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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

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The PhD thesis and its summary may be consulted at the scientific library of the Academy of Sciences of Moldova and at A. N. A. C. E. C. Web page (www.cnaa.md).

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CONCEPTUAL MILESTONES OF RESEARCH

Relevance and importance of the problem. Polynuclear homo- and heterometallic d/d-f coordination compounds have become a focus of interest due to their highly versatile structural chemistry and great potentials in “intelligent” information storage devices, molecular spintronics, and also as promising magnetocaloric materials [1-3]. For instance, they show fascinating magnetic phenomena such as single-molecule magnet behavior (SMM), macroscopic quantum tunneling of magnetization, and quantum coherence. Transition metal-based complexes have been proven to be one of the most fruitful sources of SMMs [3-5], starting from the first most known „Mn_{12}-acetate“cluster. More recently, mixed metal clusters based on 3d and 4f metals have attracted much interest 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 magnetic properties. Among 3d-4f coordination clusters that incorporate the high spin carriers such as Mn, Ni, Co, Cu or Cr ions, Fe-4f clusters remain attractive targets over the recent years. To date several Fe-4f clusters have been reported displaying SMM behavior [6], the use of magnetic Fe 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 polynuclear 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 [7-8]. The corresponding multidimensional systems lack adequate theoretical understanding even more as numerous inter- and intra-cluster interactions determine the resulting magnetism. Thus, further studies in this field are essential to obtain real control and understanding of the way that complex building blocks assemble and interact.

The main goal of this work 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 using crystal engineering principles. Thus, the following objectives have been set:

- ***development*** of crystal engineering strategies towards the synthetic approaches for the preparation of homo- and heterometallic Fe^{III}/Fe^{III}-4f clusters and coordination polymers;
- ***synthesis*** of newly designed compounds employing different carboxylate and/or *O*-based and *N*-based ligands;

- ***characterization*** of their crystalline structures, physico-chemical characteristics and chemical reactivity by using a range of research methods;
- ***examination*** of their magnetic properties by variable temperature susceptibility measurements.

Research methodology. Synthesis of coordination clusters and polymers described in this dissertation were carried out using a number of methods such as hydro(solvo)thermal, ultrasonic, microwave heating and traditional methods. In order to characterize the composition/structure and properties of the obtained complexes, modern physico-chemical methods such as elemental analysis, IR spectroscopy, X-ray crystallography, thermogravimetrical analysis (TGA) and differential thermal analysis (DTA), and magnetochemistry were used.

Scientific novelty and originality of the results consists in the elaboration of methods and conditions of syntheses for 42 new Fe^{III}/Fe^{III}-4f coordination compounds. This includes the use of conventional solution chemistry and novel synthetic procedures such as hydro(solvo)thermal synthesis, microwave and ultrasonic irradiations. This research produces homo- and heteronuclear Fe^{III}/Fe^{III}-4f compounds with a wide range of cores (di-, tri- tetra-, hexa-, hepta-, octa-, nona-, undeca-, dodeca- up to docosa- and tetracosanuclear), metal ratio and structural motifs. All compounds were crystallographically characterized by a single crystal X-ray method and magnetically studied. For the first time, a series of the largest wheel-shaped heterometallic $\{Fe_{18}Ln_6\}$-type clusters has been designed and obtained under ultrasonic treatment using in the reaction amino alcohols and carboxylate bridging ligands. 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 Fe^{III}/Fe^{III}-4f carboxylate clusters with enhanced magnetic properties and coordination polymers of Fe^{III} (0D, 1D and 3D) with notable porosity, using polynuclear Fe^{III} oxo-carboxylate precursors and *N,O*-donor ligands have been established. The prepared heterometallic $\{Fe_4Dy_2\}$, $\{Fe_6Dy_3\}$, $\{Fe_6Dy_4\}$, $\{Fe_6Tb_4\}$, $\{Fe_7Dy_4\}$, $\{Fe_{18}Dy_6\}$, and $\{Fe_{18}Tb_6\}$-type clusters showed a magnet-like behavior.

The theoretical significance of this work consists in the elaboration of the efficient synthetic routes for obtaining compounds based on Ln^{III} and Fe^{III} metals. Experimental results of structural, spectroscopic, magnetic measurements extended the knowledge of this class of compounds. 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. **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.

The main scientific results submitted for approval are: New synthetic pathways toward the preparation of Fe^{III} or Fe^{III}-Ln^{III} coordination compounds based on carboxylate and/or *N,O*-donor organic ligands was developed. Using pre-synthesized polynuclear clusters, templates, different reaction conditions and certain concentrations of reagents, 42 new compounds, including the largest Fe-Ln carboxylate wheels to date were obtained. Their structures have been determined using a single-crystal X-ray diffraction analysis. The thermal and magnetic properties of the prepared compounds have also been determined.

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 $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$ systems. The program provides accurate prediction the exchange energies in the $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$ systems.

Approval of scientific results. The main results of the thesis were presented in the form of two communication and 12 posters at national and international scientific conferences: International Conferences on Materials Science and Condensed Matter Physics (Chisinau, Moldova 2018, 2016, 2014, and 2010); 4th Central and Eastern European Conference on Thermal Analysis and Calorimetry (Chisinau, Moldova, 2017); International Scientific Conference of PhD students „Contemporary trends of development of science: views of young researchers" (Chisinau, Moldova, 2014, 2015 and 2016); XVIII-th Conference "Physical Methods in Coordination and Supramolecular Chemistry", (Chisinau, Moldova, 2015); IX COPS 2011, 9th International Symposium on Characterisation of Porous Solids (Dresden, Germany, 2011).

Scientific publications. The main results of the thesis were published in 21 scientific publications, 6 of them in journals with impact factor 1.24 - 4.85 (*Inorganic Chemistry*, *Dalton Transactions*, *Crystal Growth & Design*, *European Journal of Inorganic Chemistry*, *Zeitschrift für Anorganische und Allgemeine Chemie*) and one without co-authors in journal of A grade (*Moldavian Journal of the Physical Sciences*). Three scientific publications at conferences are also without co-authors.

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

Volume and structure of the thesis. The thesis consists of introduction, 4 chapters, general conclusions and recommendations, bibliography of 259 titles, 113 pages, 8 tables, 50 figures, 4 annexes. The results are published in 7 articles and 14 theses at conferences.

THESIS CONTENT

The **Introduction** describes the relevance and importance of the discussed issue, identifies main goals and objectives of the thesis, and describes scientific novelty and originality of the results, theoretical and practical significance, dissemination and publication of the research findings, thesis overview, keywords.

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

Chapter 1 begins with a brief introduction to the field of crystals engineering and gives the reader an idea of the chronology and milestones of the development of this discipline. The next sections are giving an in-depth review of the literature from 1921 to 2016 years to determine the state of research in the field of homo- and heterometallic Fe/Fe-Ln carboxylate clusters and coordination polymers based on clusters. Particular attention is paid to the chosen starting material and binding organic ligands that led to the obtaining of Fe/Fe-Ln carboxylate compounds. A brief structural description and information about magnetic or other properties is given to the majority of compounds. The analysis of the situation in this domain helped to find out and identify research problems. The chapter ends with conclusions.

2. EXPERIMENTAL METHODS OF SYNTHESIS AND INVESTIGATIONS

Chapter 2 begins with the information about the physico-chemical methods of investigation, equipment and instrumentation, and the technical parameters under which the analyses were performed. A single-crystal X-ray diffraction analysis, IR spectroscopy, TGA/DTA and elemental analyses were used to identify the structure and composition of the prepared coordination compounds. Figures were prepared using DIAMOND [9] and Mercury [10] programs, and cif files are available in Cambridge Structural Database (CSD) [11]. The main crystallographic data and parameters of all compounds are summarized in the Table 1. For the majority compounds were performed temperature dependent magnetic studies (ac and dc measurements). TGA/DTA measurements revealed thermal behavior of the discussed complexes. This chapter gives also an explanation about the importance of synthetic methods such as ultrasonic irradiation, microwave and hydro(solvo)thermal methods. The subsequent 4 parts give a detailed description of the preparation of 42 new homo- and heterometallic Fe^{III}/Fe^{III}-Ln^{III}-based coordination compounds.

Table 1. Crystal data and details of structural determinations for **1-42**

#	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Gr. sp.	*P*-1	$P2_1/n$	*C*2/*c*	$P2_1/n$	*P*-1	$P2_1/n$	$P2_1/n$	*I*-42*d*	$P2_1/n$	*Pa*-3	*P*-1	*P*-1	*P*4	*C*2/*c*
a (Å)	11,99(7)	12,64(7)	40,20(1)	11,347(2)	13,82(2)	12,417(9)	24,33(4)	29,277(2)	15,84(2)	24,08(1)	13,56(4)	14,17(8)	27,59(6)	32,91(8)
b(Å)	14,04(8)	10,56(6)	16,898(2)	23,957(3)	22,544(2)	21,17(2)	17,36(2)	29,277(2)	20,18(3)	24,08(1)	14,58(4)	14,71(8)	27,59(6)	10,29(3)
c (Å)	14,83(8)	17,3(1)	23,671(5)	22,575(3)	25,581(2)	14,98(1)	26,03(4)	11,41(1)	26,00(3)	24,08(1)	18,69(5)	15,54(8)	11,27(3)	27,48(7)
α (grad)	76, 9(1)	90	90	90	65,67(1)	90	90	90	90	90	97,80(5)	84,98(9)	90	90
β (grad)	70,5(1)	92,6(1)	119,96(1)	96,64(1)	83,64(1)	102,2(1)	106,55(2)	90	91,68(2)	90	101,65(5)	63,42(9)	90	101,7(5)
γ (grad)	71,3(1)	90	90	90	74,62(1)	90	90	90	90	90	114,87(4)	71,72(9)	90	90
V(Å^3)	2210,6(2)	2314(2)	13930(1)	6096(2)	7001(1)	3848,0(5)	10544(3)	9787,3(1)	8311(1)	13976(10)	3222(19)	2750(3)	8585(4)	9116(1)
R_1, wR_2 [I>2σ(I)]	0,0398, 0,1089	0,0440, 0,0919	0,0623, 0,1793	0,0444, 0,1044	0,0695, 0,1547	0,0604, 0,1629	0,0493, 0,1349	0,0536, 0,1432	0,0617, 0,1457	0,0457, 0,1060	0,1457, 0,1060	0,0566, 0,1219	0,0895, 0,2239	0,0815, 0,1829
#	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**
Gr. sp.	*P*-1	*P*-1	$P2_1/n$	$P2_1/n$	*P*6/*mcc*	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*R*-3	*P*-1	*P*-1	*P*-1
a (Å)	15,21(2)	15,139(3)	12,017(3)	14,939(3)	38,845(8)	18,42(3)	16,22(2)	16,2(1)	16,18(5)	16,22(5)	37,39(6)	15,3(2)	15,5(2)	15,73(6)
b(Å)	19,15(3)	15,192(3)	31,488(7)	26,386(5)	38,845(8)	19,44(3)	18,445(2)	18,5(1)	18,42(6)	18,47(6)	37,39(6)	23,09(2)	23,10(3)	22,86(8)
c (Å)	20,09(3)	22,806(5)	19,082(7)	15,755(3)	24,824(7)	20,30(3)	28,537(3)	27,36(2)	28,45(8)	28,51(9)	25,58(4)	24,29(2)	24,51(3)	24,56(9)
α (grad)	97,01(4)	76,867(4)	90,00	90	90	102,01(2)	106,928(2)	73,3(1)	106,9(9)	107,05(5)	90	78,06(3)	78,39(3)	78,16(1)
β (grad)	100,77(4)	74,721(4)	100,46(3)	95,29(3)	90	108,79(2)	92,016(2)	89,28(2)	91,99(8)	91,85(5)	90	81,83(3)	81,55(4)	81,10(1)
γ (grad)	108,76(4)	62,049(3)	90,00	90	120	110,86(2)	109,82 (2)	68,9(1)	109,9(8)	109,97(5)	120	76,57(3)	77,19(4)	78,16(1)
V(Å^3)	5341(14)	4437(2)	7100,4(4)	6184(2)	32439(1)	5990(14)	7598(2)	7325(9)	7542(4)	7595(4)	30974(1)	8133(14)	8311(16)	8408(5)
R_1, wR_2 [I>2σ(I)]	0,0744, 0,1538	0,1020, 0,2354	0,0922, 0,2684	0,0648, 0,1299	0,0667, 0,1942	0,0587, 0,1345	0,0851, 0,1975	0,0483, 0,0932	0,1235, 0,2795	0,1224, 0,2954	0,0623, 0,1638	0,0783, 0,2076	0,0824, 0,2224	0,0581, 0,1493
#	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**
Gr. sp.	*R*-3	*P*-1	*P*-1	*P*-1	*P*-1	*R*-3	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Pbca*	$P2_1/c$
a (Å)	37,438(6)	15,418(1)	15,699(4)	15,71(1)	16,14(9)	33,33(1)	17,1(2)	17,05(1)	16,89 (2)	17,1(1)	16,94(3)	17,00(3)	16,98(12)	17,05(5)
b(Å)	37,438(6)	23,135(1)	22,827(6)	22,83(2)	21,2(1)	33,33(1)	26,6(2)	26,71(3)	26,45(4)	26,4(1)	26,41(5)	26,39(5)	26,55(16)	18,78(3)
c (Å)	25,744(4)	24,365(1)	24,502(7)	24,52(2)	27,5(2)	30,21(1)	35,19(1)	35,25(3)	35,40(5)	35,63(2)	35,46(6)	35,34(7)	35,44(3)	36,7(11)
α (grad)	90	78,522(1)	78,730(5)	78,380(2)	98,61(2)	90	90	90	90	90	90	90	90	90
β (grad)	90	82,093(1)	81,150(5)	81,161(2)	93,3(1)	120	90	90	90,41(4)	90,3(2	90,45(3)	90,03(4)	90	92,35(3)
γ (grad)	120	76,833(1)	78,123(5)	78,225(2)	110(1)	90	90	90	90	90	90	90	90	90
V(Å^3)	31249(11)	8254,5(6)	8367(4)	8375(1)	8686(1)	29062(2)	16022(3)	16052(2)	15814(4)	16096(16)	15876(5)	15860(5)	15979(2)	11737(5)
R_1, wR_2 [I>2σ(I)]	0,0533, 0,1430	0,0598, 0,1543	0,0819, 0,2022	0,0613, 0,1386	0,0844, 0,1915	0,0738, 0,1953	0,0554, 0,1034		0,0971, 0,2268	0,0819, 0,1745	0,0816, 0,1911	0,0756, 0,1495	0,0856, 0,2438	0,0931, 0,2734

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

Chapter 3 represents the description of 15 new homometallic Fe^{III} coordination clusters (**2-16**) and three cluster-based coordination polymers (**17-19**). Compounds were obtained by the interaction of $[Fe_3O(O_2CR)_6(H_2O)_3]^+$ (R = $(Me)_3C$ (**1**) [12], $(Me)_2CH$ (**A**), $[Fe_6O_2(OH)_2(piv)_{12}]$ (**B**) or $[Fe_{14}O_{10}(OH)_4(piv)_{18}]$ (**C**) precursors with *N,O*-organic ligands such as 2,4,6-tripyridyl-s-triazine (tpt), 2,2′-dipyridylamine (dpa), 4,4′-bipyridine (4,4′-bpy), 2,2′-bipyrimidine (2,2′-bpm), triethanolamine ($teaH_3$), *N*-methyldiethanolamine ($mdeaH_2$), butyldiethanolamine ($bdeaH_2$), *N*,*N*,*N*,*N*-tetrakis(2-hydroxyethyl)ethylenediamine ($tedaH_4$), 1,1,1-tris(hydroxymethyl)ethane ($thmeH_3$), 1,2-bis(4-pyridyl)ethane (pyEt), s-triazine (str), hexamethylenetetramine (hmta) at temperatures ranging from room temperature to solvothermal heating in different media. All compounds were structurally and magnetically characterized.

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

A series of homometallic Fe^{III} coordination compounds with $\{Fe_2\}$ (**2**), $\{Fe_4\}$ (**3-5**) [13], $\{Fe_6\}$ (**6**) and $\{Fe_7\}$ (**7**) [14] cores were synthesized by the reaction of trinuclear (**1, A**) or hexanuclear (**B**) carboxylate precursors with *N*,*O*-containing organic ligands such as tpt, dpa, 2,2′-bpm and str under various reaction conditions (Figure 1).

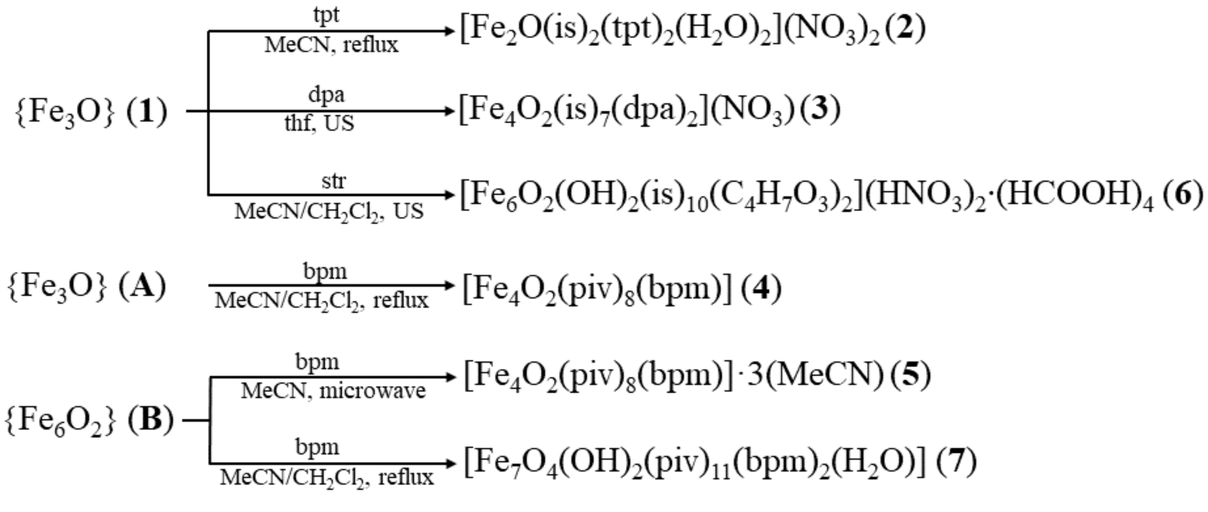


Fig. 1. Schematic syntheses of **2-7**.

The IR spectra of **1**–**7** display strong peaks of carboxylate groups in the region of 1578–1533 cm^{-1} (asymmetric stretching vibrations) and 1479–1397 cm^{-1} (symmetric stretching vibrations). The C–H asymmetric and symmetric stretching vibrations of carboxylates are observed in the range of 2973–2869 cm^{-1}. In the case of complexes **2**, **4**, **5** and **7,** the C=N stretching vibrations of aromatic rings in tpt (**2**) and bpm (**4**, **5**, **7**) ligands overlap with the asymmetric stretching bands of the carboxylates.

A single-crystal X-ray analysis showed that centrosymmetric binuclear complex **2** consists of two antiparallel $[\mathrm{Fe(is)(tpt)(H_2O)}]^{2+}$ units interconnected via sandwiched between them μ_2-O^{2-} bridge. Tetranuclear clusters **3**-**5** comprise similar central butterfly-like $\{\mathrm{Fe_4(\mu_3\text{-}O)_2}\}^{8+}$ core. The metal atoms in the core additionally bridged by seven isobutyrate (**3**) or eight pivalate (**4**, **5**) groups and two molecules of 2,2′-dpa (**3**) or one molecule of bpm (**4**, **5**) chelating the peripheral $\mathrm{Fe^{III}}$ centers. Clusters **4** (Figure 2) and **5** have the same composition but differ by the function of one pivalate group, the connectivity of the ligands, and the solvent molecules. Hexanuclear cluster **6** consists of two identical triangular $\mathrm{Fe_3(\mu_3\text{-}O)}$ fragments, where three iron(III) ions are held by μ_3-O^{2-} group. These fragments are interconnected through two bridging μ_2-OH^{-} groups. Additionally, iron atoms in each triangle are linked by three carboxylate groups and one 2-hydroxyisobutyrate ligand.

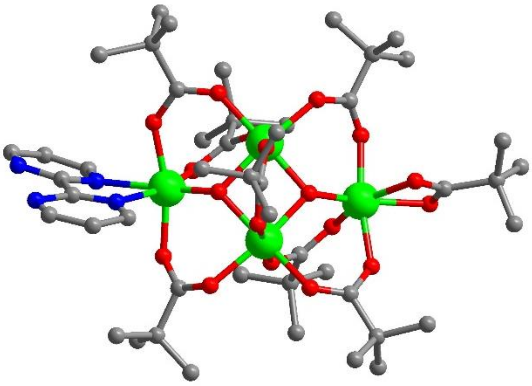


Fig. 2. Structure of **4.**

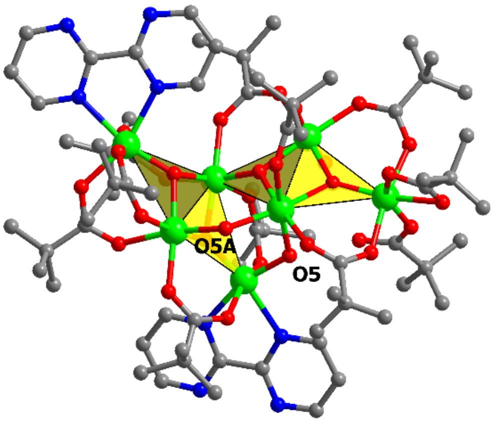


Fig. 3. The structure of **7**.

Complex **7** contains two interlocked tetranuclear $[\mathrm{Fe_4(\mu_3\text{-}O)_2}]$ butterfly-type cores composed of two edge-sharing $\{\mathrm{Fe_3(\mu_3\text{-}O)}\}$ triangles (Figure 3), crucial building blocks for the assembly of frustrated spin structures. These tetranuclear groups share a common iron atom, which serves as a “wingtip” site for the first $\{\mathrm{Fe_4O_2}\}$ group and occupies the “body” position in the other one. The two $\{\mathrm{Fe_4(\mu_3\text{-}O)_2}\}$ cores are additionally bridged by two protonated μ_2-O sites (O5/O5A).

The magnetic susceptibilities data of **4**, **5** and **7** revealed the presence of strong antiferromagnetic interaction between $\mathrm{Fe^{III}}$ ions in the examined compounds. The experimental data gave the following values of the exchange parameters for butterfly-like clusters: $J_{wb} = -72.2$ $\mathrm{cm^{-1}}$ (**4**) and $J_{wb} = -88.7$ $\mathrm{cm^{-1}}$ (**5**) for wing…body interactions. In **7**, two dominant exchange pathways of the $\{\mathrm{Fe_7O_6}\}$ core (J_1: Fe–(μ_3-O)–Fe; J_2: Fe–(μ_3-O)$_2$–Fe) have been taking into account to give $J_1 = 49.0$ $\mathrm{cm^{-1}}$ and $J_2 = 22.5$ $\mathrm{cm^{-1}}$ ($g = 1.995$) [15].

Using multitopic amino/alcohol-based ligands (teaH$_3$, mdeaH$_2$, bdeaH$_2$, tedaH$_4$, thmeH$_3$) in the reaction of precursor (**1**) or (**C**) with sodium azide or sodium dicyanamide (sca) a series of polynuclear oxo-, hydroxo-bridged compounds with {Fe$_6$} (**8**) [16], {Fe$_8$} (**9-11**) [12], {Fe$_{12}$} (**12-14**) [16] and {Fe$_{22}$} (**15**, **16**) [16] cores has been synthesized and characterized (Figure 4).

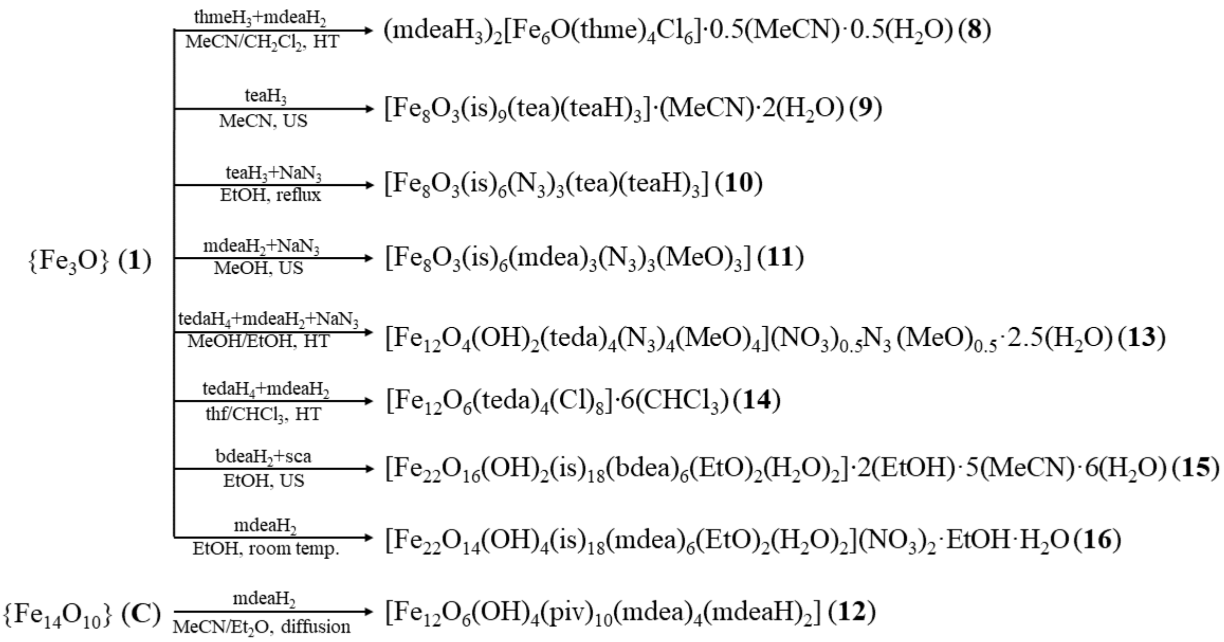
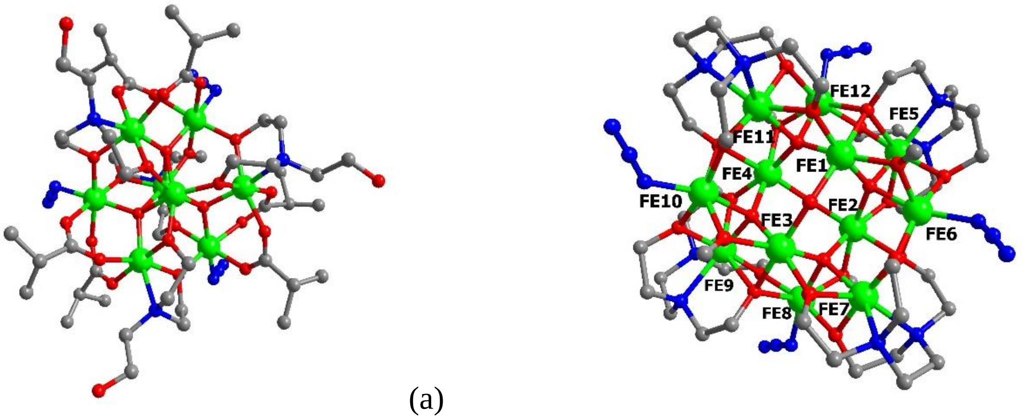


Fig. 4. Schematic syntheses of **8-16**.

The IR-spectra of **8-16** show the C–H asymmetric and symmetric stretching vibrations that were observed in the region 2969–2856 cm^{-1} for thme^{2-} and mdea^{2-} groups (**8**), methyl, methylene -(CH$_2$)- and methyne >(CH)- groups of carboxylate and polyalcohol ligands (**9-11**, **15** and **16**). Strong peaks of the coordinated asymmetric and symmetric stretching vibrations of carboxylate groups for **9-12, 15** and **16** clusters are observed in the region 1632–1542 cm^{-1} and 1429–1413 cm^{-1}, respectively.

The single-crystal X-ray analyses of a series of octanuclear clusters **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 the cubic space group *Pa*-3, whereas compound **11** in the triclinic space group *P*-1. Their cores comprise two central axial Fe^{III} ions bridged by three μ_4-O^{2-}, and each μ_4-O^{2-} furthermore bridges two peripheral Fe^{III} ions in pair, resulting in one of the three "blades" of the propeller. Figure 5a shows the molecular structure of cluster **10**. The central pair of iron ions in **9**–**11** represents the axle of the propeller with Fe···Fe distances of 2.83 Å (**9** and **10**) and 2.79 Å (**11**).

Dodecanuclear cluster **12** crystallizes in the triclinic space group *P*-1 and has C_i molecular symmetry. Twelve iron atoms form six edge-sharing {Fe$_3$O} non-equilateral triangles with a central μ_3-oxygen. The Fe···Fe distances in triangles are in the range from 2.941(2) to 3.571(2) Å.



(a) (b)

Fig. 5. Structure of **10** (a) and **13** (b).

Two other dodecanuclear clusters **13** and **14** crystallizes in the tetragonal space group *P*4 and in the monoclinic space group *C*2/*c*, respectively, and have a saddle-like non-coplanar $\{Fe_{12}\}$ ring arrangement. The core structure of **13** (Figure 5b) and **14** can be considered as the arrangement of two near-planar and about parallel $\{Fe_6\}$ areas. In **13**, Fe^{III} atoms are bridged by four μ_4-O^{2-} ions, two hydroxyl μ_2-OH^- groups and four teda^{4-} ligands, whereas four N_3^- and four MeO^- groups are completed the coordination spheres of Fe^{III} atoms. Twelve Fe^{III} atoms in **14** are linked via four μ_4-O^{2-} ions, and four teda^{4-} ligands except hydroxyl and methoxy groups that are replaced by μ_2-O^{2-} and μ_2-Cl^- ligands, respectively, to give $[Fe_{12}O_6(teda)_4(Cl)_4]^{4+}$ unit with a $\{Fe_{12}O_6\}^{24+}$ core.

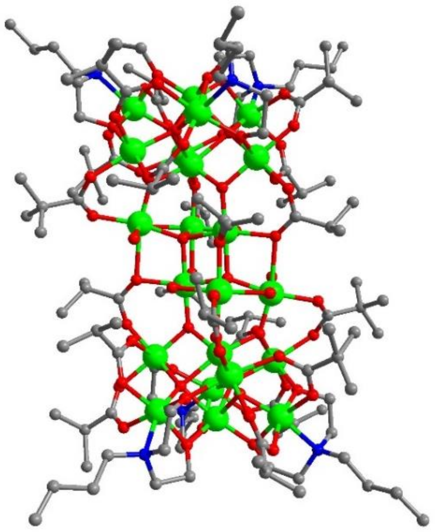


Fig. 6. Structure of **15**.

Two docosanuclear complexes **15** and **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 that form a $\{Fe_{22}(\mu_4\text{-}O)_8(\mu_3\text{-}O)_6(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_2(\mu_2\text{-}EtO)_2\}$ core in **15**, and a $\{Fe_{22}(\mu_4\text{-}O)_8(\mu_3\text{-}O)_6(\mu_2\text{-}OH)_4(\mu_2\text{-}EtO)_2\}$ core in **16**. Additional bridges between Fe^{III} atoms are provided by 18 isobutyrates and six bdea^{2-} (**15**) (Figure 6) or mdea^{2-} (**16**) ligands that are situated at the periphery of the molecules. A terminal H_2O ligand completes the coordination sphere of two Fe atoms.

The magnetic properties of clusters **8**-**16** have been analyzed. Magnetic studies revealed dominant antiferromagnetic exchange interactions between the six Fe^{III} centers in **8** (the value

$\chi_m T$ is 11.13 cm^3 K mol^{-1} at 0.1 T, which is well-below the spin-only value for six high-spin Fe^{III} centers: 26.26 cm^3 K mol^{-1}, S_{eff} = 5/2, g_{iso} = 2). Due to the similar structures of octanuclear clusters **9**–**11**, the simulated exchange parameters slightly differ for these clusters. The total number of exchange interaction parameters between 8 iron centers equals 28. The semi-empirical computer program *wxJFinder* [15] that predicts the exchange energies for the Fe-O-Fe pathways has been used to reduce the number of identical parameters based on structural information. Thus, all compounds can be described by the effective Hamiltonians that contain five independent exchange parameters J_i as depicted in Figure 7. The resulting best fit parameters are shown in Table 2. 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.

Table 2. Parameters obtained from magnetochemical analysis of **9-11**

	9	**10**	**11**
g_{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 / 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 / cm^{-1}	*NA*	*NA*	–7.5
ρ / %	0.58	0.11	0.19
SQ / % [a]	0.6	1.5	1.6

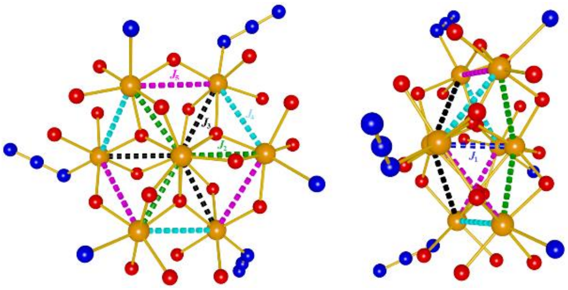


Fig. 7. Coupling scheme of **9**–**11** using the example of compound **11**: (left) front view, (right) side view.

The magnetic properties of {Fe_{12}} (**13**, **14**) and {Fe_{22}} (**15, 16**) compounds are characterized by dominant antiferromagnetic exchange interactions between the Fe^{III} centers of each compound: at 290 K the $\chi_m T$ = 22.40 (**13**), 24.30 (**14**), 32.93 (**15**) and 32.56 cm^3 K mol^{-1} (**16**) at 0.1 T, which are distinctly below the spin-only values for 12 or 22 non-interacting high-spin Fe^{III} centers equal to 52.52 and 96.29 cm^3 K mol^{-1}, respectively. At 2.0 K, they reach a value of 0.98 for **15** and 0.37 cm^3 K mol^{-1} for **16**.

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

Crystal engineering approaches for the construction of coordination polymers (CPs) based on clusters have been used. These approaches involve the use of clusters as ”nodes” and exo-bidentate organic ligands as ”linkers”. Bridging ligands occupy apical positions in the cluster replacing axillary ligands (H_2O, EtO^- *etc.*), and extending to multidimensional CPs. Thus, 1D (**17**, **18** [13]) and 3D (**19**) [17] cluster-based coordination polymers were obtained as a results of interaction of precursors **A** and **B** with pyEt, hmta and 4,4′-bpy ligands (Figure 8).

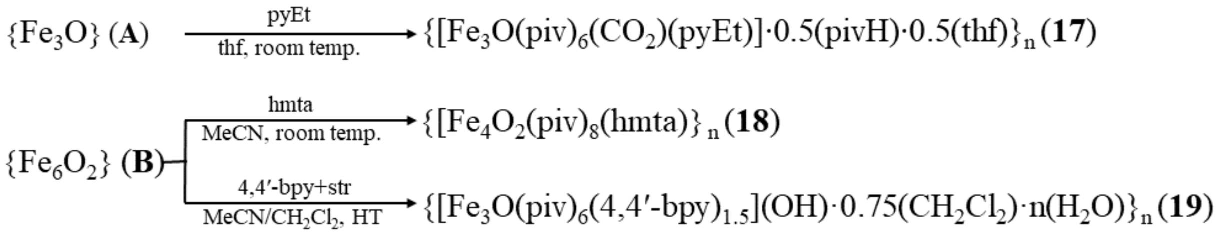
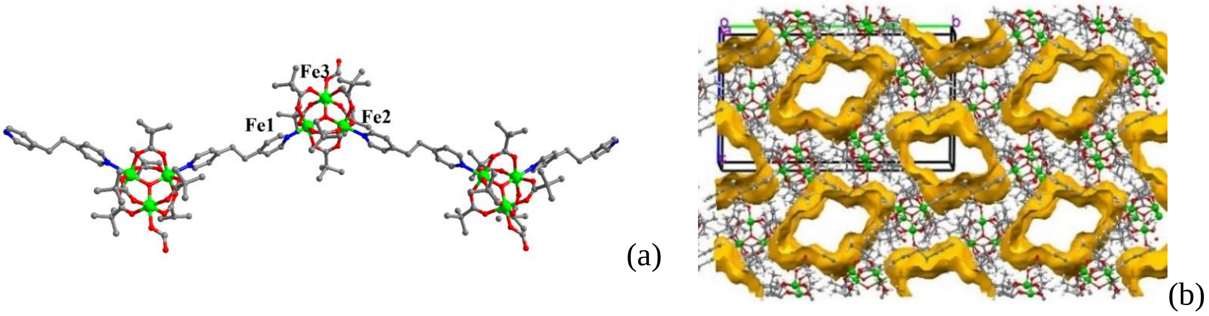


Fig. 8. Schematic synthesis of **17-19**.

The IR spectra of **17-19** showed the C–H stretching vibrations of pivalate groups appear in the region 2964–2868 cm^{-1}. Strong peaks of asymmetric and symmetric vibrations of the coordinated carboxylate groups are observed in the region 1582–1544 cm^{-1} and 1457–1415 cm^{-1}, respectively. The C=N stretching vibration of aromatic rings in **17** was observed at 1714 cm^{-1}. Several well-separated strong and sharp bands at 1250, 1056, 1024, and 987 cm^{-1} in **18** can be assigned to the C–N stretching modes of the coordinated hmta ligand.

The TGA/DTA curves of coordination polymers **18** and **19** showed that **18** is stable up to 200°C and **19** losses its weight loss as soon as heating begins. Then they decompose step by step reaching temperature 550°C (**18**) and 590°C (**19**).

A single crystal X-ray analysis revealed that **17** crystallizes in the monoclinic space group $P2_1/n$. Complex **17** consists of the trinuclear [Fe$_3$O(O$_2$CCMe$_3$)$_6$(HCO$_2$)] clusters bridged by pyEt into 1D coordination polymer of „zig-zag”- type chain (Figure 9a). Interestingly, the packing of coordination polymer **17** results in tube-like channels of diameter *ca.* 1 nm shown in Figure 9b.



(a) (b)

Fig. 9. A view of a 1D chain (a) and tube-like channels of diameter *ca*. 1 nm (b) in **17**.

The coordination polymer **18** consists of [Fe$_4$O$_2$(piv)$_8$] cluster moieties that are linked into infinite zigzag chains by the bridging hmta ligand. Four iron atoms are joined into a butterfly {Fe$_4$(μ_3-O)$_2$}$^{8+}$ core by two μ_3-oxygen atoms and seven bidentate bridging piv$^-$ ligands.

The structure of coordination polymer **19** comprises two types of identical but symmetry-independent [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.

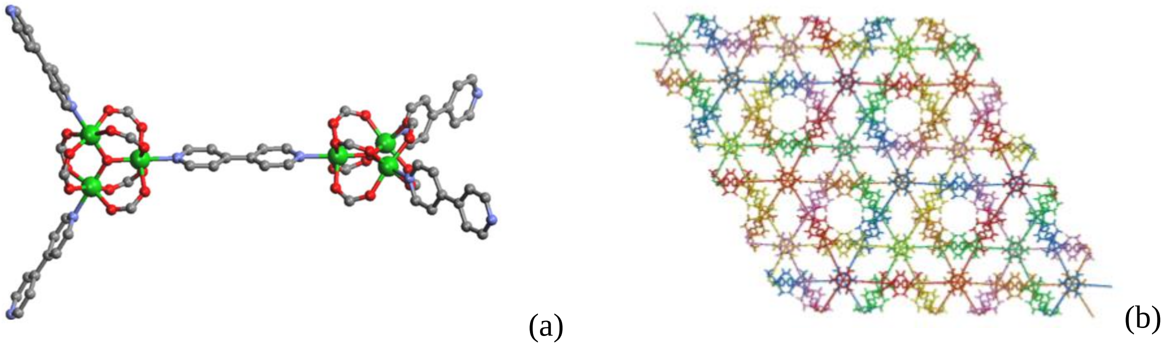

(a) (b)

Fig. 10. Four-connected binodal building block (a) and the 6-fold interpenetration of (8,3)-c networks (b) in **19**.

In **19**, neighboring 2-fold symmetry related clusters connected by 4,4′-bpy are approximately coplanar and the planes through their Fe_3O 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 10a). Such building blocks constitute a rare binodal uniform (8,3)-c (**etc**) network, Figure 10b.

Magnetic studies of 1D coordination polymer **18** indicate the presence of strong antiferromagnetic interactions in the tetranuclear cluster between body-body Fe^{III} ions with J_{bb} equal to -22 cm^{-1}, whereas the interactions between Fe-containing clusters through the hmta ligand are negligible. In the cluster-based 3D coordination polymer **19** magnetic measurements showed that both inter- and intracluster exchange interactions are antiferromagnetic: the parameters $J_1 = -0.1$ cm^{-1}, $J_2 = -27$ cm^{-1} characterize the exchange interactions through the central μ_3-O within $\{Fe_3O\}$ unit and $\lambda_{mf} = -0.609$ mol cm^{-3} *via* the 4,4′-bpy linkers.

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

In **Chapter 4** a series heterometallic wheels $\{Fe_6Dy_3\}$ (**20**), $\{Fe_6Ln_4\}$ (M = Dy (**21**), Gd (**22**), Ho (**23**), Y (**24**)), $\{Fe_{18}Ln_6\}$ (M = Dy (**25**, **26**), Gd (**27**), Tb (**28**), Sm (**29**), Eu (**30**), Ho (**31**), Y (**32**), Dy(**33**), Nd(**34**)) [18] and condensed clusters $\{Fe_4Dy_2\}$ (M= Dy (**35**), Gd (**36**), Tb (**37**), Y (**38**), Er (**39**), Tm (**40**)) $\{Fe_3MnDy_2\}$ (**41**), $\{Fe_7Dy_4\}$ (**42**) were synthesized from the reaction of precursor **1** or **B** with the different combination of organic ligands such as teaH$_3$, bdeaH$_2$, sodium azide or sodium dicyanamide (sca) under reflux or ultrasonic irradiation in MeOH/MeCN or EtOH/MeOH solutions (Figure 11). Two different series were structurally and magnetically characterized.

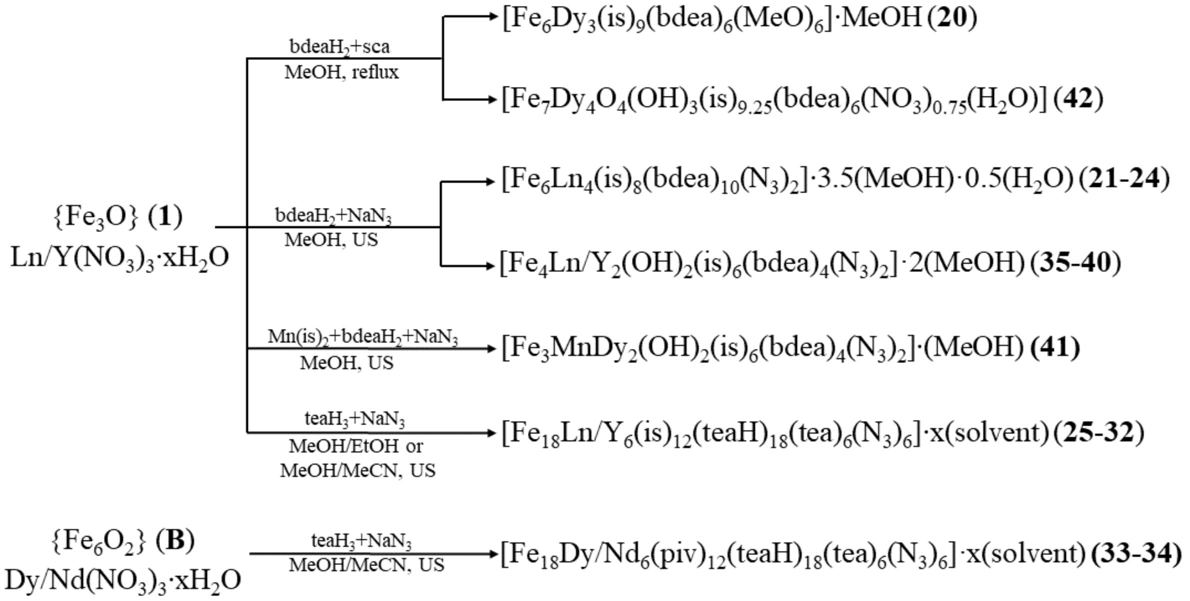


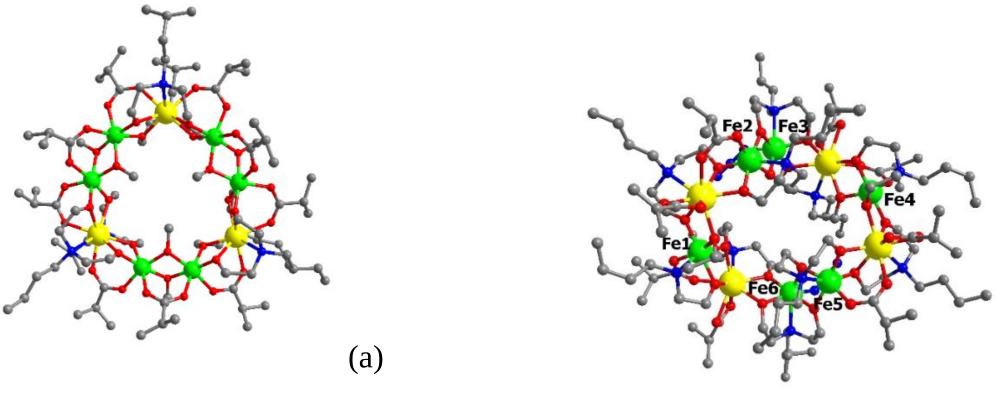
Fig. 11. Schematic synthesis of **20**-**42**.

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

The IR spectra of **20-32** and **34** display the O–H stretching vibration in the region 3438–3416 cm^{-1} caused by the presence of methanol molecules (**20-24**), uncoordinated hydroxyl groups of teaH^{2-} and solvent EtOH or H_2O 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 cm^{-1} and 1427–1411 cm^{-1}, respectively. The C–H asymmetric and symmetric stretching vibrations of methyl, methylene -(CH_2)- and methyne >(CH)- groups of carboxylates and polyalcohol ligands are observed in the range of 2964–2860 cm^{-1}.

TGA/DTA curves display that the molecular wheel **20** remain stable before the temperature of 180ºC, whereas **21-24** up to 220ºC and **25-32, 34** up to 190ºC. The loss of solvent molecules of all compounds took place in the range of 50-160ºC. The decomposition of the organic components occurs in the temperature range of 180-480ºC for **20**, 220 - 550ºC for **21-24** and 190 - 800ºC for **25-32, 34**, giving the residual weight suggests the final product of iron and lanthanide oxides. According to the TGA studies can be concluded that coordination wheels **21-24** are thermally more stable compare to others.

A single crystal X-ray analysis revealed that compound **20** crystallizes in the space group *P*-1. 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 12a) and may be considered as a 0D cyclic polymers build-up from three identical units.

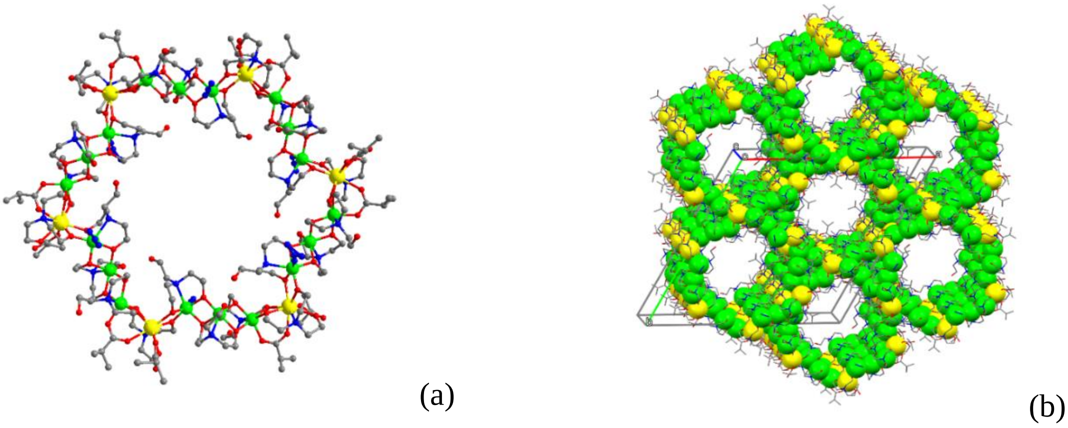


(a) (b)

Fig. 12. Structure of **20** (a) and **21** (b).

Compounds **21-24** are isomorphs, crystallize in the space group *P*-1 and have their own C_2 molecular symmetry, thus comprise two identical units. They·are wheel-shaped decanuclear clusters that built from six Fe^{III} and four M^{III} ions, which are linked by four bridging carboxylates and ten $bdea^{2-}$ ligands into a saddle–like structure with a cavity shown in Figure 12b. Four remaining isobutyrates coordinate in chelating mode to M^{III} ions. The coordination sphere of two Fe^{III} ions is completed by a monodentate coordination of azide groups.

X-ray analysis showed that **26-28, 30-33** clusters crystallize in the space group *P*-1 having their own C_i molecular symmetry. Compounds **25, 29** and **34** crystallize in the *R*-3 space group and clusters have their own C_{3i} symmetry. All compounds consist of six identical $\{Fe_3M\}$ building units organized in a $\{Fe_{18}M_6\}$ cyclic 0D structure (Figure 13a).



(a) (b)

Fig. 13. Structure of **26** (a). Formation of infinite channels in **25, 29** and **34** (b).

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, while the external diameter of these ultra-large wheels is *ca.* 3.7 nm.

The crystal structures of ultra-large wheels **25, 29** and **34** display infinite channels formation parallel to the crystal *c* axis filled by solvents molecules (Figure 13b).

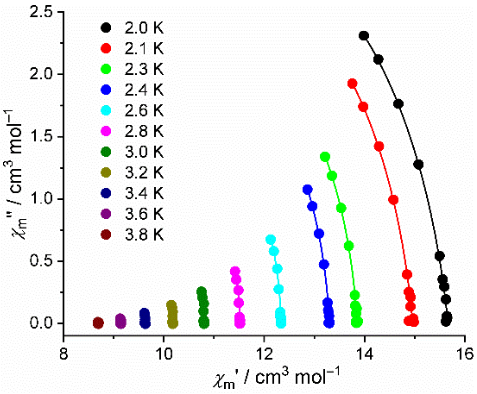


Fig. 14. Cole-Cole plot of out-of-phase *vs.* in-phase molar magnetic susceptibility of **20**.

The magnetic properties of **20-32** were investigated by both dc and ac measurements and revealed predominant strong antiferromagnetic interactions within all compounds. For {Fe$_6$Dy$_3$} (**20**) [19], the value of χ_mT is 63.25 cm^3 K mol^{-1} at 290 K which is below the range 65.29–68.41 cm^3 K mol^{-1} expected for six Fe^{III} and three Dy^{III} non-interacting centers. Ac measurements of **20** show out-of-phase magnetic susceptibility χ_m'' signals up to 3.6 K at zero bias field (Figure 14) with an effective energy barrier U_{eff} = (3.6 ± 0.2) cm^{-1}, and τ_0 = (4.9 ± 0.6)×10^{-6} s. For the heterometallic decanuclear {Fe$_6$Y$_4$} wheel (**24**), the χ_mT *vs.* T curve is characterized by a value of 21.63 cm^3 K mol^{-1} at 290 K, and continuously decreases by lowering temperature to 6.61 cm^3 K mol^{-1} at 2.0 K. The diamagnetic Y^{III} centers are exchanged by Gd^{III} centers, i.e. nearly pure spin – 7/2 centers ($g \approx 1.993$ [19]), in **22**, χ_mT = 53.86 cm^3 K mol^{-1} is well below 57.55 cm^3 K mol^{-1} at 290 K. The other two compounds of this series (**21** and **23**) reveal a similar behavior indicating predominant antiferromagnetic exchange interactions with χ_mT 78.30–82.46 cm^3 K mol^{-1} and 79.33–81.41 cm^3 K mol^{-1} at room temperature, respectively. Ac measurements of **21-24** show out-of-phase magnetic susceptibility χ_m'' signals only for **21** up to 5.5 K at zero bias field.

In heterometallic {Fe$_{18}$Ln$_6$} wheels **(25-32)** all observations indicate predominant antiferromagnetic exchange interactions within each Fe$_3$ unit (S = 5/2). The χ_mT values at 290 K of the compounds are ca. 25–30 cm^3 K mol^{-1} below the expected values for the respective non-interacting centers of a {Fe$_{18}$Ln$_6$} ring (**25**: 140.5 cm^3 K mol^{-1}, **27**: 101.2 cm^3 K mol^{-1}, **28**: 117.3 cm^3 K mol^{-1}, **29**: 57.4 cm^3 K mol^{-1}, **30**: 58.9 cm^3 K mol^{-1}, **31**: 127.2 cm^3 K mol^{-1}, **32**: 47.9 cm^3 K mol^{-1}). The analysis of **32** (comprising diamagnetic Y^{III} centers instead of lanthanides) reveals the magnetism of the Fe^{III} constituents. The best fit reproduces the experimental data, yielding g = 2.0 and the exchange parameter $J_{Fe3} = -12.4$ cm^{-1} for both intratrimer interactions as well as $\lambda_{mf} = -0.412$ mol cm^{-3}, that is, $zJ_{inter} = -0.21$ cm^{-1}. Additionally, the χ_mT 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 addition to the dc measurements, **25–32** were also tested in an ac magnetic field in absence of a static field. Only wheels **26** and **28** show an out-of-phase signal and thus slow relaxation at $T \leq 2.3$ K and $T \leq 2.6$ K, respectively, (Figure 15a, b).

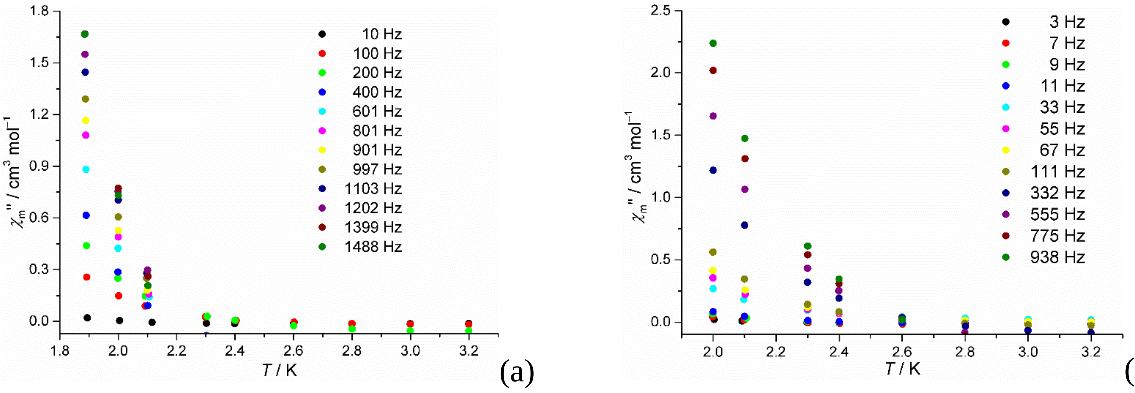


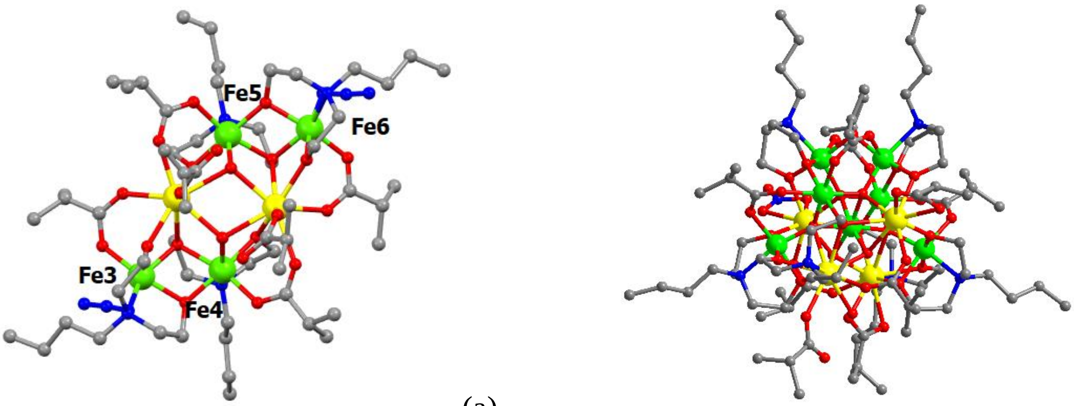
Fig. 15. Temperature dependence of out-of-phase magnetic susceptibility χ''_m of **26** (a) and **28** (b) in absence of a static field *B*.

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

The IR spectra **35-42** revealed strong peaks in the region 1588–1558 cm^{-1} and 1430–1407 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 cm^{-1}. In the range of 2962 – 2861 cm^{-1} appear the C–H asymmetric and symmetric stretching vibrations of methyl, methylene and methyne groups of carboxylates and butyldiethanolamine ligands. An intensive peak at 2059 (for **41**) and 2061 cm^{-1} (for **35-40**) corresponds to N≡N stretching vibrations of azide ligands.

TGA/DTA curves of clusters **35-41** showed that all compounds display similar thermal decomposition behaviour and molecular clusters remain stable up to the temperature of 150ºC releasing solvent molecules before 150 ºC. On further heating, the clusters start to decompose in several weakly resolved steps until 500 °C and lose organic ligands and azides (found: 64.30%; calcd: 67.66%) with residual weight of 35.7% (calcd: 35.15%).

Single-crystal X-ray diffraction measurements revealed that clusters $[Fe_4M_2(\mu_3\text{-}OH)_2(is)_6(bdea)_4(N_3)_2]\cdot MeOH$ (M= Dy (**35**), Gd (**36**), Tb (**37**), Y (**38**), Er (**39**), Tm (**40**), Fe_3Mn (**41**·2MeOH)) have a similar molecular structure, but crystallize in different space groups. Clusters **35, 36** and **41** crystallize in the space group *Pbca*, while **37-40** crystallize in the space group $P2_1/c$. All clusters **35-40** built up from four Fe^{III} and two M^{III} ions that are connected by the six is^- and four $bdea^{2-}$ ligands (Figure 16a). Cluster **41** consists of $\{Fe_3MnDy_2\}$ array. The core cluster structure in **42** consists of seven Fe^{III} ions and four Dy^{III} ions interlinked *via* four μ_4-O and three μ_3-OH groups, six is^- and six $bdea^{2-}$ ligands forming a globe-like structure with no symmetry elements (Figure 16b). The coordination environment of Dy^{III} ions is completed by the coordination of two chelating carboxylate and one nitrate groups, one monodentate aqua and one monodentate carboxylate groups. The coordination modes of isobutyrates fall into three categories: *i*) coordination in a chelating mode to three Dy^{III} ions, *ii*) coordination to one Fe^{III} and one Dy^{III} ion in a *syn,syn*–η^1:η^1:μ_2 bridging mode, *iii*) monodentate coordination to a Dy^{III} ion.



(a) (b)

Fig. 16. Molecular structure of **35** (a) and **42** (b).

Variable temperature dc magnetic susceptibility data were collected for compounds $\{Fe_4Dy_2\}$ (**35**), $\{Fe_4Gd_2\}$ (**36**), $\{Fe_4Tb_2\}$ (**37**), $\{Fe_4Y_2\}$ (**38**), $\{Fe_4Er_2\}$ (**39**), $\{Fe_4Tm_2\}$ (**40**) (Figure 17a). The $\chi_m T$ value of **38** is 14.01 cm^3 K mol^{-1} at 290 K, then it continuously decreases by lowering temperature and almost vanishes at 2.0 K (0.04 cm^3 K mol^{-1}). Comparison of the value 14.01 cm^3 K mol^{-1} at 290 K for **38** to the expected 17.51 cm^3 K mol^{-1} value for four non–interacting Fe^{III} centers (S_{Fe} = 5/2, g = 2) reveals dominant antiferromagnetic exchange interactions within the compound. This series also contains four other compounds which differ in lanthanide ions: Ln^{III} = Dy (**35**), Gd (**36**), Tb (**37**), Er (**39**), Tm (**40**) and Dy (**41**). For all compounds the $\chi_m T$ values at 290 K (41.16 cm^3 K mol^{-1} (**35**), 29.24 cm^3 K mol^{-1} (**36**), 37.15 cm^3 K mol^{-1} (**37**), 36.37 cm^3 K mol^{-1} (**39**), 27.32 cm^3 K mol^{-1} (**40**), 41.97 cm^3 K mol^{-1} (**41**)) are lower than the respective values expected for four Fe^{III} and two Ln^{III} non–interacting centers: 43.53–45.61 cm^3 K mol^{-1}, 33.15 cm^3 K mol^{-1}, 41.04–41.53 cm^3 K mol^{-1}, 39.61–40.08 cm^3 K mol^{-1}, 31.57 cm^3 K mol^{-1} and 42.15–44.36 cm^3 K mol^{-1} [19]. Therefore, the exchange interactions between the centers of the compounds are predominantly antiferromagnetic. Ac measurements show out-of-phase magnetic susceptibility χ_m'' signals only for **35** up to 5.5 K (see Figure 17b) and for **41** up to 4.4 K at zero bias field.

Dc magnetic susceptibility data of $\{Fe_7Dy_4\}$ **42** revealed both predominant antiferromagnetic and additionally weaker ferromagnetic exchange interactions. The $\chi_m T$ *vs*. T curves exhibit values 66.42 cm^3 K mol^{-1} and 65.42 cm^3 K mol^{-1} at 290 K for 0.1 and 1.0 Tesla, which are well below the range 82.68–86.84 cm^3 K mol^{-1} that is expected for seven Fe^{III} and four

Dy^{III} non-interacting centres. Cooling beyond 50 K reveals maxima at both applied magnetic fields indicating the presence of ferromagnetic exchange interaction pathways (Figure 17c). Ac measurements show out-of-phase magnetic susceptibility χ_m'' signals up to 12 K at zero bias field (Figure 17d) with an effective energy barrier U_{eff} = (15.0 ± 0.2) cm^{-1}, and an attempt time of τ_0 = (3.7 ± 0.2)×10^{-6} s.

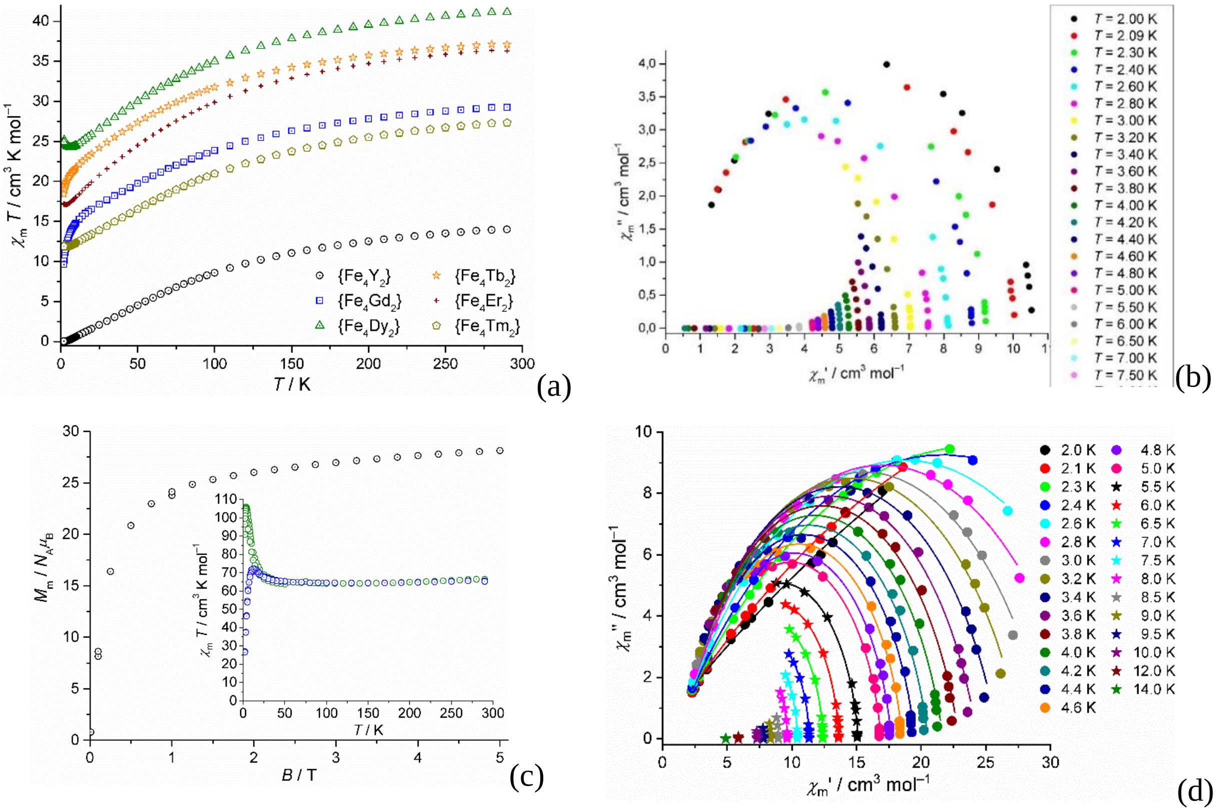


Fig. 17. Dc magnetic data of {Fe$_4$M$_2$} (**35-40**) (a) and {Fe$_7$Dy$_4$} (**42**) (c): temperature dependence of $\chi_m T$ at 0.1 Tesla. Ac magnetic data of {Fe$_4$Dy$_2$} (**35**) (b) and {Fe$_7$Dy$_4$} (**42**) (d).

OVERALL CONCLUSIONS AND RECOMMENDATIONS

The *solved scientific problem* consists in establishment of optimal and effective synthetic conditions for the obtaining of 42 new homo- and heterometallic Fe^{III}/Fe^{III}-4f coordination clusters and cluster-based coordination polymers with porosity, using pre-synthesized tri-, hexa- and tetradecanuclear oxo-carboxylate precursors and *N*-based and *O*-based organic ligands.

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

1. An extensive series of homo- and heterometallic Fe^{III}/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. The physico-chemical properties and structural features of all synthesized compounds have been studied by a range of methods such as elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, thermogravimetrical analysis (TGA) and differential thermal analysis (DTA).
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 $[Fe_{18}M_6(is)_{12}(Htea)_{18}(tea)_6(N_3)_6]\cdot n$(solvent) ($M^{III}$ = Dy (**25**, **26**), Gd (**27**), Tb (**28**), Sm (**29**), Eu (**30**), Ho (**31**) and Y (**32**)) compounds.
3. The optimal and effective synthetic pathways for the obtaining of cluster-based coordination polymers with porosity using pre-synthesized polynuclear carboxylate precursors and *N*-donor linkers have been found. This approach leaded to the formation of one- and three-dimensional coordination networks by connection the $\{Fe_3O\}$- and $\{Fe_4O_2\}$-type oxo-carboxylate clusters.
4. Detailed studies of magnetic properties (dc and ac) of new prepared 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 $\{Fe_4\}$ (**4**, **5**), $\{Fe_7\}$ (**7**), $\{Fe_6\}$ (**8**), $\{Fe_{12}\}$ (**13**, **14**), and $\{Fe_{22}\}$ (**15**, **16**)), oxo-tetranuclear $\{Fe_4O_2\}$ (**18**) and oxo-trinuclear $\{Fe_3O\}$ (**19**) cluster-based coordination polymers, as well as in heterometallic wheel-shaped $\{Fe_6Dy_3\}$ (**20**), $\{Fe_6M_4\}$ (**21-24**), $\{Fe_{18}M_6\}$ (**25-32**) and condensed $\{Fe_4M_2\}$ (**35-40**), $\{M_4Dy_2\}$ (**41**) (M^{III} = Fe, Mn) and $\{Fe_7Dy_4\}$ (**42**) compounds. Additionally, ferromagnetic exchange interactions were found in the ring structures $\{Fe_{18}Ln_6\}$

(Ln^{III} = Dy (**25**, **26**), Gd (**27**), Tb (**28**), Ho (**31**)) and condensed cluster {Fe_7Dy_4} (**42**). In a series of {Fe_8O_3} (**9-11**) propeller-like clusters magnetic studies confirm the presence of antiferromagnetic exchange interactions dominating along the edges of the propeller, while a moderate ferromagnetic interaction is found along the propeller axis.

5. Coordination compounds with Dy^{III} and Tb^{III} ions, e.g. the wheel-shaped charge-neutral {Fe_6Dy_3}-(**20**), {Fe_6Dy_4}- (**21**), {$Fe_{18}Dy_6$}- (**26**), {$Fe_{18}Tb_6$}- (**28**) type clusters and the condensed {Fe_4Dy_2}- (**35**), {M_4Dy_2}(M^{III} = Fe, Mn) (**41**) and {Fe_7Dy_4}- (**42**) type clusters were found to exhibit a magnet-like behavior. Susceptibility measurements (ac) show out-of-phase magnetic susceptibility χ_m'' signals from 2.0 K (**26**, **28**) 3.6 K (**20**), 4.4 K (**41**), 5.5 K (**21, 35**), and up to 12 K (**42**) at zero bias field, 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 τ_0 = (4.9 ± 0.6)$\times10^{-6}$ s (**20**), (1.1 ± 0.2)$\times10^{-6}$ (**35**) and (3.7 ± 0.2)$\times10^{-6}$ s (**42**).
6. 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 $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$ system.

PRACTICAL RECOMMENDATIONS

For the construction of Fe^{III} porous coordination polymers, it is recommended to use in the reaction 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 reveal the origin of magnetic interactions in Fe/Fe-Ln compounds, crystalline materials are the desirable products which should be characterized throughout by X-ray crystallography. Moreover, 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 the preparation of these compounds diamagnetic ions such as Y^{III} or Gd^{III}.

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.

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3. **Botezat O.** et al. „Thermal properties of heterometallic Fe(III)-Ln(III) carboxylate wheels and clusters.” 4th Central and Eastern Conference on Thermal Analysis and Calorimetry. August 28-31, 2017. Republic of Moldova, p. 409.
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14. **Botezat O.** et al. „Coordination polymer composed of trinuclear iron(III) carboxylate clusters and 1,2-bis-(4-pyridyl)ethane spacer ligands". The 5th Conference on Materials Science and Condensed Matter Physics MSCMP 2010, Chisinau, Republic of Moldova, 2010. MSP 8P., p. 77.

ADNOTARE

Botezat Olga, “Ingineria cristalelor clusterilor de carboxilat şi polimerilor coordinativi homometalici Fe^{III} şi heterometalici Fe^{III}/4f: sinteza, caracterizarea şi studiul proprietăţilor”, teză de doctor în ştiinţe 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: ştiinţe ale naturii.

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

Noutatea şi originalitatea ştiinţifică constă în elaborarea metodelor și condițiilor de sinteză, inclusiv sinteze hidro(solvo)termale, cu microunde şi ultrasonice, ce au rezultat cu obținerea a 42 compuși noi de Fe^{III}/Fe^{III}-4f. Pentru prima dată au fost obținuți compuși inelari heterometalici cu nuclearitatea $\{Fe_{18}Ln_6\}$. În baza rezultatelor a fost analizată influența naturii metalelor și liganzilor asupra compoziţiei, structurii și proprietăţilor magnetice ale compușilor Fe/Fe-Ln.

Problema ştiinţifică soluţionată. 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 $\{Fe_4Dy_2\}$, $\{Fe_6Dy_3\}$, $\{Fe_6Dy_4\}$, $\{Fe_6Tb_4\}$, $\{Fe_7Dy_4\}$, $\{Fe_{18}Dy_6\}$ 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 cunoştinţele 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 ştiinţifice. 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 $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$.

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 Fe^{III}/Fe^{III}-4f 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 $\{Fe_4Dy_2\}$, $\{Fe_6Dy_3\}$, $\{Fe_6Dy_4\}$, $\{Fe_6Tb_4\}$, $\{Fe_7Dy_4\}$, $\{Fe_{18}Dy_6\}$, and $\{Fe_{18}Tb_6\}$-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 $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$ 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 $\{Fe_{18}Ln_6\}$. 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 $\{Fe_4Dy_2\}$, $\{Fe_6Dy_3\}$, $\{Fe_6Dy_4\}$, $\{Fe_6Tb_4\}$, $\{Fe_7Dy_4\}$, $\{Fe_{18}Dy_6\}$ and $\{Fe_{18}Tb_6\}$ 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 $Fe^{III}(\mu_{2+n}\text{-}O)Fe^{III}$.

BOTEZAT OLGA

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144.07 - SOLID STATE CHEMISTRY

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Autoreferatul tezei de doctor în științe chimice

CHIȘINĂU, 2019