fe}(8)}{\text{Th}(2) = \text{Th}(4)}$ | 3.469(3) |
| 1b(4) = O(33) Th(4) $O(20)$ | 2.320(12) | Fe(4)=N(4) | 2.213(14) | $10(3) \cdots 10(4)$ Tb(2) Eq(8) | $\frac{3.8937(14)}{2.460(2)}$ |
| 10(4) = O(30) Th(4) $O(21)$ | 2.343(13) | Fe(3)=O(42) | $\frac{1.933(12)}{1.962(12)}$ | $\frac{10(3)\cdots Fe(\delta)}{Fb(4)-Fc(7)}$ | 3.409(3) |
| 10(4) = O(31) Tb(4)=O(23) | 2.30/(11) 2.368(11) | Fe(5)=O(25) | 1.902(12) 1.085(11) | $\frac{10(4)\cdots\Gamma C(7)}{\Gamma D(4)\cdots \Gamma C(6)}$ | 3.304(3) |
| 10(4) 0(23) | 2.300(11) | $\frac{10(3)-0(40)}{100000000000000000000000000000000000$ | 1.703(11) | 10(4) | 3.403(3) |
| Y(1) = O(22) | 2 291(8) | Y(4) = O(24) | 2 430(8) | $F_{e}(5) - O(41)$ | 2 ()88(8) |
| Y(1) - O(15) | 2.271(0) | Y(4) - O(41) | 2.561(8) | Fe(5) = N(13) | 2.000(0) |
| Y(1) - O(13) | 2.314(0) | Fe(1) = O(1) | 1 942(8) | Fe(6) - O(39) | 1 989(8) |
| Y(1) - O(3) | 2.351(9) | Fe(1) = O(17) | 1 977(9) | Fe(6) = O(29) | 2.012(9) |
| Y(1) - O(10) | 2.360(10) | Fe(1) = O(15) | 1 996(9) | Fe(6) = O(40) | 2.015(9) |
| | 2.500(10) | | 1,770(7) | | 2.012(7) |

| Y(1) - O(2) | 2.390(8) | Fe(1) - O(4) | 1.997(9) | Fe(6) - N(16) | 2.021(11) |
|---------------|-----------|---------------|-----------------------|----------------------|----------------------|
| Y(1)-O(1) | 2.404(9) | Fe(1) - O(16) | 2.102(8) | Fe(6)-O(41) | 2.099(8) |
| Y(1)-O(20) | 2.574(8) | Fe(1) - N(1) | 2.257(10) | Fe(6) - N(12) | 2.199(11) |
| Y(2) = O(11) | 2.263(8) | Fe(2) - O(18) | 1.953(8) | Fe(7) - O(24) | 1.953(8) |
| Y(2) - O(18) | 2.295(8) | Fe(2) - O(5) | 2.013(9) | Fe(7) = O(45) | 1.962(8) |
| Y(2) = O(19) | 2.328(8) | Fe(2) - N(5) | 2.017(10) | Fe(7) = O(32) | 1.987(8) |
| Y(2) - O(6) | 2.338(9) | Fe(2) = O(17) | 2.022(8) | Fe(7) - O(43) | 2.004(9) |
| Y(2) - O(1) | 2.361(8) | Fe(2) - O(16) | 2.101(8) | Fe(7) - O(44) | 2.104(9) |
| Y(2) - O(7) | 2.366(9) | Fe(2) - N(2) | 2.229(11) | Fe(7) - N(14) | 2.247(9) |
| Y(2) - O(2) | 2.430(8) | Fe(3) = O(2) | 1.938(8) | Fe(8) = O(46) | 1.956(8) |
| Y(2) - O(16) | 2.566(8) | Fe(3) = O(19) | 1.983(8) | Fe(8) = O(35) | 2.021(9) |
| Y(3) - O(27) | 2.261(8) | Fe(3) - O(8) | 1.984(9) | Fe(8) - O(45) | 2.023(8) |
| Y(3) - O(42) | 2.290(8) | Fe(3) - O(21) | 1.986(9) | Fe(8) - N(19) | 2.028(10) |
| Y(3) - O(46) | 2.317(9) | Fe(3) - O(20) | 2.108(8) | Fe(8) - O(44) | 2.095(9) |
| Y(3) - O(36) | 2.352(8) | Fe(3) - N(3) | 2.228(9) | Fe(8) = N(15) | 2.228(10) |
| Y(3) - O(24) | 2.369(8) | Fe(4) - O(22) | 1.975(8) | $Y(1)\cdots Fe(1)$ | 3.378(3) |
| Y(3) = O(25) | 2.374(9) | Fe(4) = O(21) | 2.025(9) | $Y(1) \cdots Fe(4)$ | 3.466(3) |
| Y(3) = O(23) | 2.431(8) | Fe(4) = O(9) | 2.025(9) | $Y(1) \cdots Y(2)$ | 3.893(3) |
| Y(3) - O(44) | 2,553(8) | Fe(4) - N(8) | 2.032(11) | $Y(2) \cdots Fe(3)$ | 3 386(3) |
| Y(4) = O(39) | 2.278(8) | Fe(4) = O(20) | 2.072(8) | $Y(2) \cdots Fe(2)$ | 3.452(3) |
| Y(4) = O(33) | 2.307(8) | Fe(4) - N(4) | 2.07(10) | $Y(3)\cdots Fe(5)$ | 3 408(3) |
| Y(4) - O(43) | 2 312(8) | Fe(5) = O(23) | 1 948(8) | $Y(3) \cdots Fe(8)$ | 3 473(3) |
| Y(4) - O(31) | 2 346(9) | Fe(5) = O(42) | 1.988(8) | $Y(4)\cdots Fe(7)$ | 3.175(3) 3.378(2) |
| Y(4) - O(30) | 2 356(9) | Fe(5) = O(26) | 1 993(9) | $Y(4)\cdots Fe(6)$ | 3 469(3) |
| Y(4) - O(23) | 2.359(8) | Fe(5) = O(40) | 2,006(8) | $Y(3) \cdots Y(4)$ | 3 910(3) |
| 1(1) 0(23) | 2.309(0) | | 1 39 | 1(3) 1(1) | 5.910(5) |
| Er(1) = O(15) | 2.274(9) | Er(4) = O(24) | 2.388(8) | Fe(5) = O(38) | 2,101(10) |
| Er(1) = O(22) | 2.278(9) | Er(4) - O(38) | 2.543(9) | Fe(5) = N(11) | 2.219(12) |
| Er(1) = O(13) | 2.284(10) | Fe(1) = O(15) | 1 960(9) | Fe(6) = O(40) | 1.975(10) |
| Er(1) = O(10) | 2.327(9) | Fe(1) - N(5) | 1.900(9) 1.999(12) | Fe(6) = O(39) | 2.015(9) |
| Er(1) = O(3) | 2.342(9) | Fe(1) - O(4) | 2.012(10) | Fe(6) = O(27) | 2.017(10) |
| Er(1) = O(2) | 2.351(9) | Fe(1) = O(16) | 2.016(9) | Fe(6) = N(15) | 2.025(13) |
| Er(1) = O(1) | 2.404(9) | Fe(1) = O(17) | 2.078(10) | Fe(6) = O(38) | 2.061(10) |
| Er(1) = O(17) | 2.555(9) | Fe(1) - N(1) | 2.227(12) | Fe(6) = N(12) | 2.229(12) |
| Er(2) = O(11) | 2.257(10) | Fe(2) = O(2) | 1.963(9) | Fe(7) = O(43) | 1.969(10) |
| Er(2) - O(18) | 2.274(9) | Fe(2) - O(18) | 1.981(9) | Fe(7) - O(24) | 1.970(9) |
| Er(2) - O(20) | 2.296(9) | Fe(2) - O(16) | 1.985(9) | Fe(7) - O(42) | 1.983(9) |
| Er(2) = O(7) | 2.323(10) | Fe(2) = O(5) | 1.989(10) | Fe(7) = O(30) | 1.992(9) |
| Er(2) - O(1) | 2.359(9) | Fe(2) - O(17) | 2.082(9) | Fe(7) = O(41) | 2.090(9) |
| Er(2) - O(6) | 2.359(9) | Fe(2) - N(2) | 2.220(13) | Fe(7) - N(13) | 2.228(12) |
| Er(2) - O(2) | 2.415(9) | Fe(3) - O(20) | 1.951(10) | Fe(8) - O(44) | 1.966(10) |
| Er(2) = O(21) | 2.559(9) | Fe(3) = O(19) | 2.000(9) | Fe(8) = O(31) | 1.995(10) |
| Er(3) = O(35) | 2.237(10) | Fe(3) - N(8) | 2.011(13) | Fe(8) = N(18) | 2.018(12) |
| Er(3) - O(44) | 2.271(9) | Fe(3) - O(8) | 2.029(9) | Fe(8) - O(43) | 2.020(9) |
| Er(3) - O(37) | 2.287(9) | Fe(3) - O(21) | 2.099(9) | Fe(8) = O(41) | 2.082(9) |
| Er(3) = O(32) | 2.323(10) | Fe(3) - N(3) | 2.234(12) | Fe(8) = N(14) | 2.209(12) |
| Er(3) - O(24) | 2.337(9) | Fe(4) = O(1) | 1.955(9) | $Er(1)\cdots Fe(4)$ | 3.365(2) |
| Er(3) - O(25) | 2.346(9) | Fe(4) = O(22) | 1.973(9) | $Er(1) \cdots Fe(1)$ | 3.455(2) |
| Er(3) - O(23) | 2.397(9) | Fe(4) - O(19) | 1.979(9) | $Er(1)\cdots Er(2)$ | 3.8684(11) |
| Er(3) - O(41) | 2.533(9) | Fe(4) - O(9) | 1.979(9) | $Er(2)\cdots Fe(2)$ | 3.382(2) |
| Er(4) - O(33) | 2.281(10) | Fe(4)–O(21) | 2.077(10) | $Er(2)\cdots Fe(3)$ | 3.461(2) |
| Er(4) - O(40) | 2.282(9) | Fe(4)-N(4) | 2.240(12) | Er(3)···Fe(5) | 3.361(2) |

| Er(4)–O(42) | 2.290(11) | Fe(5)-O(39) | 1.959(10) | $\operatorname{Er}(3)\cdots\operatorname{Fe}(8)$ | 3.441(2) |
|----------------------------|-------------------------------|----------------------------------|-------------------------------|---|------------------------|
| Er(4)–O(28) | 2.328(10) | Fe(5)-O(23) | 1.961(9) | $\operatorname{Er}(3)\cdots\operatorname{Er}(4)$ | 3.8478(11) |
| Er(4)–O(29) | 2.349(9) | Fe(5) - O(37) | 1.983(10) | $Er(4)\cdots Fe(7)$ | 3.365(2) |
| Er(4)–O(23) | 2.363(8) | Fe(5) - O(26) | 1.985(9) | $Er(4)\cdots Fe(6)$ | 3.449(2) |
| | | Compound | d 40 | | |
| Tm(1)-O(22) | 2.271(11) | Tm(4) - O(24) | 2.396(12) | Fe(5)-O(41) | 2.042(12) |
| Tm(1)-O(13) | 2.274(11) | Tm(4)-O(41) | 2.548(11) | Fe(5)-N(13) | 2.191(16) |
| Tm(1)-O(15) | 2.288(12) | Fe(1)-O(1) | 1.961(11) | Fe(6)-O(39) | 1.964(12) |
| Tm(1)-O(3) | 2.323(13) | Fe(1)-O(17) | 1.972(12) | Fe(6)-O(29) | 1.992(13) |
| Tm(1)-O(10) | 2.327(12) | Fe(1)-O(15) | 1.975(13) | Fe(6)-N(16) | 2.010(17) |
| Tm(1)-O(2) | 2.351(10) | Fe(1)-O(4) | 1.979(13) | Fe(6)-O(40) | 2.026(12) |
| Tm(1) - O(1) | 2.390(10) | Fe(1)-O(16) | 2.117(12) | Fe(6)-O(41) | 2.070(13) |
| Tm(1)-O(20) | 2.577(11) | Fe(1) - N(1) | 2.280(14) | Fe(6)-N(12) | 2.215(16) |
| Tm(2)-O(18) | 2.261(11) | Fe(2)–O(18) | 1.955(11) | Fe(7)-O(32) | 1.956(12) |
| Tm(2)-O(11) | 2.274(12) | Fe(2) - O(17) | 1.982(12) | Fe(7)–O(24) | 1.964(11) |
| Tm(2)-O(19) | 2.312(12) | Fe(2) - N(5) | 2.003(15) | Fe(7)-O(45) | 1.970(12) |
| Tm(2)–O(1) | 2.322(10) | Fe(2)–O(5) | 2.028(12) | Fe(7)-O(43) | 1.981(13) |
| Tm(2)–O(7) | 2.333(12) | Fe(2)–O(16) | 2.081(13) | Fe(7)-O(44) | 2.100(14) |
| Tm(2)–O(6) | 2.347(12) | Fe(2) - N(2) | 2.235(16) | Fe(7)-N(14) | 2.237(15) |
| Tm(2)–O(2) | 2.361(9) | Fe(3)-O(2) | 1.934(11) | Fe(8)–O(46) | 1.936(12) |
| Tm(2)-O(16) | 2.529(11) | Fe(3)–O(21) | 1.957(12) | Fe(8)–N(19) | 1.988(16) |
| Tm(3)–O(27) | 2.270(12) | Fe(3) - O(19) | 1.978(13) | Fe(8)–O(45) | 2.002(13) |
| Tm(3)-O(46) | 2.286(13) | Fe(3)-O(8) | 2.011(14) | Fe(8)-O(35) | 2.035(15) |
| Tm(3)-O(42) | 2.286(12) | Fe(3) - O(20) | 2.092(12) | Fe(8)-O(44) | 2.094(14) |
| Tm(3) - O(36) | 2.314(12) | $\frac{\text{Fe}(3)-N(3)}{N(3)}$ | 2.230(15) | Fe(8)-N(15) | 2.204(17) |
| Tm(3) - O(24) | 2.344(12) | Fe(4) - O(9) | 1.972(13) | $Tm(1)\cdots Fe(1)$ | 3.347(3) |
| Tm(3) - O(25) | 2.347(12) | Fe(4) - O(22) | 1.986(11) | $Tm(1)\cdots Fe(4)$ | 3.445(3) |
| Tm(3) - O(23) | 2.385(12) | Fe(4) - O(21) | 1.994(13) | $Tm(1)\cdots Tm(2)$ | 3.8154(12) |
| Tm(3) - O(44) | 2.542(12) | Fe(4) - N(8) | 2.037(16) | $Tm(2)\cdots Fe(3)$ | 3.349(3) |
| Tm(4)=O(33) | $\frac{2.239(11)}{2.269(12)}$ | Fe(4) = O(20) | $\frac{2.053(12)}{2.246(14)}$ | $\operatorname{Im}(2)\cdots\operatorname{Fe}(2)$ | 3.438(3) |
| 1m(4) = O(43) | $\frac{2.268(13)}{2.204(14)}$ | Fe(4)=N(4) | 2.246(14) | $\operatorname{Im}(3)\cdots\operatorname{Fe}(5)$ | 3.358(3) |
| Tm(4)=O(39) | $\frac{2.294(14)}{2.201(11)}$ | Fe(5)=O(40) | $\frac{1.955(12)}{1.062(12)}$ | $\operatorname{Tm}(3)\cdots\operatorname{Fe}(8)$ | 3.449(3) |
| Tm(4)=O(30) Tm(4)=O(31) | 2.301(11) 2.312(12) | Fe(5)=O(25) | 1.902(12) 1.078(13) | $\operatorname{Tm}(3) \cdots \operatorname{Tm}(4)$ $\operatorname{Tm}(4) = \operatorname{Fo}(7)$ | 3.8200(14) 3.357(3) |
| Tm(4) = O(31) | 2.313(12) 2.328(11) | $F_{2}(5) = O(42)$ | $\frac{1.978(13)}{1.000(13)}$ | Tm(4) = Fo(6) | 3.337(3) |
| 1111(4) O(23) | 2.338(11) | $\frac{\Gamma(3)}{Compound}$ | 1.990(13) | 1111(4)1(e(0) | 3.434(3) |
| $D_{v(1)=O(7)}$ | 2 290(9) | Fe(3) = O(22) | 1 994(9) | $F_{e}(1) = O(21)$ | 2 142(9) |
| Dy(1) = O(15) | 2.200(9) | Fe(3) = O(10) | 2 003(9) | Fe(1) = N(1) | 2.142(9) 2 259(10) |
| Dy(1) = O(17) | 2.315(8) | Fe(3) = O(21) | 2.066(9) | Fe(2) = O(1) | 1.948(8) |
| Dy(1) = O(3) | 2.335(9) | Fe(3) - N(10) | 2.000(2) | Fe(2) = O(19) | 1.974(9) |
| Dy(1) = O(2) | 2.348(8) | Mn(1) - O(20) | 1.932(9) | Fe(2) = O(6) | 1.974(9) |
| Dy(1) = O(5) | 2.372(8) | Mn(1) - O(12) | 1 979(11) | Fe(2) = O(17) | 1 974(9) |
| Dy(1) = O(1) | 2.415(8) | Mn(1) = N(7) | 1.983(14) | Fe(2) = O(18) | 2.070(9) |
| Dy(1) - O(21) | 2.535(8) | Mn(1) - O(19) | 1.987(10) | Fe(2) = N(5) | 2.243(10) |
| Dy(2)-O(22) | 2.299(11) | Mn(1)–O(18) | 2.160(10) | Fe(3)-O(2) | 1.955(8) |
| Dy(2) - O(13) | 2.305(10) | Mn(1)-N(6) | 2.248(12) | Fe(3) - O(16) | 1.963(8) |
| Dy(2)–O(20) | 2.324(9) | Dy(1)-O(7) | 2.290(9) | Fe(3)-O(22) | 1.994(9) |
| Dy(2)-O(11) | 2.337(10) | Dy(1)-O(15) | 2.307(8) | Fe(3)-O(10) | 2.003(9) |
| Dy(2)-O(9) | 2.357(9) | Dy(1)-O(17) | 2.315(8) | Fe(3)-O(21) | 2.066(9) |
| Dy(2)-O(1) | 2.368(8) | Dy(1)-O(3) | 2.335(9) | Fe(3)-N(10) | 2.233(13) |
| Dy(2)–O(2) | 2.429(8) | Dy(1)-O(2) | 2.348(8) | Mn(1)–O(20) | 1.932(9) |
| Dy(2)–O(18) | 2.525(9) | Dy(1)-O(5) | 2.372(8) | Mn(1)-O(12) | 1.979(11) |
| $F_{e}(1) = O(15)$ | 1 033(8) | $D_{v}(1) = O(1)$ | 2 /15(8) | Mn(1) - N(7) | 1.983(14) |
|--------------------|-----------|-------------------|-----------|---------------------|------------|
| Fe(1) = N(2) | 1.930(0) | Dy(1) = O(21) | 2.535(8) | Mn(1) - O(19) | 1.987(10) |
| Fe(1) - O(4) | 1 990(8) | Dy(2) - O(22) | 2.299(11) | Mn(1) - O(18) | 2 160(10) |
| Fe(1) = O(16) | 2,005(9) | Dy(2) = O(13) | 2.305(10) | Mn(1) = N(6) | 2.248(12) |
| Fe(1) = O(21) | 2.142(9) | Dy(2) - O(20) | 2.324(9) | $Dv(1)\cdots Fe(2)$ | 3 3914(18) |
| Fe(1) = N(1) | 2.259(10) | Dy(2) = O(11) | 2.337(10) | $Dy(1)\cdots Fe(1)$ | 3.4704(19) |
| Fe(2) = O(1) | 1.948(8) | Dy(2) - O(9) | 2.357(9) | $Dy(1)\cdots Dy(2)$ | 3.8731(9) |
| Fe(2) - O(19) | 1.974(9) | Dy(2) - O(1) | 2.368(8) | $Dv(2)\cdots Fe(3)$ | 3.391(2) |
| Fe(2) - O(6) | 1.974(9) | $D_{v(2)} - O(2)$ | 2.429(8) | $Dv(2)\cdots Mn(1)$ | 3.477(2) |
| Fe(2) - O(17) | 1.974(9) | Dy(2) - O(18) | 2.525(9) | $Dy(1)\cdots Fe(2)$ | 3.3914(18) |
| Fe(2)-O(18) | 2.070(9) | Fe(1)-O(15) | 1.933(8) | $Dy(1)\cdots Fe(1)$ | 3.4704(19) |
| Fe(2) - N(5) | 2.243(10) | Fe(1) - N(2) | 1.980(12) | $Dy(1)\cdots Dy(2)$ | 3.8731(9) |
| Fe(3)-O(2) | 1.955(8) | Fe(1)-O(4) | 1.990(8) | $Dy(2)\cdots Fe(3)$ | 3.391(2) |
| Fe(3)-O(16) | 1.963(8) | Fe(1)-O(16) | 2.005(9) | $Dy(2)\cdots Mn(1)$ | 3.477(2) |
| | | Compound | d 42 | · · | |
| Dv(1) - O(14) | 2.297(12) | Dv(4) - O(34) | 2.304(12) | Fe(4)-O(33) | 2.032(11) |
| Dy(1)-O(28) | 2.325(10) | Dy(4)-O(37) | 2.316(11) | Fe(4)–O(10) | 2.081(11) |
| Dy(1)-O(15) | 2.352(12) | Dy(4)-O(11) | 2.366(13) | Fe(4)-N(4) | 2.268(14) |
| Dy(1)-O(5) | 2.403(9) | Dy(4)-O(6) | 2.369(11) | Fe(5)–O(2) | 1.935(10) |
| Dy(1)-O(31) | 2.433(11) | Dy(4)-O(5) | 2.397(10) | Fe(5)-O(36) | 1.944(11) |
| Dy(1)-O(39) | 2.458(10) | Dy(4)-O(12) | 2.503(11) | Fe(5)-O(35) | 2.001(11) |
| Dy(1)-O(27) | 2.509(10) | Dy(4)-O(27) | 2.572(10) | Fe(5)-O(40) | 2.002(11) |
| Dy(1)-N(1) | 2.728(13) | Fe(1)-O(1) | 1.882(10) | Fe(5)-O(17) | 2.081(13) |
| Dy(1)-O(1) | 2.777(10) | Fe(1)-O(31) | 2.012(10) | Fe(5) - N(5) | 2.264(13) |
| Dy(2)-O(36) | 2.266(11) | Fe(1)-O(32) | 2.012(12) | Fe(6)-O(3) | 1.931(12) |
| Dy(2)–O(21) | 2.273(11) | Fe(1)-O(7) | 2.023(10) | Fe(6)-O(2) | 1.996(10) |
| Dy(2)–O(32) | 2.295(11) | Fe(1)-O(28) | 2.024(11) | Fe(6)-O(18) | 2.015(13) |
| Dy(2)–O(2) | 2.367(10) | Fe(1) - N(3) | 2.241(14) | Fe(6)-O(33) | 2.023(11) |
| Dy(2)–O(4) | 2.379(11) | Fe(2)-O(1) | 1.918(10) | Fe(6)-O(26) | 2.070(10) |
| Dy(2)-O(19) | 2.405(15) | Fe(2)–O(6) | 2.021(10) | Fe(6)-O(30) | 2.098(11) |
| Dy(2)-O(20) | 2.522(12) | Fe(2)-O(9) | 2.031(11) | Fe(7)-O(3) | 1.887(11) |
| Dy(2)-O(30) | 2.560(10) | Fe(2)–O(35) | 2.050(12) | Fe(7)-O(37) | 1.999(13) |
| Dy(2)-N(7V) | 2.94(4) | Fe(2)–O(8) | 2.061(10) | Fe(7)-O(38) | 2.013(12) |
| Dy(3)-O(29) | 2.328(11) | Fe(2)–O(27) | 2.096(11) | Fe(7)–O(29) | 2.031(12) |
| Dy(3)–O(4) | 2.352(9) | Fe(3)-O(1) | 1.995(10) | Fe(7)-O(25) | 2.036(11) |
| Dy(3)–O(22) | 2.363(11) | Fe(3)–O(3) | 1.998(10) | Fe(7) - N(6) | 2.199(13) |
| Dy(3)-O(23) | 2.392(11) | Fe(3)-O(5) | 1.999(10) | $Dy(1)\cdots Fe(1)$ | 3.216(2) |
| Dy(3)-O(30) | 2.441(12) | Fe(3)-O(2) | 2.009(11) | $Dy(1)\cdots Dy(4)$ | 3.9773(11) |
| Dy(3)–O(24) | 2.451(12) | Fe(3)-O(6) | 2.013(10) | $Dy(3)\cdots Fe(7)$ | 3.184(2) |
| Dy(3)-O(38) | 2.454(10) | Fe(3)-O(4) | 2.017(9) | $Dy(4)\cdots Fe(3)$ | 3.357(2) |
| Dy(3)-O(3) | 2.635(10) | Fe(4)-O(6) | 1.922(11) | $Dy(4)\cdots Fe(4)$ | 3.395(3) |
| Dy(3)-N(2) | 2.641(14) | Fe(4)-O(34) | 1.932(13) | $Fe(2)\cdots Fe(3)$ | 2.926(3) |
| Dy(4)–O(13) | 2.275(14) | Fe(4)–O(40) | 2.002(12) | $Fe(3)\cdots Fe(6)$ | 2.933(3) |

| | | , | () | 0 | | |
|--|--|---|----------------------|-----------|--|--|
| D−H···A | d(D–H) | $d(H \cdots A)$ | $d(D \cdots A)$ | ∠(DHA) | | |
| Compound 9 | | | | | | |
| O35-H35EO30 | 0.95 | 1.97 | 2.752(10) | 138.6 | | |
| O35–H35DO27 ^{#1} | 0.85 | 1.99 | 2.840(11) | 179.5 | | |
| O34–H34BO15 | 0.95 | 2.27 | 2.881(11) | 121.0 | | |
| O34–H34AO35 ^{#2} | 0.95 | 1.92 | 2.762(14) | 146.8 | | |
| O30–H30AO15 ^{#3} | 0.82 | 1.90 | 2.718(8) | 172.8 | | |
| O27–H27O34 ^{#4} | 0.82 | 1.89 | 2.696(13) | 167.1 | | |
| O24–H24O21 ^{#4} | 0.82 | 1.95 | 2.754(7) | 167.1 | | |
| #1 -x+1,-y+1,-z+1 # | $\frac{1}{2} - x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ | /2 #3 -x+1/2,y-1/2,- | z+1/2 #4 -x+3/2,y-1/ | /2,-z+1/2 | | |
| Compound 10 | | | | | | |
| O9–H9N3 ^{#3} | 0.82 | 2.10 | 2.868(6) | 156.0 | | |
| O9–H9N4 ^{#3} | 0.82 | 2.61 | 3.190(6) | 129.4 | | |
| O9A–H9AN5 ^{#4} | 0.82 | 2.40 | 3.147(17) | 152.5 | | |
| O9B-H9BN5 ^{#4} | 0.82 | 2.46 | 2.95(2) | 119.0 | | |
| #3 x, $-y+1/2$, $z-1/2$ #4 y-1/2, $-z+1/2$, $-x$ | | | | | | |

Annexe 2. Hydrogen bond distances (Å) and angles (°) in 9 and 10

Annexe 3. Infrared spectra of 1-32, 34-42 complexes



Fig. A3.1. IR spectrum of [Fe₃O(is)₆(H₂O)₃](NO₃)·(H₂O)₂·(MeCN)₂ (1).



Fig. A3.2. IR spectrum of $[Fe_2O(is)_2(tpt)_2(H_2O)_2](NO_3)_2(2)$.



Fig. A3.3. IR spectrum of [Fe₄O₂(is)₇(dpa)₂]NO₃ (**3**).



Fig. A3.6. IR spectrum of [Fe₇O₅(piv)₁₁(bpm)₂(H₂O] (7).



Fig. A3.7. IR spectrum of $(mdeaH_3)_2[Fe_6O(thme)_4Cl_6] \cdot 0.5(MeCN) \cdot 0.5(H_2O)$ (8).



Fig. A3.8. IR spectrum of $[Fe_8O_3(is)_9(tea)(teaH)_3]$ ·(MeCN)·2(H₂O) (9).



Fig. A3.9. IR spectrum of [Fe₈O₃(is)₆(tea)(teaH)₃(N₃)₃] (10).



Fig. A3.10. IR spectrum of $[Fe_8O_3(is)_6(mdea)_3(N_3)_3(MeO)_3]$ (11).



Fig. A3.11. IR spectrum of $[Fe_{12}O_6(OH)_4(piv)_{10}(mdea)_4(mdeaH)_2]$ (12).





Fig. A3.13. IR spectrum of [Fe₁₂O₆(teda)₄(Cl)₈]·6(CHCl₃) (14).



Fig. A3.14. IR spectrum of $[Fe_{22}O_{16}(OH)_2(is)_{18}(bdea)_6(EtO)_2(H_2O)_2] \cdot 2(EtOH) \cdot 5(MeCN) \cdot 6(H_2O)$



Fig. A3.15. IR spectrum of [Fe₂₂O₁₄(OH)₄(is)₁₈(mdea)₆(EtO)₂(H₂O)₂](NO₃)₂·EtOH·H₂O (**16**).



Fig. A3.16. IR spectrum of $\{[Fe_3O(piv)_6(CO_2)(pyEt)] \cdot (pivH)_{0.5} \cdot (thf)_{0.5}\}_n$ (17).



Fig. A3.17. IR spectrum of $[Fe_4O_2(piv)_8(hmta)]_n$ (18).



Fig. A3.18. IR spectrum of $\{[Fe_3O(piv)_6(4,4'-bpy)_{1.5}](OH) \cdot 0.75(CH_2Cl_2) \cdot n(H_2O)\}_n$ (19).



Fig. A3.19. IR spectrum of $[Fe_6Dy_3(is)_9(bdea)_6(MeO)_6]$ ·MeOH (20).



Fig. A3.20. IR spectrum of $[Fe_6Dy_4(is)_8(bdea)_{10}(N_3)_2]$ ·MeOH (21).



Fig. A3.21. IR spectrum of $[Fe_6Gd_4(is)_8(bdea)_{10}(N_3)_2]$ ·MeOH (22).



Fig. A3.22. IR spectrum of [Fe₆Ho₄(is)₈(bdea)₁₀(N₃)₂]·MeOH (23).



Fig. A3.23. IR spectrum of $[Fe_6Y_4(is)_8(bdea)_{10}(N_3)_2]\cdot MeOH~(\textbf{24}).$



 $Fig. \ A3.24. \ IR \ spectrum \ of \ [Fe_{18}Dy_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot 6(MeOH) \cdot \ 30(H_2O) \ (\textbf{25}).$



Fig. A3.25. IR spectrum of [Fe₁₈Dy₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·MeCN·8(H₂O) (26).



Fig. A3.26. IR spectrum of $[Fe_{18}Gd_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·MeCN·10(H₂O) (27).



Fig. 3.27. IR spectrum of $[Fe_{18}Tb_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot 2(MeCN) \cdot 8(MeOH) \cdot 7.5(H_2O)$ (28).



Fig. A3.28. IR spectrum of $[Fe_{18}Sm_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot 6(MeOH) \cdot 21(H_2O)$ (29).



2500 2000 Wellenzahlen (cm-1) Fig. A3.30. IR spectrum of [Fe₁₈Ho₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·MeCN·3(MeOH)·11(H₂O) (**31**).

30 -



Fig. A3.31. IR spectrum of $[Fe_{18}Y_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot 2(MeCN) \cdot 2(MeOH) \cdot 14(H_2O)$ (32).



Fig. A3.32. IR spectrum of $[Fe_{18}Nd_6(piv)_{12}(teaH)_{18}(tea)_6(N_3)_6] \cdot 3(MeCN) \cdot 12.5(MeOH) \cdot 6(H_2O)$ (34).



Fig. A3.33. IR spectrum of $[Fe_4Dy_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (35).









Fig. A3.37. IR spectrum of $[Fe_4Er_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (39).



Fig. A3.38. IR spectrum of $[Fe_4Tm_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (40).



Fig. A3.39. IR spectrum of $[Fe_3MnDy_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (41).





Annexe 4. Thermogravimetric spectra of 1-11, 13-15, 18-32 and 35-41 complexes

Fig. A4.1. TGA/DTA curves of a $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot (H_2O)_2 \cdot (MeCN)_2$ (1).



Fig. A4.2. TGA/DTA curves of a [Fe₂O(is)₂(tpt)₂(H₂O)₂](NO₃)₂ (**2**).









Fig. A4.5. TGA/DTA curves of a $[Fe_4O_2(piv)_8(bpm)] \cdot 3(MeCN)$ (5).



Fig. A4.6. TGA/DTA curves of a [Fe₆O₂(OH)₂(is)₁₀(C₄H₆O₃)₂](NO₃)₂·4(HCOOH) (**6**).



Fig. A4.7. TGA/DTA curves of a [Fe₇O₄(OH)₂(piv)₁₁(bpy)₂(H₂O)] (7).



Fig. A4.8. TGA/DTA curves of a $(mdeaH_3)_2[Fe_6O(thme)_4Cl_6]\cdot 0.5(MeCN)\cdot 0.5(H_2O)$ (8).



Fig. A4.9. TGA/DTA curves of a $[Fe_8O_3(is)_9(tea)(teaH)_3] \cdot (MeCN) \cdot 2(H_2O)$ (9).



Fig. A4.10. TGA/DTA curves of a [Fe₈O₃(is)₆(tea)(teaH)₃(N₃)₃] (10).







Fig. A4.12. TGA/DTA curves of a

 $[Fe_{12}O_4(OH)_2(teda)_4(N_3)_4(MeO)_4](NO_3)_{0.5} \cdot N_3 \cdot (MeO)_{0.5} \cdot 2.5(H_2O) \ \textbf{(13)}.$







Fig. A4.14. TGA/DTA curves of a

 $[Fe_{22}O_{16}(OH)_2(is)_{18}(bdea)_6(EtO)_2(H_2O)_2] \cdot 2(EtOH) \cdot 5(MeCN) \cdot 6(H_2O) \text{ (15)}.$



Fig. A4.15. TGA/DTA curves of a [Fe₄O₂(piv)₈(hmta)]_n (18).



Fig. A4.16. TGA/DTA curves of a { $[Fe_3O(piv)_6(4,4'-bpy)_{1.5}](OH) \cdot 0.75(CH_2Cl_2) \cdot n(H_2O)$ } n (19).



Fig. A4.17. TGA/DTA curves of a [Fe₆Dy₃(is)₉(bdea)₆(MeO)₆]·MeOH (**20**).



Fig. A4.18. TGA/DTA curves of a $[Fe_6Dy_4(is)_8(bdea)_{10}(N_3)_2]$ ·MeOH (21).



Fig. A4.19. TGA/DTA curves of a $[Fe_6Gd_4(is)_8(bdea)_{10}(N_3)_2]$ ·MeOH (22).





Fig. A4.21. TGA/DTA curves of a $[Fe_6Y_4(is)_8(bdea)_{10}(N_3)_2]$ ·MeOH (24).



Fig. A4.22. TGA/DTA curves of a first polymorph

 $[Fe_{18}Dy_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]\cdot 6CH_3OH\cdot 30H_2O~(\textbf{25}).$



Fig. A4.23. TGA/DTA curves of a $[Fe_{18}Dy_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (26).



Fig. A4.24. TGA/DTA curves of a $[Fe_{18}Gd_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (27).



Fig. A4.25. TGA/DTA curves of a [Fe₁₈Tb₆(is)₁₂(teaH)₁₈(tea)₆(N₃)₆]·x(solvents) (**28**).



Fig. A4.26. TGA/DTA curves of a $[Fe_{18}Sm_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (29).



Fig. A4.27. TGA/DTA curves of a $[Fe_{18}Eu_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (30).



Fig. A4.28. TGA/DTA curves of a $[Fe_{18}Ho_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (31).



Fig. A4.29. TGA/DTA curves of a $[Fe_{18}Y_6(is)_{12}(teaH)_{18}(tea)_6(N_3)_6]$ ·x(solvents) (32).



Fig. A4.30. TGA/DTA curves of a $[Fe_4Dy_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (35).



Fig. A4.31. TGA/DTA curves of a $[Fe_4Gd_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (36).



Fig. A4.32. TGA/DTA curves of a $[Fe_4Tb_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (37).



Fig. A4.33. TGA/DTA curves of a $[Fe_4Y_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (38).



Fig. A4.34. TGA/DTA curves of a $[Fe_4Er_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (39).



Fig. A4.35. TGA/DTA curves of a $[Fe_4Tm_2(OH)_2(is)_6(bdea)_4(N_3)_2]$ ·MeOH (40).



Fig. A4.36. TGA/DTA curves of a $[Fe_3MnDy_2(OH)_2(is)_6(bdea)_4(N_3)_2] \cdot MeOH$ (41).

DECLARATION ON THE ASSUMPTION OF RESPONSIBILITY

I, the undersigned, Botezat Olga, declare on my own responsibility that the materials presented in the thesis are the result of my own research and scientific achievements. I realize that otherwise will suffer the consequences in accordance with the legislation in force.

Botezat Olga Data: 21.02.2019

11. Off

CURRICULUM VITAE

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|---------------|--|
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EDUCATION DEGREES

| 2012-present | University of the Academy of Science of Moldova, PhD Student Scientific Supervisor: assoc. prof., Ph.D. Victor Kravtsov and Scientific |
|--------------|---|
| | Consultant: assoc. prof., Ph.D. Svetlana Baca. |
| 2008-2009 | University of the Academy of Science of Moldova, Chisinau, Master's |
| | Degree in Chemistry Specialisation in Coordination Chemistry |
| | Dissertation title: The synthesis and study of Fe ^{III} carboxylate clusters and |
| | coordination polymers based on them |
| | Scientific Supervisor: Dr. Svetlana Baca. |
| 2003-2008 | Tiraspol State University, Faculty of Bio-Chemistry, Chisinau, Undergraduate |
| | degree in Chemistry |
| | Dissertation title: <i>The synthesis and investigation of</i> Fe ^{III} <i>carboxylate complexes</i> with N donor ligger de |
| | with Iv-aonor liganas. |
| | Scientific Supervisors: Dr. Svetiana Baca& Dr. Eugenia Melentiev. |

EMPLOYMENTS

| 06/2010 - | Scientific | Researcher | - | Institute | of | Applied | Physics, | Moldova | Academy | of |
|-----------|------------|------------|---|-----------|----|---------|----------|---------|---------|----|
| present | Sciences. | | | | | | | | | |
| | | | | | | | | | | |

09/2008 - *Researcher* - Institute of Chemistry. Moldova Academy of Sciences. 06/2010

Scholarship, Grands, Awards

- 2015 The 65th Lindau Nobel Laureate Meetings 2015. (65 Nobel Laureates and 650 young researchers participated in the 65th Lindau Nobel Laureate Meeting Interdisciplinary: Physiology/Medicine, Physics, Chemistry) Germany, Lindau from 28.06.2015 to 3.07. 2015
- **2013-2015 DAAD scholarship**. Project "Sandwich Model": *Crystal engineering and study of coordination polymers based on 3d-, 3d-4f, and 4f-metal-based carboxylate clusters*).
 - 2012 Research Grant from Swiss National Science Foundation for three months

study visit to the Department of Chemistry and Biochemistry, University of Bern, Switzerland from *1.06.2012* to *15.08.2012*

Title: "Magnetic coordination polymers from nanosized clusters" (Host: Prof. S. Decurtins)

AREA OF SCIENTIFIC INTEREST

synthesis, structural characterization and physical properties of the polynuclear carboxylate complexes;

preparation and investigation of metal coordination polymers

synthesis and physical properties of complexes based on homo- or heterometallic transition and 4f –metals.

RESEARCH EXPERIENCE

synthesis of coordination compounds, including synthesis of initial organic polydentate, polyfunctional ligands; hydro- and solvothermal synthesis, experience with inert- atmosphere manipulation techniques;

characterization of obtained compounds by IR, mass-spectrometry and thermogravimetric methods;

investigation of catalytic properties of the 3d-Fe-metal complexes.

PARTICIPATION IN RESEARCH PROJECTS

- **2016-2017** CSSDT (16.80013.5007.04/Ro). New non-toxic aromatic carboxylate derivatives with role in plant growth regulation: from synthesis and structural investigations to biological tests (CAREPLANT), head Ph.D. Pavlina Bourosh
 - **2017** CSSDT (16.80012.02.05F). Design, preparation and study of metal-organic mixed-ligand materials with useful properties based on transition metals and polydentate ligands, head Lilia Croitor, Ph.D.
- **2016-2017** CSSDT (16.00353.50.05A). Crystal engineering approach for design and tuning the architecture of functional metal-organic materials, head Ph.D. Victor Kravtsov

2014-2017 Scopes, project (IZ73Z0_152404/1). "Synthesis, Experimental and Theoretically Study of Bistable Magnetic Materials Based on 3d and 3d-4f Exchange Coupled Clusters: Prospects for Practical Applications" supported by the Swiss National Scientific Foundation. Director de project: Dr. Svetlana Baca.

- **2016** The Grant for Young Scientists (15.819.02.03F). Director de proiect: Dr. Lilia Croitor.
- 2014-2015 STAT PROGRAMM. (CSSDT 14.518.02.04A) "Ingineria cristalelor la crearea materialelor metaloorganice cu proprietăți cooperative" din cadrul Programului de Stat "Designul substanțelor chimice și dirijarea arhitecturii materialelor pentru diverse aplicații") Director de proiect: dr. șt. fiz.-mat. Victor Kravţov.

PUBLICATIONS:

- 7 publications in the International Journals with Impact Factor from 1.249 to 4.85.
- **14 scientific publications** at the international Confrences.

Acknowledgements

I would like to thank people, without them, the implementation of this work would not be possible. First, I would like to express my deepest gratitude to two my advisors, Dr. Victor Kravtsov and Dr. Svetlana Baca, for being open for my questions and provide quick professional help, that they shared their knowledges and experience with me. I appreciate them for the excellent guidance and for the outstanding support during my studies.

I also wish to say big thanks to Prof. Dr. Paul Kögerler (Germany, Aachen, RWTH University of Inorganic chemistry) for work opportunity in his laboratory, thereby making possible to synthesize more complexes and perform magnetic studies of obtained compounds. I am very grateful to Dr. Jan van Leusen for assistance in the field of magnetization and description of the magnetic properties of the resulting compounds; it is an essential and important contribution to my thesis. I want to thank Dr. Natalia Izarova for providing single crystal X-Ray diffraction analyses and elemental analyses for some of my compounds. I would also like to acknowledge the help of all members of the Laboratory of Molecular magnetism I was working with, in particular Brigitte, Christine, Tim and Sebastian (Aachen, Germany).

Special acknowledgement goes to group of Prof. Dr. Ulli Englert (Aachen, Germany) for performing single-crystal X-Ray diffraction analyses for my compounds.

I want to give special thanks to Laboratory of Physical Methods of Solid State Investigation "Tadeusz Malinowski" for supporting me during my PhD studies, in particular Dr. Bourosh Polina for her professional consultancy.

I would like to express huge gratitude to DAAD for given scholarship (2013-2015) within two years and with that get great opportunity to perform the experimental part for my PhD Thesis.

I am deeply grateful to my husband and my mother for their invaluable and helpful support during my studies and when I was writing my dissertation.