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SYNTHESIS AND CHARACTERIZATION OF COORDINATION POLYMERS OF Zn(II) AND Cd(II) BASED ON AZINE AND AZOMETHINE BRIDGING LIGANDS

141.01. INORGANIC CHEMISTRY

Summary of the doctoral thesis in chemical sciences

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The thesis was developed in the Doctoral School of Chemical Sciences of the State University „Dimitrie Cantemir" and the Institute of Chemistry, member of the academic consortium.

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The doctoral thesis and summary can be consulted at the National Library of the Republic of Moldova, „Andrei Lupan" Scientific Library, USM Library and on the website of the ANACEC (http://www.cnaa.md/) and on the USM website (http://usm.md/).

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CONCEPTUAL FRAMEWORK OF THE RESEARCH

The actuality of the research topic. Coordination polymers (*CPs*) and metal-organic frameworks (*MOFs*) are currently among the most prolific research areas in the field of inorganic chemistry and crystal engineering. The properties of *CPs* such as low density, large surface area, pore function regulation and structural flexibility offer them the possibility to be applied in gas storage, catalysis, magnetism, optics, electrical conductivity and so on. Numerous studies report rigid *MOFs* as porous materials with the desired pore volume and selectivity in adsorption [1, 2]. Post-synthetic modification is an alternative method for the formation of functional *CPs*. Using this method, the nature of the pores is modified after the synthesis of coordination polymer, thus allowing the introduction of sensitive groups in the crystal structures [3]. Luminescent *CPs* and *MOFs* have found promising applications in imaging, optoelectronics, as well as in solid state lighting devices and as sensors. Lately, luminescent *CPs* have stimulated considerable interest as excellent materials for sensor applications due to their ability to detect hazardous, volatile and explosive chemicals.

The purpose of this work is synthesis and characterization of coordination polymers based on Zn(II)/Cd(II) ions and azine/azomethine bridge ligands of N,N'-donor type in combination with various inorganic and organic ligands, study of photoluminescence and sorption properties of synthesized compounds and their desolvated forms.

Proposed research objectives:

- synthesis of coordination polymers based on Zn(II)/Cd(II) ions using the mixed ligand synthetic approach including azine and azomethine bridge ligands type N,N'-donors and various inorganic anions or organic anionic ligands from the carboxylate class;
- studying the crystal structure and elucidation of the role of the anionic ligand and the solvent in the extension and modeling of the polymeric structure;
- functionalization of the synthesized compounds by processes of elimination or substitution of guest molecules from the as-synthesised crystalline forms;
- investigation of thermal and chemical stability;
- investigation of structure-property correlation, especially in the case of the manifestation of photoluminescence and sorption properties.

The research hypothesis assumes that the synthetic approach using mixed ligands including azines/azomethines bridged type, in combination with inorganic or organic anionic ligands, provides high efficacy for the regulation of polymeric coordination structures based on zinc(II) and cadmium(II) cations, and a spectrum of properties such as photoluminescence and sorption.

Protocol of the research methodology. The research methodology involves the synthesis of *CPs* and the investigation of structure-property correlation and establishing the role of the basic components for this purpose. Diffusion methods were used primarily to obtain monocrystalline compounds. The synthetic approach involving the use of mixed inorganic/organic ligands blends allowed the structural and compositional diversification of the newly synthesized compounds. The selection of bridged ligands such as azines/azomethines is justified by their aability to form polymeric coordination structures, with cavities and by their photoluminescent properties. Elucidation of structural architectures was achieved by a single-crystal X-ray diffraction. Investigation of properties of the compounds was performed by FTIR, UV-Vis, NMR, AAS spectroscopy, XRPD analysis, thermal analysis etc. Greater attention has been paid to the investigation of photoluminescent properties. The post-synthetic modification of compounds was achieved by processes of desolvation or removal of the guest molecules from the cavities of crystal structures. The sorption capacity for some compounds was measured by adsorption of N_2, or solvent molecules accompanied by recording of optical signals to identify sensitive compounds in such processes. The stability of compounds was investigated by thermal analysis, accompanied by PXRD data and UV-Vis spectroscopic measurements.

SYNTHESIS OF CHAPTERS

The work consists of introduction, 4 chapters, general conclusions and recommendations, bibliography of 264 titles, 126 pages of basic text, 103 figures, 4 tables and 5 annexes.

In this work we proposed the use of bridged azine and azomethine ligands as basic ligands for the synthesis of coordination compounds with polymeric structure. The choice for this class of ligands is motivated by the fact that azines/azomethines are among the ligands required in construction of MOFs, as they can function as pillars that offer the possibility to regulate pore size and the inclusion of guest molecules. On the other hand, extended π-conjugated systems comprising aromatic rings conjugated with C=N bonds serve as safe premises for the manifestation of luminescent properties [4]. For this purpose, five azine and two azomethine ligands were synthesized. Four N,N'-donor ligands 1,2-bis(pyridin-3-ylmethylene)hydrazine (*3-bphz*), 1,2-bis(pyridin-4-ylmethylene)hydrazine (*4-bphz*), 1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (*3-bpmhz*) and 1,2-bis(1-(pyridin-4-yl)ethylidene) hydrazine (*4-bpmhz*) are part of the azine family and are known in the literature as effective coordination bridging ligands. Complexes with these ligands were shown to be used to obtain luminescent materials with potential applications in the field of sensors [5, 6]. Another lesser known azomethine linker, N^1,N^4-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine (*bda4bPy*), used in synthetic reactions proved to be less stable, an azomethine bond has been solvolized which led to the obtaining of four coordination compounds containing the ligand N-((pyridin-4-yl)methylene)benzene-1,4-diamine (*bda4Py*). This fact motivated us to synthesize this individual ligand, which, according to the verification in the Cambridge Structural Database, revealed no reported compounds on its base so far. A novelty is the synthesis of the ligand 1,2-bis(benzoic-4-ylmethylene acid)hydrazine (*4-dbahz*) containing two terminal carboxylic groups, the structure of which was demonstrated by a single crystal X-ray diffraction. Based on this ligand, a unique Cd(II)-based 3D coordination polymer of was obtained.

The choice of Zn(II) and Cd(II) cations is motivated by the fact that the coordination compounds with these metals are of major interest for their luminescent properties and useful applications in the field of optics. The metallic ions Zn(II) and Cd(II) with d^{10} close shell can adopt coordination geometries from tetrahedral to pentagonal bipyramid being suitable for obtaining luminescent complexes based on luminophore ligands [7-9]. In addition to the bridging role offered by azomethine linkers, inorganic or organic auxiliary ligands also play a key role in the expansion of coordination polymers and the formation of structures of different dimensionality. In this sense, starting from the Zn(II) and Cd(II) salts, we proposed, by changing the inorganic anion in the salt composition, to direct the dimensionality of the coordination polymers. Also, another reason for this strategy is to investigate the property-structure correlation and the role of the anion in this regard, especially in the case of the manifestation of photoluminescent properties. This technique allowed us to follow the evolution of polymeric structures, but also the adjustment of properties depending on the anionic ligand used.

1. COORDINATION POLYMERS. GENERAL CHARACTERIZATION. PROPERTIES AND APPLICATIONS

Chapter 1 presents general theoretical and practical approaches in the field of *CPs* with reference to the terminology and hierarchical classification of *CPs*, structure and dimensionality, methods of synthesis and post-synthetic modification, conformational and supramolecular isomerism for rigid and flexible *CPs* and *MOFs*, properties and applications. The class of azomethine ligands as basic precursors for *CPs* synthesis is also described, as well as the class of carboxylate and sulfate anions as co-ligands. Examples from the literature of *CPs* containing mixed ligands from the class of azines and carboxylates based on zinc(II) and cadmium(II) cations and properties of these CPs are described.

2. METHODS OF SYNTHESIS, ANALYSIS AND RESEARCH

Chapter 2 describes the syntheses of azine and azomethine ligands, the syntheses of complex combinations based on zinc(II)/cadmium(II) cations with inorganic or organic anions and azine/azomethine ligands. At the end, the methods of analysis and the devices used to characterize the compounds are described.

3. COORDINATION POLYMERS OF Zn(II) AND Cd(II) CONSTRUCTED FROM AZINE/AZOMETHINE BRIDGE N,N'-DONOR LIGANDS AND INORGANIC ANIONS

Chapter 3 describes the *CPs* obtained from azine/azomethine bridge N,N'-donor ligands and inorganic anions derived from the respective salts, zinc(II)/cadmium(II) iodide, nitrate and sulphate. The description of crystal structures of monocrystalline complexes, FTIR, UV-Vis, NMR spectroscopic characterization is presented. The role of anionic ligands in the expansion of polymeric structure and in manifestation of photoluminescent properties is described. Also, the comparative photoluminescent properties of synthesized compounds and their desolvated forms are investigated. The thermal and chemical stability of synthesized compounds and ligands is investigated. The chromatic properties and the origin of color for some crystals of the reported compounds are described.

3.1. 1D coordination polymers derived from Zn(II)/Cd(II) iodide and azine ligands

The use of halogenated salts CdI_2 and ZnI_2 in combination with azine luminophore ligands of N,N'-donor type led to six 1D *CPs* with similar structures (Figure 1). The formation of polymer chains is due to azine bridging ligands provided the function of expanding the polymer in one dimension while bulky iodide anions coordinate to the metal exclusively in monodentate mode as terminal ligands, and. The effective packing of polymer chains contributed to the obtaining of compact crystal structures.

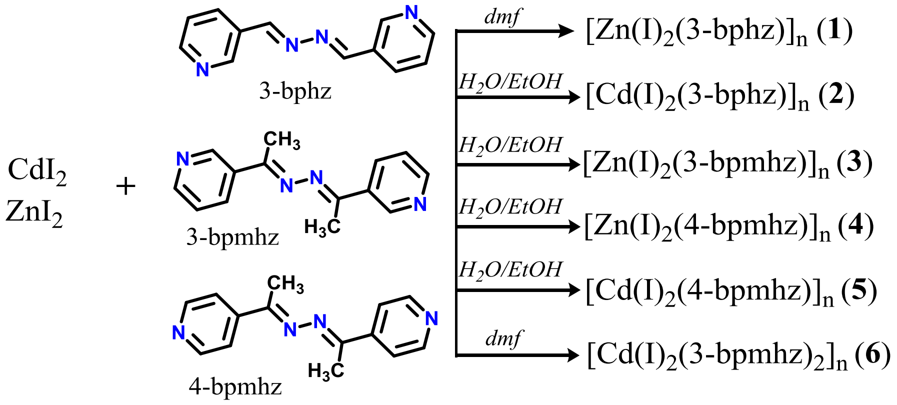
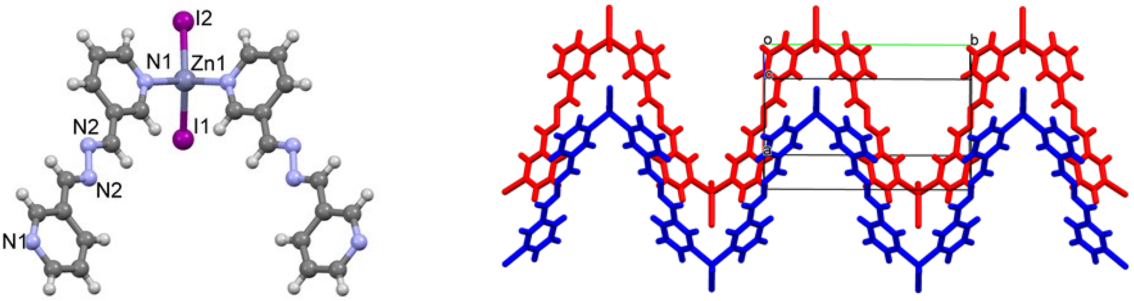


Fig. 1. Scheme of synthesis of compounds 1-6.

Compounds **1-5** have zig-zag coordination chains, in which the metal atom adopts a tetrahedral configuration comprising the set of N_2I_2 donor atoms going from two iodide anions and two azine ligands. Unlike compounds **1-5**, in **6** the Cd(II) atom adopts an N_4I_2 octahedral geometry by coordinating four *3-bpmhz* bidentate-bridging ligands and two iodide anions.



(a) **(b)**

Fig. 2. (a) Fragment of the coordination chain in compound 1; (b) packing of chains.

3.2. 1D and 2D coordination polymers derived from Zn(II)/Cd(II) nitrates and azine ligands

Next, in order to expand and diversify the polymeric structures, the halide salts were replaced with cadmium and zinc nitrates, in reactions with the same azine ligands, *3-bphz*, *3-bpmhz* and *4-bpmhz*. As a result, five *CPs* with different crystal structures were obtained (Figure 3).

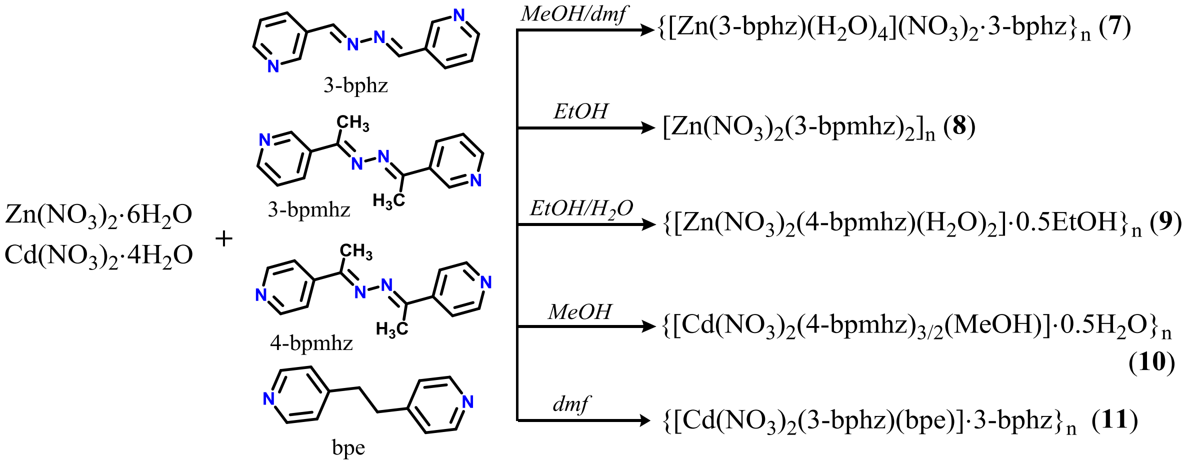
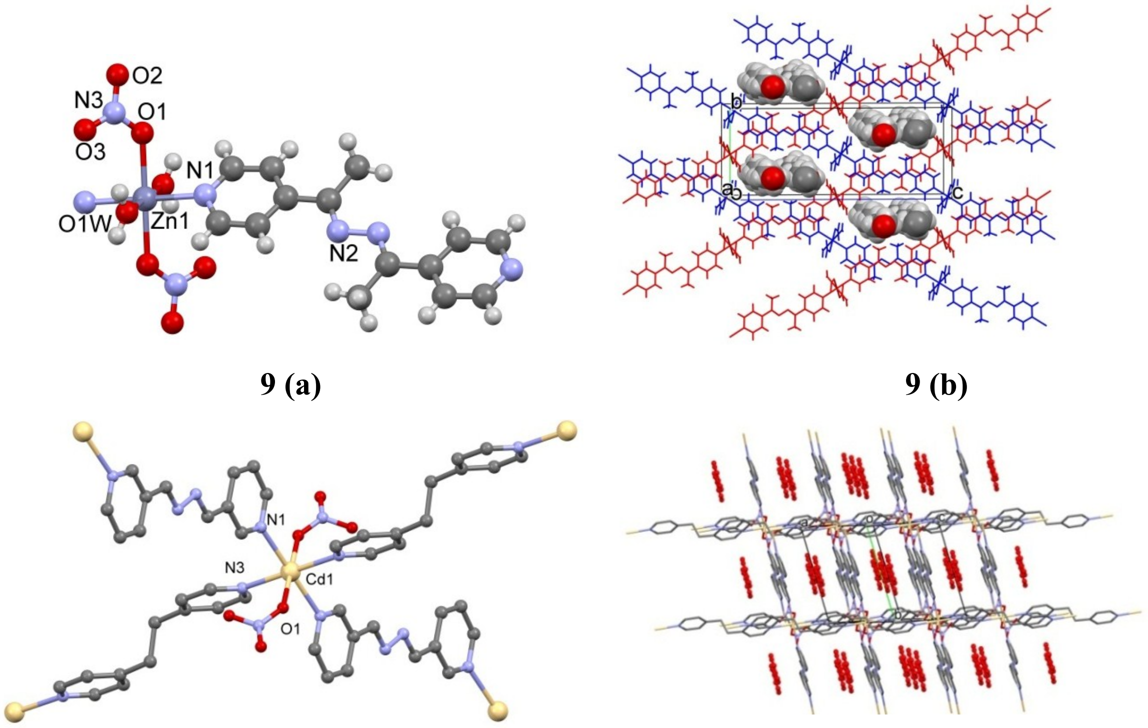


Fig. 3. Synthesis scheme of compounds 7-11.

Zn(II)-based compounds **7-9** have 1D structures, while compounds **10** and **11** based on the more voluminous Cd(II) cation, have expanded in the form of 2D coordination networks. In all compounds the azine ligands act as bridges, and the nitrate anion does not participate in the coordination polymer extension. In compound **7**, the nitrate anions are occupying positions in the external coordination sphere, and in the rest of compounds the nitrate anion coordinates in monodentate mode to the metal cations. Only in compound **10** one anion coordinates in bidentate-chelate mode, and the other – in monodentate mode to the Cd(II) cation. In compound **10**, the Cd(II) cation is heptacoordinated and adopts an N_2O_5 pentagonal-bipyramidal geometry, while in the rest of compounds the metal atoms adopt octahedral geometries. Compounds **9** and **11** have channel-shaped cavities where EtOH solvent molecules in **9** and *3-bphz* ligand molecules in **11** are located (Figure 4). In compound **10**, the interpenetration of the coordination networks did not allow the formation of cavities in the crystal. Compound **8**, similar to **6**, containing the same azine ligand, is a double linear chain with twisted *3-bpmhz* ligands.



9 (a) **9 (b)**

11 (c) **11 (d)**

Fig. 4. (a) The coordination environment of Zn(II) in 9 and (c) of Cd(II) in 11; (b), (d) crystal packing indicating the guest molecules of EtOH in 9 and 3-bphz in 11.

IR spectra confirm the presence of organic ligands and constituent nitrate anions. Stretching bands for nitrate anions are positioned at $\nu_{as}(NO)$ ~ 1418 cm^{-1} and $\nu_s(NO)$ ~ 1300 cm^{-1}. For **9** the band ν(OH) 3000-3600 cm^{-1} is broad and intense as a result of the formation of hydrogen bonds between the EtOH and H_2O component molecules. The water molecules have a low intensity band $\delta(H_2O)$ at 1654 cm^{-1} for **9** and 1666 cm^{-1} for **10**. The UV-Vis spectra recorded for compounds **9-11** indicate similar spectral profiles corresponding to the component azine ligands, with maxima originating from the transition $n \rightarrow \pi^*$ specific to the chromophore group C=N.

3.3. Conformational isomerism of azine ligands and effects on crystal color

Surprisingly, crystals **6** and **8** containing the *3-bpmhz* yellow ligand are colorless. This irregularity is explained by the conformational isomerism of the *3-bpmhz* ligand. When the ligand twists from the planar *transoid* conformation to the nonplanary *cisoid* conformation around N-N bonds, the conjugation system along the azine chain becomes deformed, leading to the absence of color.

3.4. Thermochromic stability and temperature spectroscopic investigation

The thermochromic behavior of colorless crystals **6** and **8** was investigated by their subjecting to heating. The crystals were heated in two stages. At the first stage, the compounds were heated at 110 °C for one hour, as a result the surface of the crystals deteriorated with the appearance of a yellow tint. Subsequently, the crystals were heated for another two hours at this temperature. Eventually, the crystals of compound **6** turned yellow, and crystals **8** turned white. In the IR spectra recorded for these crystals after heating, differences were observed in the displacement of wave numbers and intensity for some spectral bands compared to the spectra recorded before heating, which indicates that the compounds undergo structural changes under these conditions.

3.5. Sulphate anion - generator of coordination polymeric architectures for Zn(II)/Cd(II) ions with azine ligands

Reactions of Zn(II) or Cd(II) sulphates with *3-bphz*, *4-bphz*, *3-bpmhz* and *4-bpmhz* semi-rigid azine ligands resulted in eight coordination compounds including two discrete compounds and six *CPs* of different dimensions (Figure 5). Only in compounds **12** and **14** the sulfate anion is found in the outer sphere.

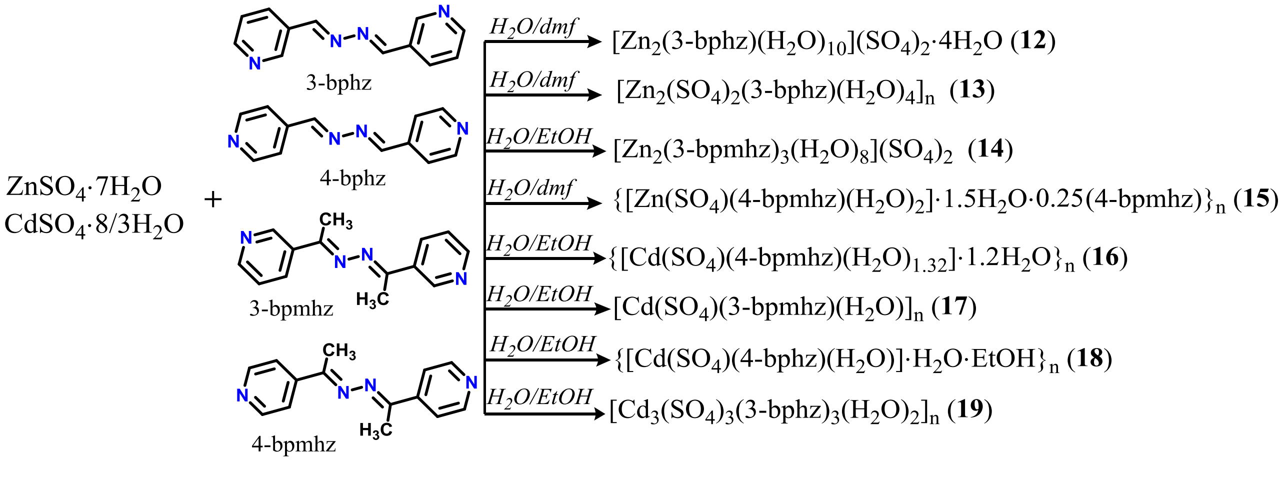
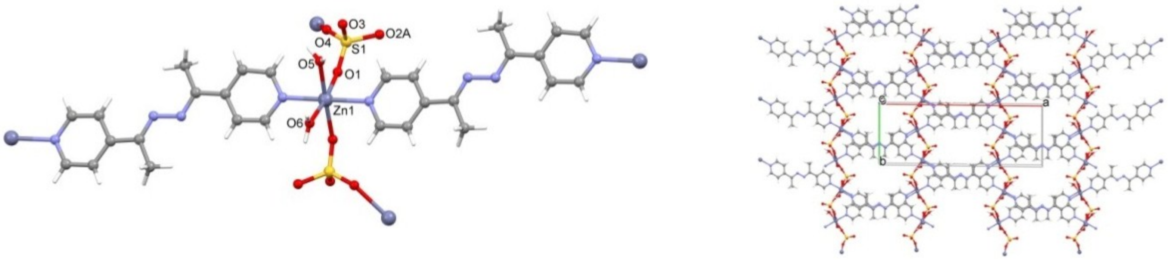


Fig. 5. Synthesis scheme of compounds 12-19.

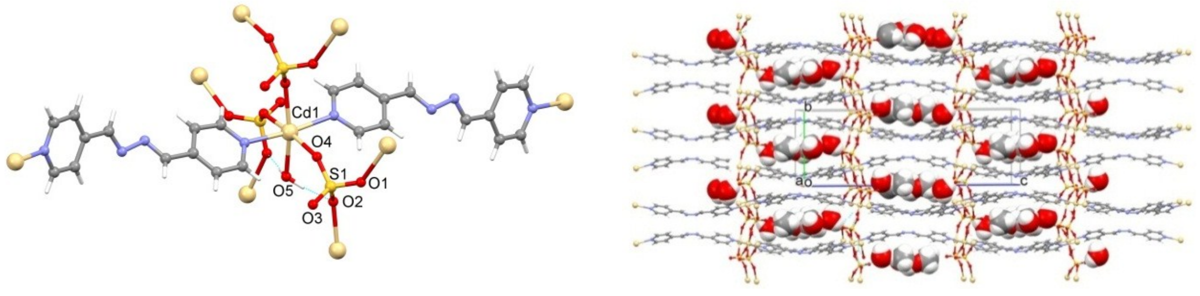
The ionic crystals of compounds **12** and **14** are constructed of binuclear Zn(II) cations and sulfate anions. In the 2D coordination polymer **13** the sulfate anions coordinate directly to the metal due to the substitution of three water molecules in the starting salt, and one water molecule was substituted by the *3-bphz* ligand leading to the formation of the 2D network. With the *4-bpmhz* ligand, two isostructural 2D coordination polymers **15** and **16** were obtained. The sulfate anions connect two metals forming a helical inorganic chain $[ZnSO_4(H_2O)_2]_n$ in **15**. These chains are linked by bridged azine ligands and form a layer-like network (Figure 6). The packing of the networks led to the formation of channels in which a mixture of water and azine molecules is located in compound **15** and only water molecules in **16**.



(a) **(b)**

Fig. 6. (a) Coordination environment of Zn(II) ion in 15; (b) network representation.

In compounds **17-19** the sulfate anion connects three metal atoms leading to the formation of 2D inorganic metal-sulfate network, which being interconnected by azine ligands lead to the formation of 3D metal-organic networks. The network topology for **18** coincides perfectly with **17**. Similarly, the Cd(II) cation is hexacoordinated, the N_2O_4 coordination polyhedron results from two *4-bphz* ligands, three sulfate anions, and one water molecule (Figure 7, a), and the crystal is constructed of the same inorganic layers $[CdSO_4(H_2O)]_n$ linked by *4-bphz* pylons. The *4-bphz* ligand adopts a more distorted chain conformation. The structure shows the alternation of wide pores in which water and ethanol molecules are located, and narrow empty ones (Figure 7, b). The voids in the crystal comprise ~ 21% or 382,65 Å^3 of the volume of the elementary cell.



(a) **(b)**

Fig. 7. (a) Coordination environment of Cd(II) ion in 18; (b) crystal packing with indication of EtOH solvating molecules.

Recorded IR spectra confirm the presence of azine ligands and sulfate anion in the series of compounds **12-19**. Depending on position of sulphate anion, either coordinated to metal or situated in the outer sphere, the characteristic bands of sulphate group were registered at distinct values in the IR spectra. From four to six bands ν_1 and ν_3(SO) can be identified in the range 950-1200 cm^{-1}. The azomethine band (C=N) characteristic for *3-bphz* and *4-bphz* ligands is identified for compounds **12**, **13**, **18** and **19** at ~ 1630 cm^{-1}. For compounds **14-17** this band is identified in the range 1611-1615 cm^{-1}. In the region 3030-3100 cm^{-1} there are 2-3 ν(CH) bands of medium intensity.

3.6. Binuclear and polymeric coordination compounds of Zn(II) and Cd(II) based on N-((pyridin-4-yl) methylene)benzene-1,4-diamine ligand obtained *in situ*

Next, our interest was focused on a longer and more rigid π-conjugated linker, N^1,N^4-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine (*bda4bPy*). Attempts have been made to obtain new *CPs* of Zn(II) and Cd(II) with this ligand. Instead, four coordination compounds containing the ligand N-((pyridin-4-yl)methylene)benzene-1,4-diamine (*bda4Py*) were obtained as a product of the partial solvolysis of the *bda4bPy* ligand in the reaction medium (Figure 8).

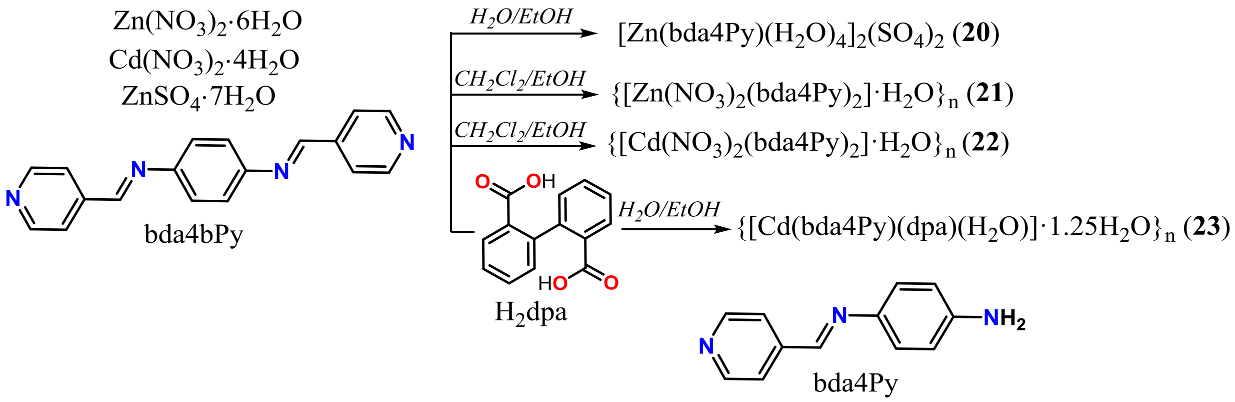
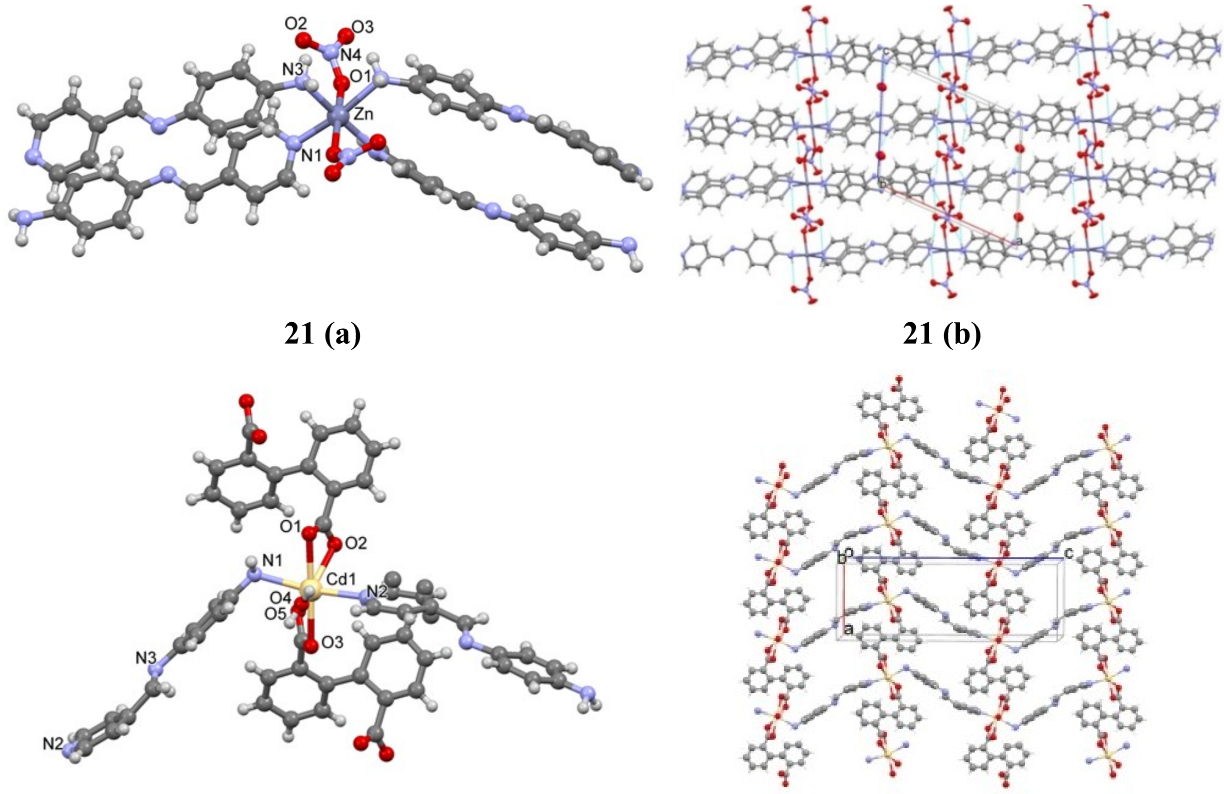


Fig. 8. Synthesis scheme of compounds 20-23.

Compound **20** is a binuclear complex of Zn(II), with sulfate anions found in the outer coordination sphere, and the organic ligand acts in a bridging mode. Compounds **21** and **22** are isomorphous, differ only by the metal cation and have 1D polymeric structures in the form of a linear double chain. Nitrate anions coordinate monodentate to the metal, and the organic ligand acts in a bridging mode (Figure 9, a, b). Compound **23** was obtained by substituting of inorganic anion from the initial cadmium nitrate salt with the *dpa* dicarboxylate anion. As a result, in this compound both organic ligands play bridging role, which led to the formation of the 2D polymer structure (Figure 9, c, d). The packing of coordination networks in this compound ensured the formation of cavities in which disordered water molecules are located.

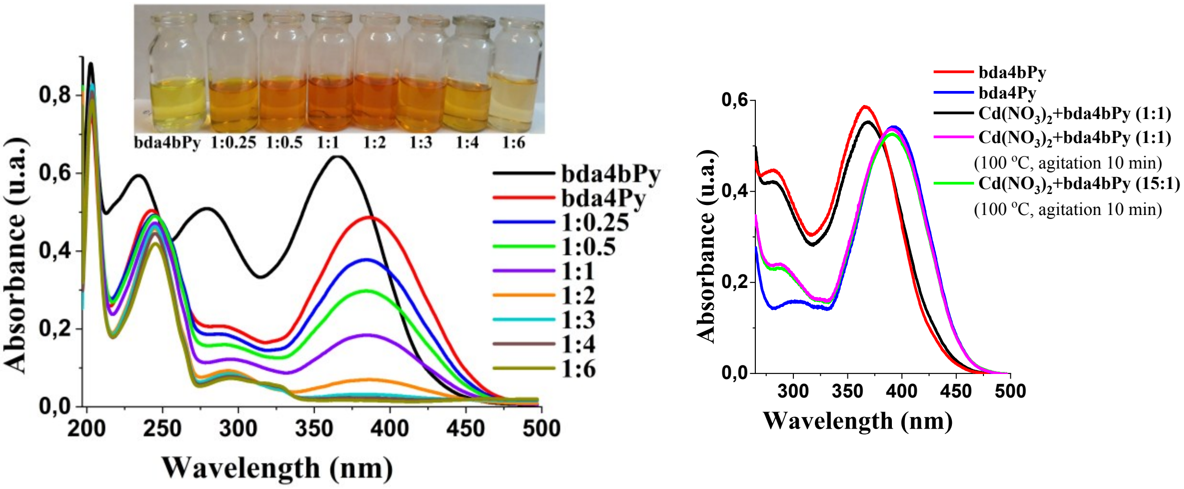


21 (a) **21 (b)**

23 (c) **23 (d)**

Fig. 9. (a) Coordination environment of Zn(II) in 21 and (c) of Cd(II) in 23; (b), (d) crystal packing in 21 and 23.

Investigation of solvolytic stability of azomethine ligands. Solvolytic reactions with the participation of azomethine ligands, produced during the synthesis of compounds, led us to study the stability limits of these ligands depending on the pH of the solution and the concentration of the metal cation. This monitoring was performed using UV-Vis spectroscopy. These ligands reveal a specific absorption band that is attributed to the chromophore group C=N and corresponds to the electronic transition $n \rightarrow \pi^*$, for *bda4bPy* λ_{max} is at 365 nm, and for *bda4Py* $\lambda_{max} = 386$ nm (Figure 10, a). The solvolytic stability of ligands was investigated in acidic solutions prepared with 0,1 M HCl. Starting from the ligand-acid molar ratio of 1:0,25, the color of the solution changed from yellow to orange, and the recorded curve is outlined with the same profile as the *bda4Py* chromophore, but of lower intensity. According to these measurements, it was found that the compound *bda4bPy* has a low solvolytic stability in the acid medium, so that at the molar ligand-acid ratio of 1:3 practically the entire amount of the compound *bda4bPy* is solvolized. Chromophore stability was also elucidated in the presence of Cd(II) cations (Figure 10, b). For this, cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$ was used in admixture with the *bda4bPy* ligand in various molar ratios. It was found that by heating the solution of the 1:1 mixture of salt and ligand at 100 °C for 10 min, the solvolysis of the *bda4bPy* ligand takes place and the increase of the concentration of Cd(II) metal ions does not cause the solvolysis of the second azomethine group, the color of the solution remains stable, orange (last curve measured, molar ratio Cd(II):ligand 15:1).



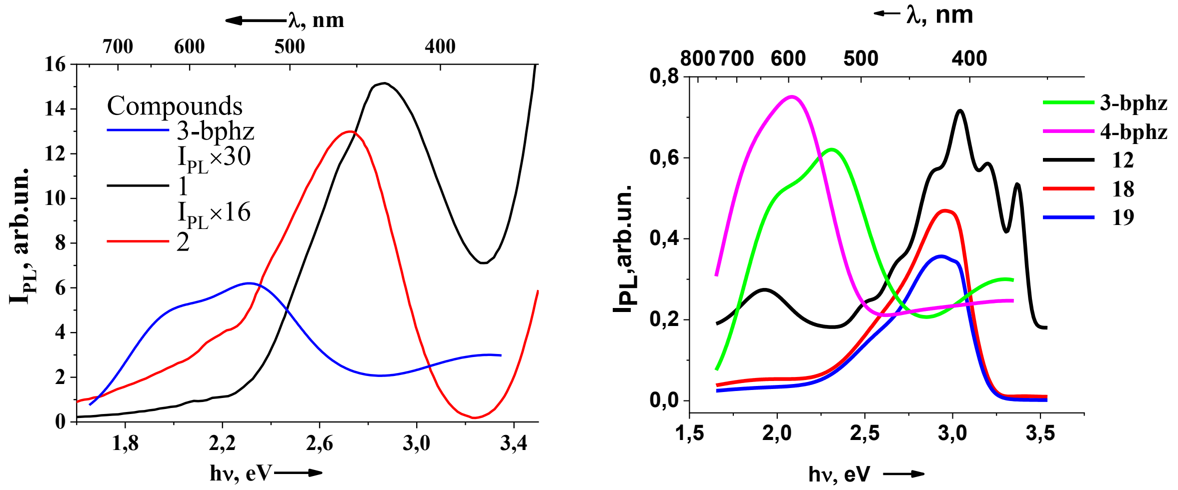
(a) (b)

Fig. 10. UV-Vis spectra for *bda4bPy* and *bda4Py* ligands; (a) investigation of the solvolytic stability of ligands in acidic medium and (b) in cadmium nitrate solution.

3.7. Photoluminescent properties and thermal stability of compounds containing inorganic anions.

The photoluminescent activity in these series of compounds is mainly determined by azine/azomethine ligands and is dictated by the crystal packing and the favorable location of luminophores. Since azine ligands are the sources of emission processes in the studied compounds, the emission spectra of *CPs* are correlated with the emission of individual luminophores. The individual *3-bphz*, *4-bphz*, *4-bpmhz* and *3-bpmhz* ligands reveal emission bands with maxima at 540, 600, 575 and 583 nm respectively, which can be attributed to intraligand π*···π transitions. In the series of iodides with compact crystal packing and without crystallization solvents emissions have higher intensities than the individual azine ligands. Compounds **1** and **2** show emission maxima shifted to the blue region of the spectrum relative to the ligand, at 435 and 460 nm, respectively (Figure 11, a). As the coordination polymers extend to 3D networks in the case of sulfates, there is a significant decrease in PL emission (Figure 11, b), lower than luminophore ligands, which originates in the less dense crystal lattice with the presence of cavities containing solvent molecules. Most compounds show significant displacements to the blue region with maximum emission, that are located at 408 nm for **12**, 369 nm for **15**, 439 nm for **16** and 414 nm for **17-19**, in correspondence with the displacement in the blue zone previously recorded in *CPs* with non-methylated ligands.

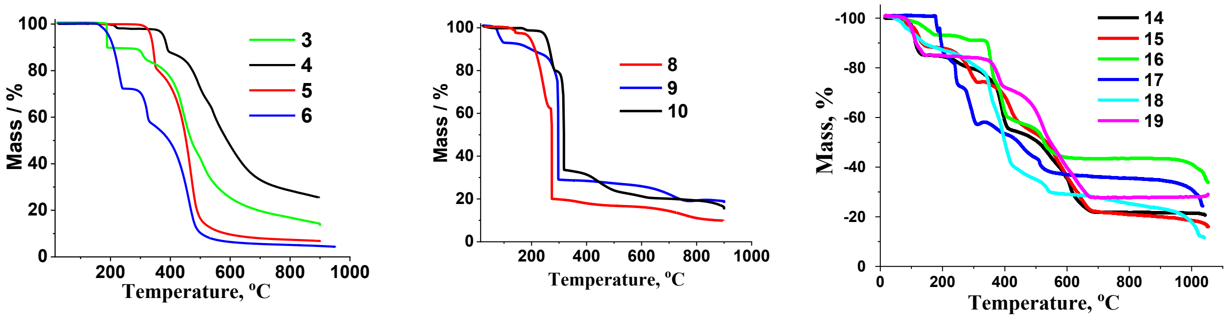
Only for **14** the position of emission maximum practically coincides with the pure ligand, which clearly indicates the origin of the ligand-based emission. Desolvation of these compounds reveals a slight increase in emission intensity. The emission curves in the iodide and nitrate series have similar profiles with maxima in the yellow region of the spectra, and in the case of sulphates there is a shift towards the blue region in relation to the luminophore ligands.



(a) **(b)**

Fig. 11. Comparative PL spectra: (a) for compounds 1, 2 and the *3-bphz* ligand; (b) for 3-6, *4-bpmhz* and *3-bpmhz* ligands.

The study of thermoanalytic curves has shown that the thermal stability in these series of compounds is dependent on the nature of the anion. Thus, the complexes derived from nitrate salts have reduced stability compared to the rest (Figure 12). From the TG curves it is found that they decompose violently with drastic loss of mass (~ 60%) at a temperature of ~ 300 °C. In the case of iodide complexes, decomposition is slower and begins at higher temperatures. Compounds derived from sulfate salts are shown to be the most stable with profiles of more varied TG curves that record significant mass losses up to ~ 600 °C.



(a) **(b)** **(c)**

Fig. 12. Decomposition TG curves for compounds: (a) 3-6; (b) 9-10; (c) 14-19.

4. COORDINATION POLYMERS OF Zn(II) AND Cd(II) CONSTRUCTED FROM AZINE/AZOMETHINE N,N'-DONOR LIGANDS AND CARBOXYLATES

Chapter 4 deals with issues similar to chapter 3 with reference to compounds containing organic anionic ligands included by the substitution of inorganic anions from the initial salt. The possibilities of coordination mono- and dicarboxylic acids (acetic, 2-thiophenecarboxylic, 2-aminobenzoic, sebacic, isophthalic, homophthalic, 4,4'-biphenyldicarboxylic) for the expansion of polymeric structures are described. Compounds containing cavities are investigated in order to identify porous materials with sorption and photoluminescence properties.

4.1. Polymer chains containing 2-thiophenecarboxylate ligand

Starting from Zn(II) or Cd(II) nitrate salts in reaction with sodium 2-thiophenecarboxylate and four azine ligands *4-bphz*, *4-bpmhz*, *3-bphz* and *3-bpmhz*, seven 1D *CPs* were obtained (Figure 13). In all compounds, azine as a bidentate bridging ligands ensure the expansion of polymers, while different mono/binuclear metal nodes demonstrate the coordination capabilities of metals that influence crystal packing. The bond distances and angles in the metal coordination polyhedra of **24-30** have similar values. In all these compounds the crystal packing is generally regulated by weak intermolecular forces. The polymer chains of compounds **24-28** are packed in parallel mode in crystal, while in compounds **29** and **30** they are packed in a criss-cross mode with formation of large channels, where the guest molecules (4-bpmhz/water) serve as templates for directing the crystal packings. Compound **29** demonstrated the ability to replace guest molecules and cation exchange.

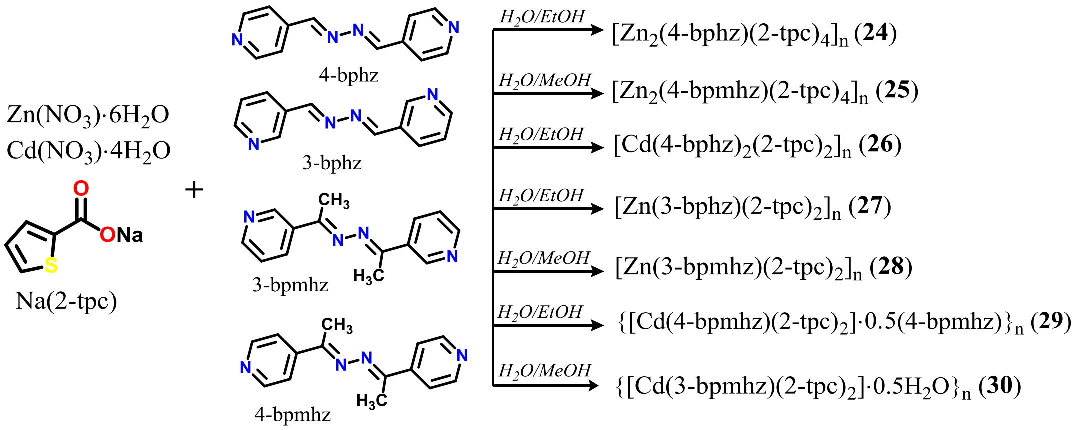
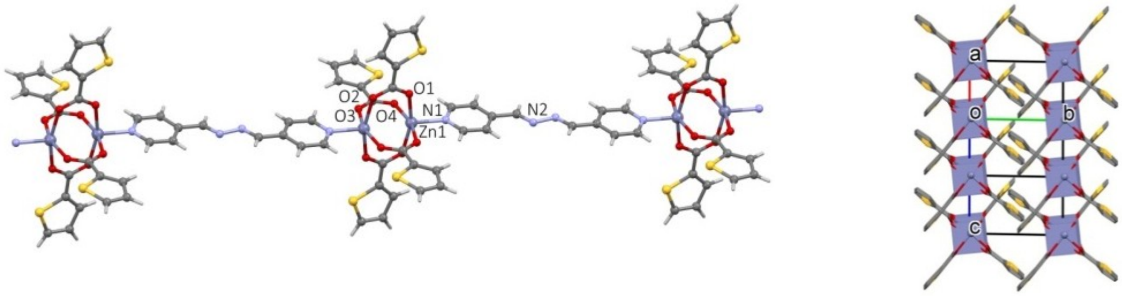
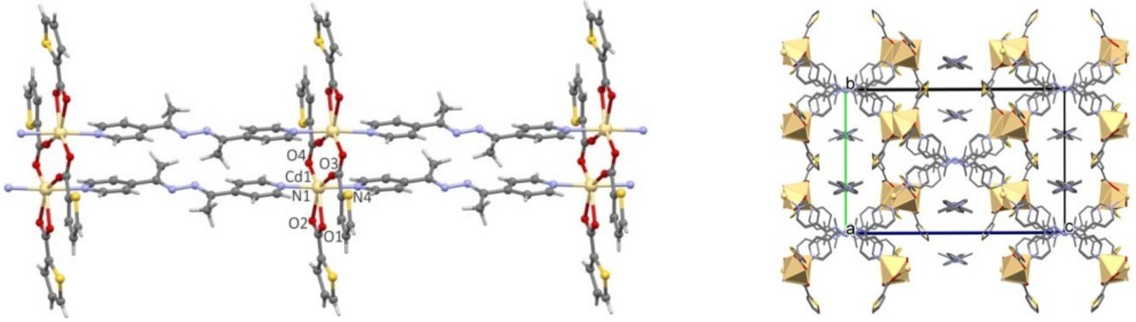


Fig. 13. Synthesis scheme of compounds 24-30.

Compounds **24** and **25** are isostructural, both contain a Zn(II) cation, two *2-tpc* residues and half of the *4-bphz*/*4-bpmhz* chromophore in the asymmetric parts of the unit cells. In linear chains, the binuclear building units $[M_2(CO_2)_4]$ of a paddle-wheel type alternate with *4-bphz*/*4-bpmhz* bridging ligands (Figure 14, a). Zn(II) cations adopt NO_4 pyramidal-tetragonal geometries. Compounds **28-30**, containing methylated chromophores, have similar double chains ladder-like structures with binuclear building units $[M_2(CO_2)_4]$. In all compounds one *2-tpc* residue coordinates in bidentate-chelate, another one – in a bidentate-bridging mode (Figure 14, c). In compounds **29** and **30**, the coordination chains are packed in criss-cross mode, due to the template functions of the guest molecules, identified as *4-bpmhz* chromophore in **29** and water molecules in **30**.



24 (a) **24 (b)**



29 (c) **29 (d)**

Fig. 14. (a), (c) Fragments of the coordination chain in 24 and 29; (b), (d) packing of chains.

The crystal structure of compound **29** contains channels in which uncoordinated *4-bpmhz* guest molecules are located. Elimination of these molecules led to the obtaining of the activated form **29a**. The N_2 adsorption isotherm for activated product **29a** recorded at 77 K (Figure 15) reveals a type V isotherm and indicates a negligible adsorption for N_2. The calculated BET area is 22 m^2/g. The distribution of pore volume by radius indicates the presence of mesopores, and the total pore volume is also relatively small, 0,113 cm^3/g.

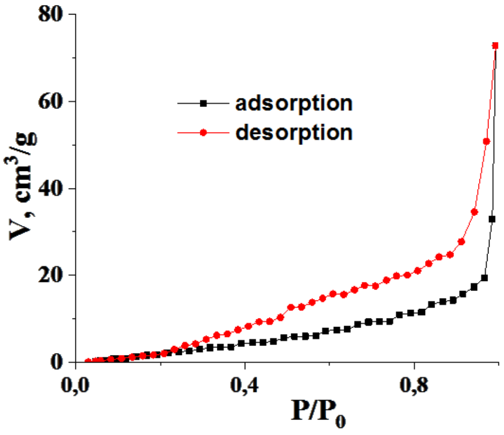


Fig. 15. Adsorption-desorption isotherms of N_2 at 77 K for 29a.

Solvent sorption properties. Figure 16 (a), (b) shows the comparative images of the synthesized crystals **29** and the activated form **29a**, accompanied by the corresponding IR spectra that are displayed with similar profiles. The sorption capacity of the activated compound **29a** was also investigated for small molecules using as solvents, formamide and isobutanol, and the FTIR/NMR spectroscopic techniques elucidated these processes. The presence of solvent molecules in the cavities of the compound was identified in the recorded IR and NMR spectra. The presence of isobutanol was confirmed by the ν(OH) band at 3385 cm^{-1} and the ν(CH) bands at 2952-2871 cm^{-1} (Figure 16, c). In the case of formamide, the bands ν(C=O) at 1700 cm^{-1} and ν_{as}(NH), ν_{s}(NH) at 3308 and 3169 cm^{-1} are clearly visible (Figure 16, d).

Cation exchange capacity. The product **29a** was introduced into the aqueous solution of $Cu(NO_3)_2$ of 0,2 M concentration for two weeks. The crystals changed color from yellow-orange to green (Figure 16, e), and the atomic absorption spectroscopy (AAS) indicated the substitution of Cd(II) cations by Cu(II) in a proportion of about 99%. The structural stability of compound **29** in post-synthetic modification processes was determined using the XRPD technique. PXRD patterns for modified products indicate that their crystallinity is maintained.

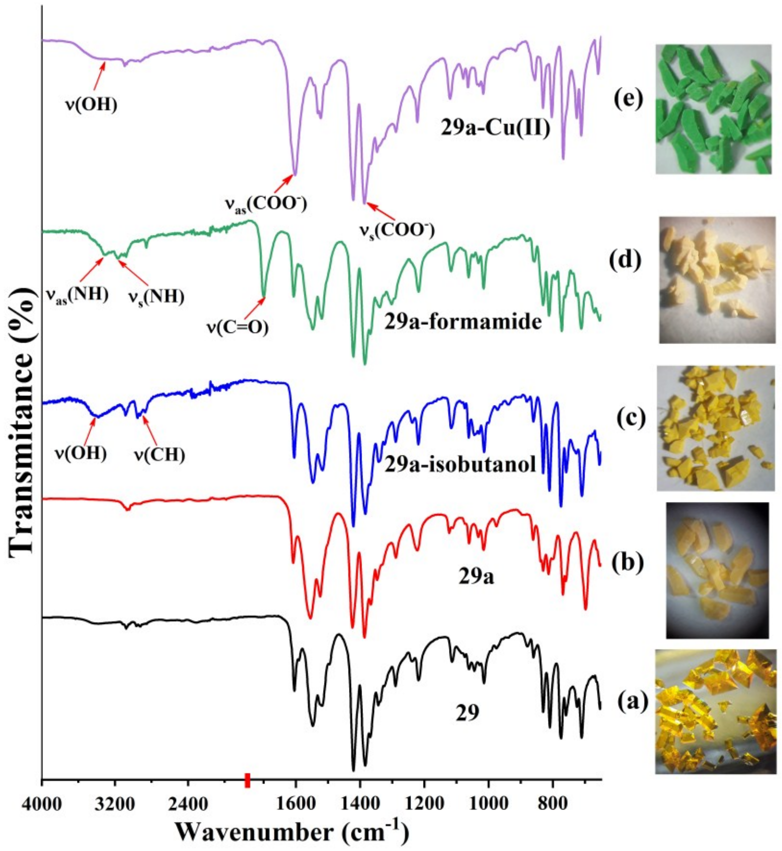


Fig. 16. IR spectra and images for compound 29 and its modified forms: (a) 29; (b) 29a activated; (c) 29a-isobutanol; (d) 29a-formamide; (e) product 29a-Cu(II).

4.2. Coordination polymers containing mono- and dicarboxylate ligands

The potential of various mono- and dicarboxylic acids in the formation of polymeric structures based on azine ligands was further investigated. The syntheses derived from the precursors indicated in Figure 17 resulted in eight *CPs*.

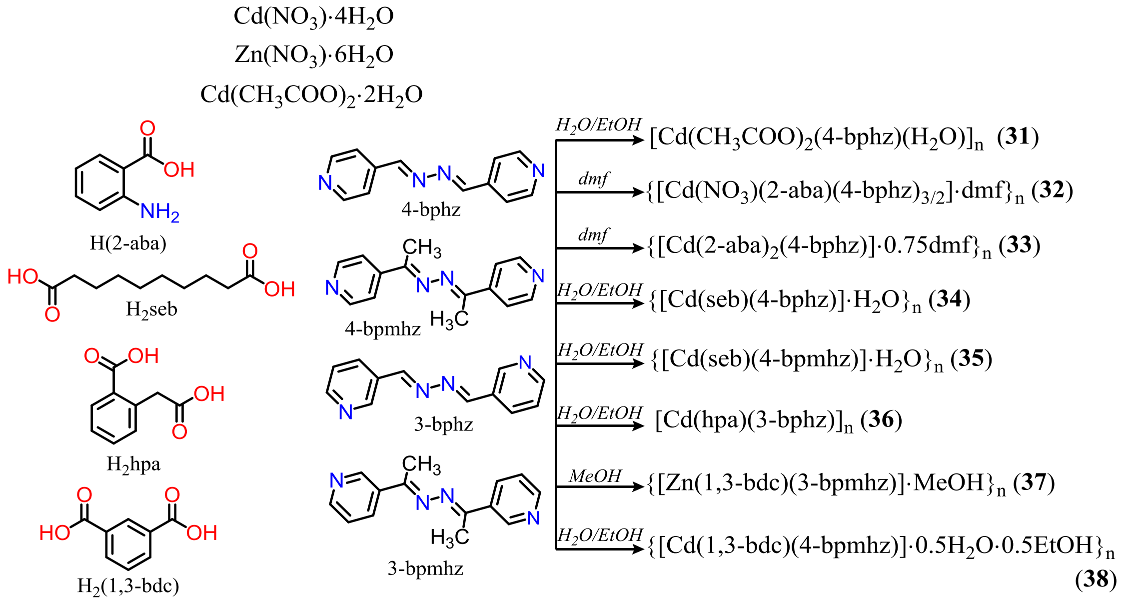
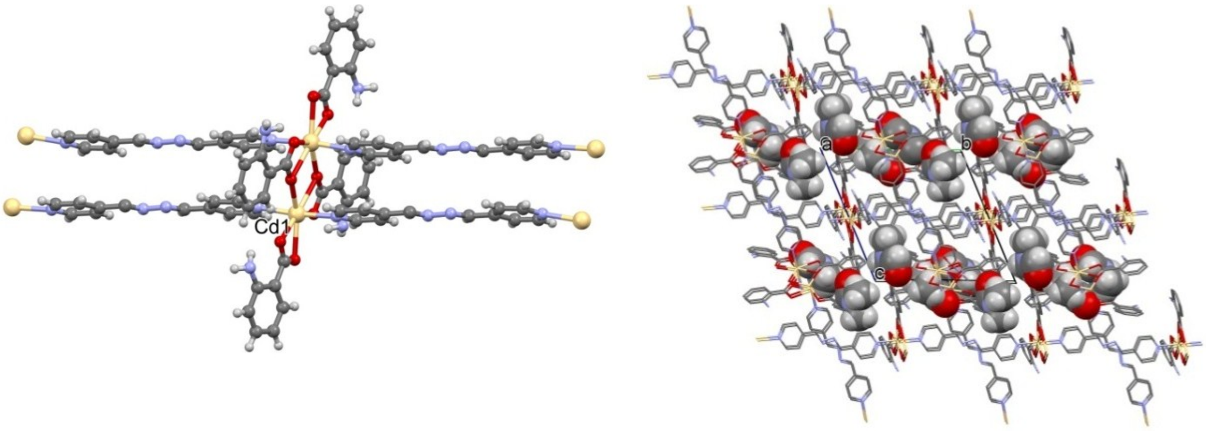
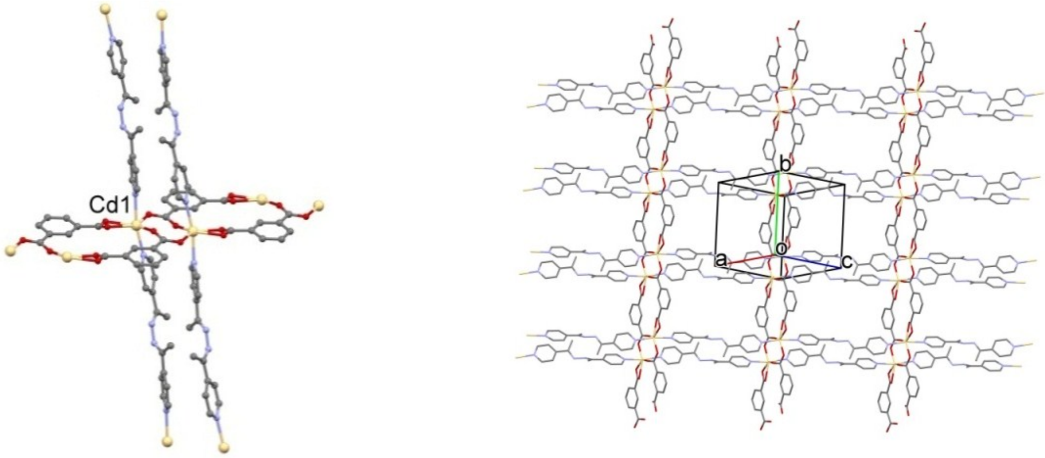


Fig. 17. Synthesis scheme of compounds 31-38.

Starting from the simplest monocarboxylated ligand, acetate, then using in the syntheses 2-aminobenzoic acid, were obtained *CPs* **31-33** with 1D structure. By replacing the monocarboxylate ligands with dicarboxylate ones originated from sebacic, homophthalic and isophthalic acids, were obtained 2D *CPs* **34-38**. The decisive role of the second carboxylic group in the structure extension is evident from *CP* 1D **33** with double chain type structure (Figure 18, a) together with the described structural analogs based on 2-thiophenecarboxylate, all compounds obtained with the use of monocarboxylic acids, look like structural precursors to 2D networks. The five 2D **34-38** isostructural networks are similarly constructed of double chain structures based on metal building blocks $[M_2(CO_2)_4]$ interconnected by azine ligands as double pillars (Figure 18, c, d). 2D networks host solvent molecules in the interlayer space. The favorable cross-packing of one-dimensional CP **33** with the inclusion of *dmf* molecules in the pores (Figure 18, b) allowed following the solvent exchange processes that took place without degradation of the coordination chains. Depending on the coordination modes of the carboxylate group, the stretching bands ν_{as} and ν_s are positioned at particular values in the spectrum, $\nu_{as}(COO^-) \sim 1550$ cm^{-1} and $\nu_s(COO^-) \sim 1380$ cm^{-1}. The characteristic band of azomethine groups $\nu(C{=}N)$ can be identified in the range ~ 1633–1608 cm^{-1}. Solvent molecules *dmf* show an intense band $\nu(C{=}O)$ at 1669 cm^{-1} for compound **33** and less intense band at 1663 cm^{-1} for **32**.



33 (a) **33 (b)**



38 (c) **38 (d)**

Fig. 18. (a) Fragment of the coordination chain in 33; (b) crystal packing indicating the *dmf* solvation molecules in 33; (c) fragment of the coordination network in 38; (d) representation of the coordination network in 38

The cross-packing of the double chains in compound **33** led to the formation of channels in which the *dmf* guest molecules are located. This compound has a structure similar to *CP* **29**, which has demonstrated the ability to replace guest molecules. This property was also investigated for compound **33**. For this purpose, the crystals of compound **33** were immersed in MeOH, EtOH and H_2O solvents. Post-synthetic changes were examined by IR spectroscopy and XRPD analysis (Figures 19, 20). The recorded IR spectra clearly indicated the replacement of the dimethylformamide molecules with those solvents. The ν(C=O) band disappeared from the spectrum, and the solvent molecules can be identified by the broad band ν(OH) in the region ~ 3500-3000 cm^{-1} and the band ν(C-O) at ~ 990 cm^{-1}. Changes in the stretching bands of the amino and carboxylate groups were also recorded, probably caused by the formation of hydrogen bonds with solvent molecules. Comparison of XRPD patterns indicates that the compound retains its crystallinity after these changes (Figure 20).

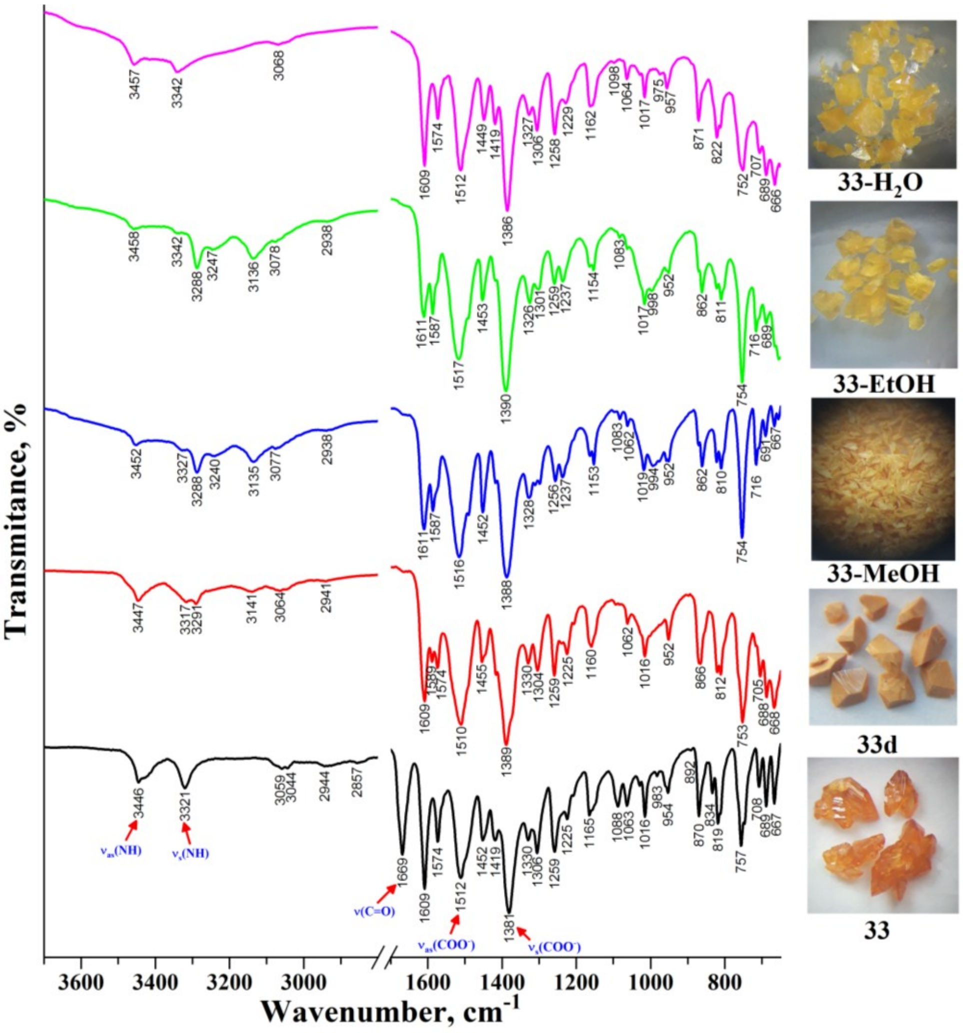


Fig. 19. IR spectra and crystal images for compound 33 and modified products 33d, 33-MeOH, 33-EtOH and 33-H$_2$O.

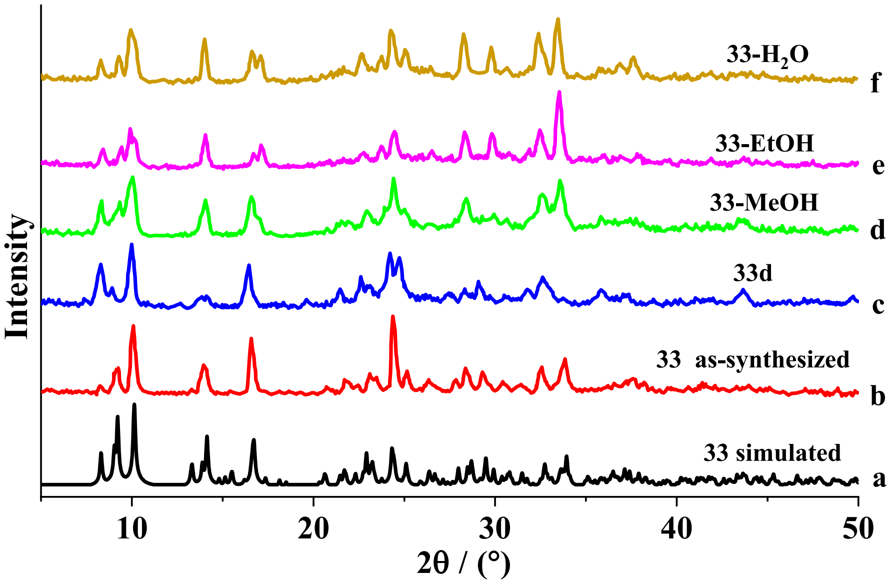


Fig. 20. PXRD diffractograms for compound 33 and modified products 33d, 33-MeOH, 33-EtOH and 33-H$_2$O.

4.3. Coordination polymers containing 4,4'-biphenyldicarboxylate ligand

The selection of spaced dicarboxylic ligands offers the possibility of obtaining structures with large cavities. Subsequently, the use of 4,4'-biphenyl dicarboxylic acid in combination with the methylated azine ligands *3-bpmhz*, *4-bpmhz* and azomethine *bda4bPy* resulted in three 3D *CPs* according to the scheme in Figure 21. A 3D *CP* of Cd(II) was obtained with the newly synthesized dicarboxylic azine ligand *4-dbahz*.

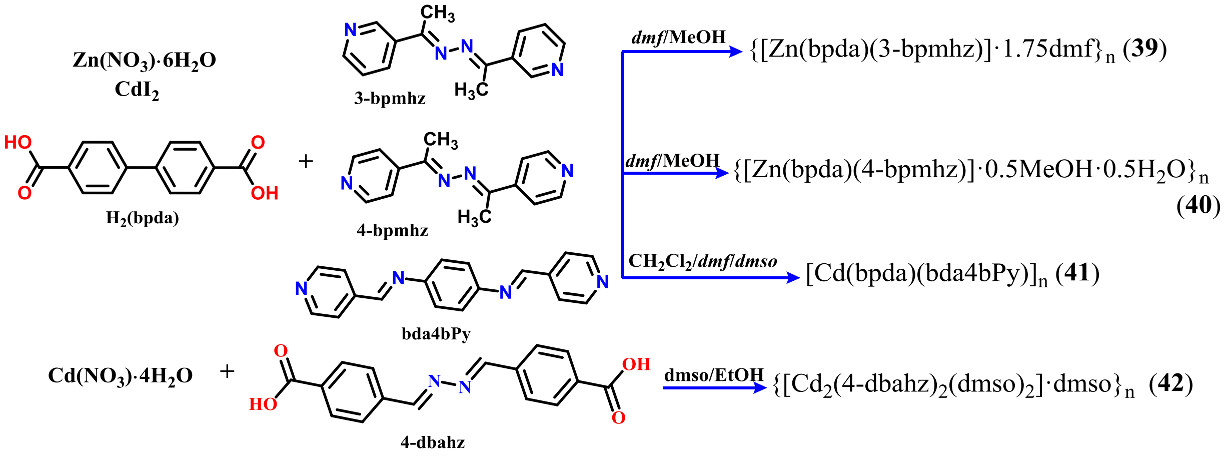
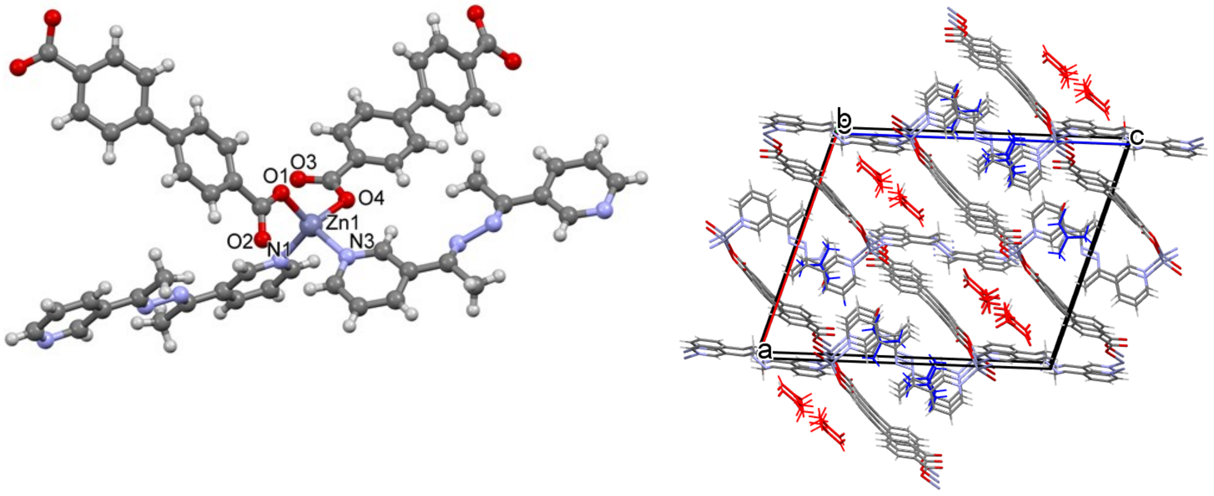


Fig. 21. Synthesis scheme of compounds 39-42.

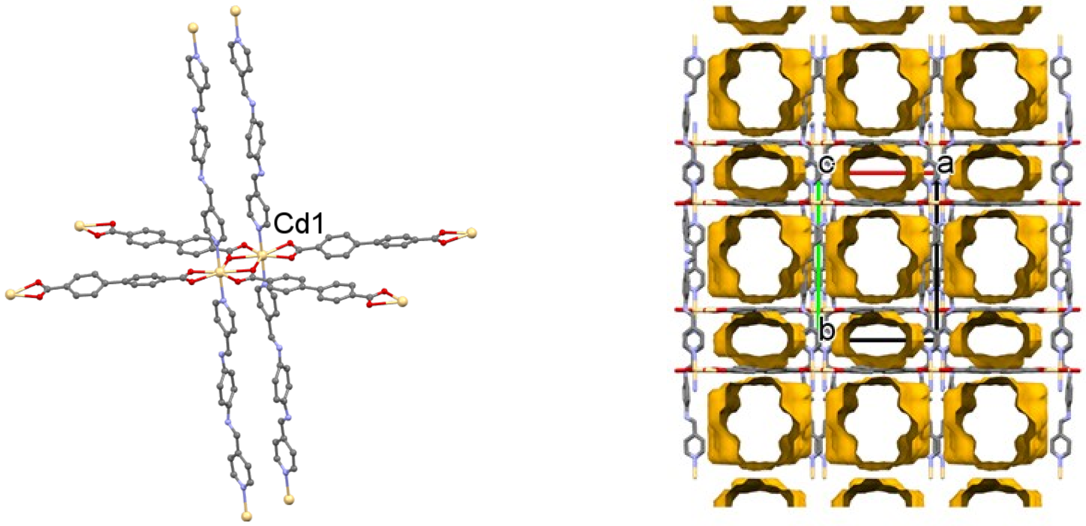
In compound **39** to each Zn(II) cation coordinate in monodentate modes two *bpda* carboxylate ligands and two *3-bpmhz* azine ligands. The Zn(II) cation adopts an N_2O_2 tetrahedral geometry (Figure 22, a) generating a 3D diamond-type network with large-channel which constitute 26,1% (842,74 Å^3) of the elementary unit cell volume (Figure 22, b) where *dmf* molecules are located.



(a) **(b)**

Fig. 22. (a) Coordination environment of Zn(II) cation in compound 39; (b) crystal packing indicating the included *dmf* molecules.

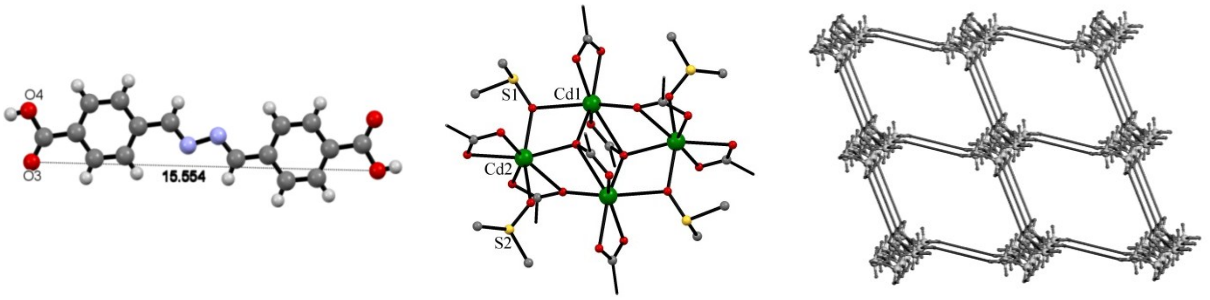
In compound **40** to the Zn cation coordinates three dicarboxylate ligands, one monodentate and the other two bidentate-bridging with the formation of the binuclear unit. They form a 2D zinc-dicarboxylate network, these networks are interlinked by azine ligands leading to the formation of the 3D network. The interpenetration of these networks has led to a significant reduction in the area accessible to the solvent. In compound **41**, similar to **40**, a 2D Cd-dicarboxylate network is formed containing binuclear clusters $[Cd_2(CO_2)_4]$, and the perpendicularly positioned *bda4bPy* pylon ligands form a three-dimensional network. These networks interpenetrate in the crystal and led to the formation of wide and narrow channels. The voids represent 39,7% or 1723,6 Å^3 of the elementary cell volume (Figure 23).



(a) **(d)**

Fig. 23. (a) Representation of the Cd (II) binuclear node in 41; (b) image of 3D networks indicating the areas accessible for solvent.

A new azinic dicarboxylic ligand 1,2-bis(benzoic-4-ylmethylene acid)hydrazine (***4-dbahz***) was obtained from the condensation reaction between 4-carboxybenzaldehyde and hydrazine sulfate (Figure 24, a). The reaction between *4-dbahz* and $Cd(NO_3)_2\cdot 4H_2O$ in the solvent mixture *dmso*:EtOH resulted in a 3D CP with the composition $\{[Cd_2(4\text{-dbahz})_2(dmso)_2]\cdot dmso\}_n$ (**42**). Compound crystallizes in the triclinic system. The coordination network is constructed of centrosymmetric tetranuclear clusters $[Cd_4(COO)_8]$ with Cd···Cd distances of 3,93, 3,98 and 6,62 Å. Each metal atom adopts a pentagonal-bipyramidal coordination geometry O_7 deriving from four *4-dbahz* ligands and a bridging *dmso* molecule for Cd1, and for Cd2 from three *4-dbahz* ligands and two *dmso* molecules, bridging and monodentate coordinated (Figure 24, b). Clusters connected by *4-dbahz* ligands led to a 3D network of the *α-Po* type (Figure 24, c).

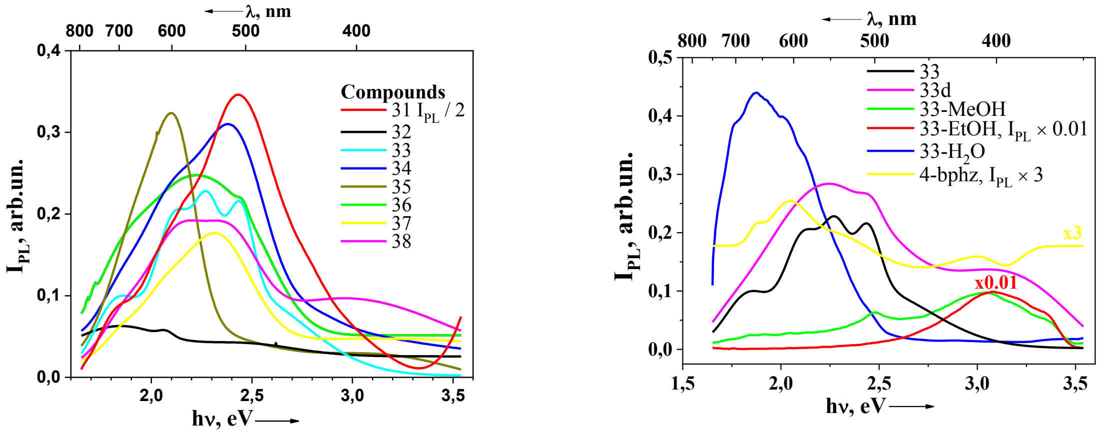


(a) **(b)** **(c)**

Fig. 24. (a) Structure of *4-dbahz* ligand; (b) structure of the tetranuclear cluster $[Cd_4(COO)_8]$ in compound 42; (c) fragment of 3D coordination network in 42.

4.4. Photoluminescent properties of compounds containing carboxylate anions

Comparative examination of photoluminescent spectra in the range of carboxylated compounds reveals low emissions that originate in crystal packing with arrangement of chromophores in ways unfavorable for strong emission and the presence of solvent-filled cavities. As we move from synthesized compounds to their desolvated forms, we observe the retention of profiles of the PL spectra for **32/32d**, **33/33d** and **37/37d** and the redistribution of emission peak position for **38/38d**, accompanied by a significant increase in emission intensity for desolvated forms which allow to suggest these systems as sensors for small molecules. Because the main emission intensity for samples **31-38** is concentrated in the range of 500-600 nm (Figure 25, a), they can be considered as useful materials for obtaining yellow and yellow-green light sources. The emission spectra for the solvent-exchanged forms of compound **33** show the sensitivity of this compound in the process of exchange of guest molecules, especially the compound shows a high selectivity for ethanol molecules (Figure 25, b). These measurements reveal that the compound could be applied in the field of sensors for the detection of small molecules.



(a) **(b)**

Fig. 25. PL spectra: (a) compounds 31-38; (b) compound 33 and its modified forms.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

1. Synthetic methods involving slow diffusion of reactants or slow evaporation of the solvent are effective for the synthesis of Zn(II)/Cd(II) coordination polymers with mixed azine/azomethine ligands such as N,N'-donors and various inorganic anions, or organic carboxylates. As a result, 42 coordination compounds were obtained, among which 21 compounds are 1D CPs, 11 are 2D CPs, 7 are 3D CPs and 3 binuclear compounds.
2. Analyzing the role of structural components in the extension of coordination polymers, it was established that azine/azomethine ligands play the bidentate bridging role, and the inorganic/organic anionic ligand plays a significant role in these reactant systems. Bulky iodide anions, coordinated monodentately to the metal, direct the coordination of azine bridging ligands in only one direction, with the formation of coordination chains (**1-6**). Nitrate anions also do not act in bridging mode, but there is a tendency towards the formation of 2D coordination networks for Cd(II) compounds (**10** and **11**). The sulfate anion as a polydentate ligand led to the formation of 2D and 3D networks (**13**, **15-19**). In compounds containing monocarboxylate ligands (**23-33**), single chains or double chains of ladder type are formed from building blocks $[M_2(CO_2)_4]$. In compounds with dicarboxylate ligands (**34-38**), the second carboxylate group connects the double chains and leads to the formation of 2D networks. Compounds containing the biphenyl dicarboxylate ligand (**39-42**) generate metal-carboxylate networks, which are further interconnected by N,N'-donor pylon ligands that led to the formation of 3D metal-organic networks. In compound **42**, the carboxylate groups and Cd(II) cations form tetranuclear clusters $[Cd_4(COO)_8]$, which are interconnected by dicarboxylate ligands to form the 3D network. In some cases it has been established that polar solvents such as *dmf* and water can prevent the coordination of bridging ligands to metal, thus impeding the formation of the coordination polymer (compounds **12**, **14** and **20**).
3. The possibility of forming, with these structural components, compounds with cavities containing included crystallization molecules has been demonstrated, so the cross-packing of the chains in 1D coordination polymers (**9**, **15**, **16**, **29**, **30**, **32** and **33**) led to the formation of channels, in 2D compounds (**11**, **23**, **34**, **35**, **37** and **38**) the networks packing generate channels or inter-layer cavities, and the packing of the 3D networks (**18**, **39-42**) also resulted in the formation of cavities with crystallization solvents. In 3D compound **41** voluminous voids were formed which occupy ~ 40% of the volume of the elementary cell.
4. It has been demonstrated that the photoluminescent activity in these series of compounds, containing Zn(II)/Cd(II) cations with complete electronic configuration d^{10}, is mainly determined by azine/azomethine ligands and dictated by crystal packing and luminophores placement. The series of iodides with compact crystal packing and without crystallization

solvents have higher intensities than the individual azine ligands. As the coordination structures extended to 3D networks, a significant decrease in PL emission was found, lower than the luminophore ligands, which originates from the less dense crystal lattice with the presence of cavities containing solvent molecules that work as emission quenchers. Desolvation of compounds containing inorganic anions reveals an insignificant increase in emission intensity. The emission curves in the iodide and nitrate series have similar profiles with maxima in the yellow region of the spectrum, and in the case of sulphates there is a shift towards the blue region in relation to the luminophore ligands. In the case of desolvated compounds containing carboxylate anions, the spectral profiles are retained or the position of the emission peaks is redistributed accompanied by a significant increase in intensity, which allows suggesting these systems as sensors for small molecules or yellow and yellow-green light sources.

5. For *CPs* 1D **29** and **33**, which contain wide channels, the selective absorption and exchange capacity of the guest molecules, such as the sorption of the molecules of isobutanol, formamide and water, methanol, ethanol, respectively, has been demonstrated. In compound **29** the exchange of Cd(II) cations with Cu(II) cations was demonstrated.
6. The chromatic particularity of colorless crystals **6** and **8** was demonstrated based on the conformational isomerism of azine ligand. The twisting of the ligand from the planar transoid conformation to the non-planar cisoid conformation around the N-N bond causes deformation of the conjugation system along the azine chain, leading to the absence of color for these crystals compared to the rest which are yellow-orange.
7. The study of thermoanalytic curves has shown that the thermal stability in these series of compounds is dependent on the nature of the anion. Thus, complexes with nitrate anions have low stability. Iodide-containing complexes decompose more slowly and at higher temperatures, and sulfate-containing complexes are most stable with more complex TG curve profiles.
8. The chemical stability of azomethine ligands has been elucidated. It has been shown that the azomethine bipyridine ligand under the conditions of synthesis undergoes solvolytic cleavage of the azomethine bond and leads to the formation of complexes with the azomethine pyridine derivative ligand. It has been established that the solvolysis reaction is a synthetic condition necessary to obtain complexes with this ligand.
9. The analysis of the IR spectra, recorded for the compounds, is in accordance with the information provided by the crystallographic data and indicates the particularities of coordination of ligands to metal. Thus, it was found that the monodentate coordination of the carboxylate group (**27** and **39**) shifts the $\nu_s(COO^-)$ band to smaller wave numbers (1360 cm^{-1}), in relation to the values for bidentate coordination (~ 1385 cm^{-1}). It was also found that this band is shifted to higher wave numbers (~ 1415 $cm-^1$) in compounds with aliphatic carboxylates (**31**, **34** and **35**).

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Patent application:

LOZOVAN Vasile, FONARI Marina, KRAVȚOV Victor, SIMINEL Nikita, COROPCEANU Eduard, KULIKOVA Olga, COSTRIUCOVA Natalia; *Polimer coordinativ unidimensional al cadmiului(II) în baza liganzilor 1,2-bis(piridin-4-ilmetilen)hidrazină și acid 2-aminobenzoic, care manifestă capacitate de schimb de solvenți și activitate fotoluminescentă*. Nr. 6732, 16 oct. 2020.

ADNOTARE

la teza cu titlul „**Sinteza și caracterizarea polimerilor coordinativi ai Zn(II) și Cd(II) în baza liganzilor punte azinici și azometinici**”, înaintată de pretendentul **LOZOVAN Vasile**, pentru conferirea gradului științific de doctor în științe chimice, la specialitatea 141.01. “Chimie Anorganică”.

Structura tezei: Teza a fost realizată în cadrul Institutului de Chimie, laboratorul Chimie Coordinativă. Lucrarea este scrisă în limba română și constă din introducere, 4 capitole, concluzii generale și recomandări, bibliografie din 264 de titluri, 126 pagini text de bază, 103 figuri și 4 tabele. Rezultatele obținute au fost publicate în 27 lucrări științifice, inclusiv: o cerere de brevet de invenție; 6 articole recenzate în reviste cotate în baza de date ISI și SCOPUS; 20 rezumate prezentate și publicate la Conferințe Naționale și Internaționale.

Cuvinte-cheie: sinteză, polimeri coordinativi, liganzi azinici și azometinici, structură cristalină, caracterizare spectroscopică, fotoluminescență.

Scopul lucrării constă în sinteza și caracterizarea polimerilor coordinativi în baza cationilor Zn(II)/Cd(II) și liganzilor punte azinici și azometinici de tipul N,N'-donori în comun cu diferiți liganzi anorganici și organici, studierea proprietăților fotoluminescente și de sorbție.

Obiectivele cercetării: sinteza polimerilor coordinativi în baza cationilor Zn(II)/Cd(II) utilizând liganzi punte azinici/azometinici de tipul N,N'-donori și diferiți anioni anorganici sau organici; studierea structurii cristaline și analiza rolului ligandului anionic și solventului în extinderea și modelarea structurii polimerice; funcționalizarea compușilor sintetizați prin procedee de eliminare sau substituire a moleculelor oaspete; investigarea stabilității termice și chimice; investigarea corelației structură-proprietate în funcție de liganzii componenți, în special în cazul manifestării proprietăților fotoluminescente și de sorbție.

Noutatea și originalitatea științifică: utilizând săruri anorganice de Zn(II)/Cd(II), liganzi punte azinici/azometinici și liganzi de tip carboxilat au fost obținuți, prin metoda difuziei lente a soluțiilor reactante sau evaporării lente a solventului, 42 compuși coordinativi dintre care 39 sunt cu structură polimerică uni-, bi- și tridimensională.

Problema științifică soluționată constă în identificarea materialelor cu structură poroasă, cu capacitate de sorbție a moleculelor mici și cu proprietăți fotoluminescente.

Semnificația teoretică constă în elucidarea modalității de autoasamblare a polimerilor coordinativi și stabilirea rolului ligandului anionic și solventului în extinderea și modelarea polimerilor coordinativi. De asemenea, a fost elucidată corelația structură-proprietate în compușii sintetizați și posibilitățile de ajustare a dimensiunii porilor în funcție de liganzii utilizați.

Valoarea aplicativă a lucrării constă în extinderea gamei de compuși cu structură poroasă în bază de polimeri coordinativi ai cadmiului(II) și zincului(II) cu proprietăți fotoluminescente și capacitate de sorbție și schimb a moleculelor de dimensiuni mici.

Implementarea rezultatelor științifice. Rezultatele științifice au fost utilizate parțial în procesul instructiv-educativ desfășurat în cadrul UST. Activitatea fotoluminescentă și capacitatea de sorbție și schimb ale moleculelor oaspete sugerează posibilitatea utilizării compușilor coordinativi cu structură poroasă în domeniul senzorilor pentru detectarea moleculelor de dimensiuni mici.

АННОТАЦИЯ

к диссертации „**Синтез и характеристика координационных полимеров Zn(II) и Cd(II) на основе азиновых и азометиновых мостиковых лигандов**”, представленной **ЛОЗОВАН Василием**, соискателем на степень доктора химических наук по специальности 141.01. “Неорганическая Химия”.

Структура диссертации: Диссертация выполнена в Институте Химии, в лаборатории Координационной Химии. Написана на румынском языке и состоит из введения, 4 глав, общих выводов и рекомендаций, библиографии из 264 наименований, 126 страниц основного текста, 103 рисунков и 4 таблиц. Полученные результаты опубликованы в 27 научных работах, в том числе: заявку на выдачу патента; 6 статей в рецензируемых журналах, включенных в базы данных ISI и SCOPUS; 20 тезисы докладов представлены и опубликованы на Национальных и Международных Конференциях.

Ключевые слова: синтез, координационные полимеры, азиновые лиганды, кристаллическая структура, спектроскопическая характеристика, фотолюминесценция.

Целью диссертации является синтез и характеристика координационных полимеров на основе катионов Zn(II)/Cd(II) и азиновых и азометиновых мостиковых лигандов типа N,N'-доноров, вместе с различными неорганическими и органическими лигандами, исследование эмиссионных и сорбционных свойств.

Задачи исследования: синтез координационных полимеров на основе солей цинка(II) и кадмия(II) с использованием метода смешанных лигандов, включая азиновые и азометиновые мостиковые лиганды типа N, N'-доноры и различные неорганические или органические анионные лиганды; изучение кристаллических структур новых соединений и исследование роли анионного лиганда и растворителя в расширении и моделировании полимерной структуры; функционализация синтезированных соединений процессами удаления или замещения гостевых молекул; исследование термической и химической стабильности; исследование корреляции структура-свойство по компонентным лигандам, особенно в случае проявления фотолюминесцентных и сорбционных свойств.

Научная новизна и оригинальность: начиная с неорганических солей цинка(II) и кадмия(II) и продолжая замещением неорганического аниона органическими анионами, было получено 42 координационных соединения на основе азиновых и азометиновых мостиковых лигандов, из которых 39 соединений имеют одно-, двух- и трехмерную полимерную структуру.

Решенной научной задачей является идентификация материалов с пористой структурой, способных поглощать малые молекулы и обладающих фотолюминесцентными свойствами.

Теоретическая значимость состоит в выяснении способа самосборки координационных полимеров и установлении роли анионного лиганда и растворителя в расширении и моделировании координационных полимеров. Также выяснены корреляция структура-свойство в синтезированных соединениях и возможности регулирования размера пор в зависимости от используемых лигандов.

Практическое значение диссертации заключается в расширении круга веществ с пористой структурой на основе координационных полимеров кадмия(II) и цинка(II), обладающих фотолюминесцентными свойствами и способностью к сорбции и обмену малых молекул.

Внедрение научных результатов. Научные результаты частично использованы в учебно-воспитательном процессе, проводимом в университете UST. Фотолюминесцентная активность, а также абсорбционная и обменная способность молекул-гостей предполагают возможность использования координационных соединений с пористой структурой в области сенсоров для обнаружения малых молекул.

ANNOTATION

to the thesis entitled „**Synthesis and characterization of coordination polymers of Zn(II) and Cd(II) based on azine and azomethine bridging ligands**”, submitted by the pretender **LOZOVAN Vasile**, for conferring the scientific degree of doctor in chemical sciences, specialty 141.01. “Inorganic Chemistry”.

Thesis structure: The thesis was conducted at the Institute of Chemistry, in the Coordination Chemistry laboratory. It is written in Romanian and consists of introduction, 4 chapters, general conclusions and recommendations, bibliography of 264 titles, 126 pages of basic text, 103 figures and 4 tables. The obtained results were published in 27 scientific papers, including: a patent application, 6 articles in peer-reviewed journals listed in the ISI and SCOPUS database and 20 abstracts presented and published at National and International Conferences.

Keywords: synthesis, coordination polymers, azine and azomethine ligands, crystal structure, spectroscopic characterization, photoluminescence.

The purpose of this thesis is synthesis and characterization of coordination polymers based on Zn(II)/Cd(II) ions and azine/azomethine bridging ligands of N,N'-donor type and additional various inorganic and organic ligands, study of photoluminescence and sorption properties.

Research objectives: synthesis of coordination polymers based on Zn(II)/Cd(II) ions using the technique of mixed coligands including azine and azomethine bridging ligands at type N,N'-donors and various inorganic or organic anionic ligands; studying the crystal structure and elucidation of the role of the anionic ligand and the solvent in the extension and modeling of the polymeric structure; functionalization of the synthesized compounds by elimination or substitution of the guest molecules; investigation of thermal and chemical stability; investigation of structure-property relationship, especially in case of photoluminescence and sorption properties.

Scientific novelty and originality: starting from inorganic salts of zinc(II) and cadmium(II) and continuing with the substitution of the inorganic anion with organic anions, 42 coordination compounds were obtained based on azine and azomethine bridge ligands, of which 39 reveal 1D, 2D and 3D-dimensional polymeric structure.

The solved scientific problem consists in identifying materials with porous structure, capable absorbing small molecules and having photoluminescent properties.

The theoretical significance consists in elucidating the way of self-assembly of coordination polymers and establishing the role of anionic ligand and solvent in the extension and modeling of coordination polymers. The structure-property correlation in the synthesized compounds and the possibilities of adjusting the pore size depending on the used ligands have been also elucidated.

The applicative value of the thesis consists in the extension of the range of substances with porous structure based on coordination polymers of cadmium(II) and zinc(II) with photoluminescent properties and capacity of sorption and exchange of small molecules.

Implementation of scientific results. The scientific results were partially used in the instructive-educational process carried out at UST. The photoluminescent activity and the absorption and exchange capacity of the guest molecules suggest the possibility of using coordination compounds with porous structure as sensors for the detection of small molecules.

LOZOVAN VASILE

SYNTHESIS AND CHARACTERIZATION OF COORDINATION POLYMERS OF Zn(II) AND Cd(II) BASED ON AZINE AND AZOMETHINE BRIDGE LIGANDS

141.01. INORGANIC CHEMISTRY

Summary of the doctoral thesis in chemical sciences

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