STUDIA UNIVERSITATIS MOLDAVIAE, 2014, nr.1(71)
Seria "Ştiinţe reale şi ale naturii" ISSN 1814-3237 ISSN online 1857-498X p.142-148

SYNTHESIS AND CARACHTERIZATION OF Zn AND Cd MONO- AND BINUCLEAR COMPLEXES CONTAINING OXIME LIGANDS

Eduard COROPCEANU

Institutul de Chimie al AŞM

New zinc and cadmium mono- and binuclear complexes containing dioxime ligands were synthesized. Due to Zn and Cd affinity for oxygen and nitrogen atoms a high diversity of complexes containing dioxime ligands with varied composition and interesting architecture can be prepared. The use of bridging ligands offers good perspectives for assembly of bi- and polynuclear compounds, study of various components impact on synthesis and opens new directions for oriented and programmed synthesis of compounds with predictable properties. In such a way the use of some chelate ligands which coordinate with metal perpendicularly to the axis connecting metal atoms make lighter the crystalline structure and create cavities which can be embedded with small molecules.

Keywords: *zinc, cadmium, oxime, coordination compounds, mononuclear, binuclear.*

SINTEZA ŞI CARACTERIZAREA COMPLECŞILOR MONO- ŞI BINUCLEARI AI Zn ŞI Cd CU LIGANZI OXIMICI

Au fost elaborate noi metode de sinteză a complecşilor mono- şi binucleari ai zincului şi cadmiului cu liganzi mono- şi dioximici. Afinitatea zincului şi cadmiului atât faţă de atomul de oxigen, cât şi faţă de cel de azot permite îmbinarea în complex a liganzilor cu diversitate înaltă, fapt ce conduce la obţinerea compuşilor coordinativi cu compoziţie variată şi arhitectură interesantă. Utilizarea liganzilor cu funcţie de punte deschide perspective de asamblare a compuşilor bi- şi polinucleari, iar studiul impactului diferitelor componente ale mediului de sinteză deschide perspectiva sintezei orientate şi porgramate a compuşilor cu proprietăţi predictibile. Utilizarea unor liganzi chelanţi, care coordinează la metal perpendicular axei ce leagă atomii metalici, „afânează" structura cristalină şi creează premise favorabile pentru crearea cavităţilor în care pot fi înglobate molecule cu dimensiuni mici.

Cuvinte-cheie: *zinc, cadmiu, oxime, compuşi coordinativi, mononuclear, binuclear.*

Introduction

Zinc and cadmium compounds with oxime ligands are poorly studied, despite the fact that based on them new complexes with a varied composition, molecular architecture and useful properties, such as: luminescence, biological activity can be assembled. In the literature there is a few information on zinc compounds with oxime ligands, as for the cadmium compounds the literature data are almost missing [18,14]. In the studied compounds, both monoximes and dioximes serve as ligands. The mononuclear zinc complexes with neutral mono- and dioximes have been synthesized and studied in the presence of organic and inorganic anions [2,9,16]. Pyridinealdoximes are versatile ligands which are comfortable for the assembly of polymer and cluster complexes [13]. The advantage of the 2-pyridinealdoxime consists in the fact that both nitrogen atoms of the ligand are bonded to the central atom and form a chelate with a higher stability in comparison with complexes containing 3- and 4-pyridinealdoxime. The donor atoms of the neutral pyridinealdoximes in metal complexes are both nitrogen atoms of oxime and pyridyl groups. But depending on the metal, the pyridinealdoximes coordinate differently. On the other hand, recently 1D and 2D coordination polymers obtained by coordination of the 4-pyridineamidoxime bridging function with Ag(I) and Cu(I) metal centers *via* both pyridine and oxime nitrogens were reported [15].

Phenanthroline-dicarbaldehyde dioxime complexes, which is a polydentate ligand with both metals proved to be potential agents for the hydrolysis of nucleic acid. In the case of cadmium nitrate interaction, the dioxime acts as a tetradentate ligand to form a pentagonal-bypiramidal structure. The dissociation of the oxime group into an oximate which acts as an anionic ligand has been observed within the interaction with zinc acetate, thus creating dimers and/or polymers [2]. The di- and trinuclear heterometallic complexes [3-5] containing zinc and classical or modified mono- and dioxime ligands, have been of great interest in the field of magnetochemistry for synthesis of uni-molecular magnets. The intensive study regarding the exchange interaction refers to the linear trinuclear complexes with the $d^5d^{10}d^5$ metal electron configuration. This objective was achieved by synthesizing the isostructural and isoelectronic linear $Cr^{III}Zn^{II}Cr^{III}$ and $Mn^{IV}Zn^{II}Mn^{IV}$ complex compounds containing three oximate anions as bridging ligand, where the central divalent metal ion is redox inactive. The use of oxime ligands can lead to a propeller-shaped structure in which two metal ions have deformed O_2N_4 coordination octahedral polyhedra, while the remaining ones are in a strongly distorted tetrahedral or trigonal-bipyramidal sphere [1,20].

Nowadays, the attention of researchers is pointed on preparation of complexes which posses chains with cavities where different molecules can be adsorbed. The chains formation is influenced by several factors, as follow, presence of the "guests", coordination mode of the metal atom, type of the present anion and metal-ligand relation. C. Papatriantafyllopoulou and co-workers [17] obtained successfully an 1D chain by combining the Zn metal center (or Cd) with the 2-pyridiloximic ligand which lead to an equatorial metal platform.

Our ideea to obtain complexes by combination of pyridine and carboxyl functions was supported by recent publications where some bi- and tetranuclear complexes with pyridinoxymic ligands are described [11,10]. The preparation of new mono- and binuclear complexes obtained by complexation of zinc and 3-pyridinealdoxime put in evidence some aspects of the influience under DNA structure [12].

Zinc and cadmium ions show different properties during the binding process to the oxygen, nitrogen and sulfur atoms. This fact presents a great interest as the domain of oxime chemistry but till now it is not sufficiently studied. Their geometry sphere can be tetra-, penta-, hexa-, hepta- or octahedral. Initially it was proposed to obtain mononuclear compounds with mono- and dioxime ligands. Further, based on various inorganic and organic bridging ligands it was proposed to obtain complexes with a low nuclearity, followed by coordination polynuclear compounds assembly.

Materials and General Procedures. All reagents and solvents were obtained from commercial sources and were used without further purification. Zink and cadmium complexes **1-15** were synthesized by interaction of their salts with oximic ligands (4-pyridinealdoxime, 4-pyridineamidoxime, 2-pyridinealdoxime or 1,2-cyclohexanedionedioxime) and with same organic ligands in case of complexes **10-15**, by heating and stirring in water, methanol and dimethylformamide [6-8]. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario El III elemental analyzer. The IR spectra were obtained in Nujol on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range of 400-4000 cm^{-1}. X-ray data were collected at room temperature on an Oxford Diffraction Xcalibur diffractometer equipped with CCD area detector and a graphite monochromator utilizing *Mo*Kα radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structures and to refine the model proposed were carried out with the programs SHELXS97 and SHELXL97 [19].

Results and Discussion

In order to obtain zinc and cadmium complexes was carried out a series of syntheses using various monoximes and dioximes as ligands. For example as monoximes 4-pyridinealdoxime (4-PyAO), 4-pyridineamidoxime (4-PyAmO) and 2-pyridinealdoxime (2-PyAO) were used. One of the objectives was to study the ability of coordination in the competition process between different functional groups (pyridine, oxime) from the molecules of heterofunctional ligands.

By interaction of the zinc acetate with 4-PyAO and 4-PyAmO (CH_3OH:DMF) in a 1:2 ratio the $[Zn(CH_3COO)_2(4\text{-}PyAO)_2]$ (**1**) and $[Zn(CH_3COO)_2(4\text{-}PyAmO)_2]$ complexes (**2**) have been synthesized (Fig.1) [7], wherein the central atom shows the coordination number 4. Besides the two acetate radicals to zinc atom two pyridine-oxime ligands are coordinated through the nitrogen atom of the pyridine groups. The IR spectra of these complexes confirm their structure by presence of characteristic for oxime group bands at: ~ 3350, 1699 to 1636 cm^{-1} ν (C=N), 939-929 cm^{-1} ν (NO). The presence of non-coordinating NH_2 groups in the molecule of compound **2** is proved by the presence of the signal at 3456 cm^{-1} in its IR spectrum. The bands corresponding to the oscillations of the aromatic ring are present at ~ 1600, 1100 cm^{-1}. The strong bands at ~ 1550 and 1405 cm^{-1} indicate the presence of the coordinated acetate ion.

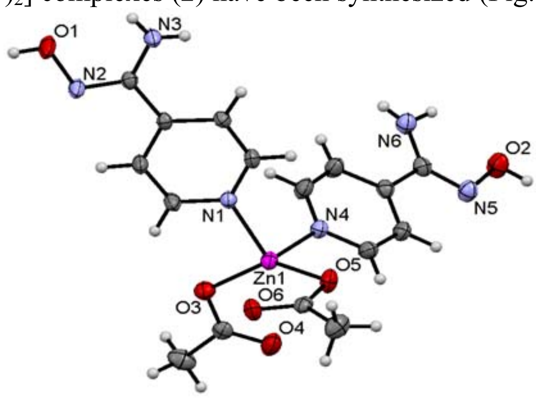


Fig.1. Molecular structure of the $[Zn(CH_3COO)_2(4\text{-}PyAmO)_2]$ complex.

The interaction of the cadmium acetate with 4-PyAO (CH_3OH:DMF) in a 1:3 ratio led to [$Cd(CH_3COO)_2$(4-PyAO)$_3$] complex (**3**), wherein the central atom shows the coordination number 5, consisting of three nitrogen atoms of the pyridine groups of the monoxime molecules and two oxygen atoms of the acetate radicals.

By the interaction of the cadmium acetate with 4-pyridialdoxime and 4-pyridineamidoxime have been synthesized the binuclear [$Cd_2(CH_3COO)_4$(4-PyAO)$_4$]·$2H_2O$ (**4**) and [$Cd_2(CH_3COO)_4$(4-PyAmO)$_4$]·DMF complexes (**5**), where the acetate ion plays the role of bridge (Fig.2). Due to the ability of the cadmium ion to have a high coordination number, in these two complexes to the complex generator coordinate seven atoms; two nitrogen atoms of the pyridine fragments of the oxime molecules and five oxygen atoms (four from two bidentate coordinate acetate radicals, and one from a coordinated bidentate oxygen atom to the neighbor cadmium atom). The presence of the amine group in complex (**5**) leads to the different molecules position in the crystal chain compared to (**4**).

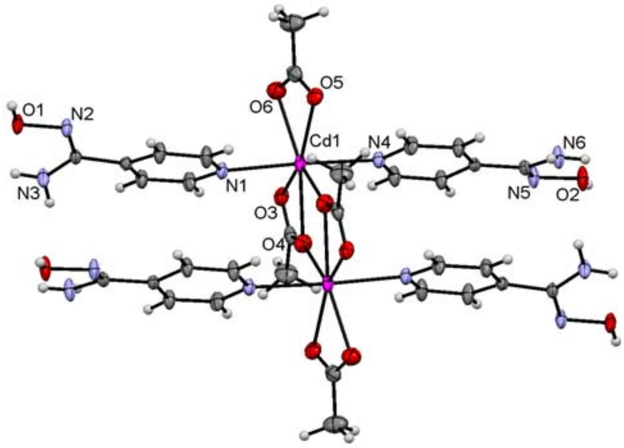


Fig.2. Molecular structure of the binuclear complex [$Cd_2(CH_3COO)_4$(4-PyAmO)$_4$].

In the IR spectra of these complexes there are present bands characteristic for the oxime group at ~ 3350, 1699 to 1636 cm^{-1}ν (C=N), 939-929 cm^{-1} ν (NO). In the spectra of the compounds (**2**) and (**5**), are observed signals at 3456 and 3406 cm^{-1}, respectively, indicating the presence of non-coordinating NH_2 groups. The bands corresponding to the oscillations of the aromatic ring are present at ~ 1600, 1100 cm^{-1}. The strong bands at ~1540 and 1405 cm^{-1} indicate the presence of coordinated acetate ion.

The use of chelate ligands involve oxime group in the formation of pseudo-metal cycles, and in such a way, by occupation of two coordination positions at the central atom leads to the modification of the steric factor which influences the spatial configuration of the complex. It has been noticed that in the case of coordination of two bidentate ligands, they can be placed in *cis*-position, a fact which may cause a cyclic structure, or a zig-zag form of the assembled complex. It has been decided to carry out the synthesis of zinc and cadmium complexes with chelate oxime ligands: 2-pyridinealdoxime and 1,2-cyclohexanedionedioxime. By the interaction of the cadmium formiate with 2-PyAO was assembled the mononuclear [$Cd(HCOO)_2$(2-PyAO)$_2$] complex (**6**), associated by intramolecular hydrogen bonds between the hydrogen atom of the oxime group and the oxygen atom of the formate radical (Fig.3) [6].

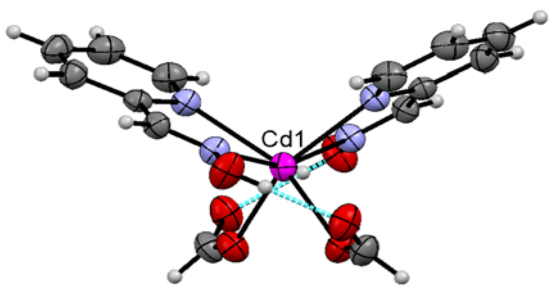


Fig.3. Structure of molecule [$Cd(HCOO)_2$(2-PyAO)$_2$].

The interaction of the zinc sulphate with 2-PyAO (CH_3OH:DMF) gave the [$(ZnSO_4)_2$(2-PyAO)$_4$] binuclear complex with a cyclic structure (**7**), wherein the sulphate anion has the bidentate bridging function.

The small number of zinc compounds with dioxime ligands and the lack of cadmium compounds is explained by the low affinity of these metal atoms to form bonds with oxime groups. To increase the efficiency of the synthesis it has been decided to use dioximes with rough frame where the oxime groups are in *cis* position which can easily form bonds with the metal atom. From this point of view, a suitable ligand is 1,2-cyclohexanedionedioxime. Based on cadmium formiate, acetate, and sulphate and zinc acetate, as well, we have been synthesized mononuclear [$Cd(HCOO)_2(NioxH_2)_2$] (**8**), [$Zn(SO_4)(NioxH_2)_2(H_2O)$]·DMF·$2H_2O$ (**9**), [$Cd(CH_3COO)_2(NioxH_2)(Im)_2$]·$H_2O$ (**10**), and [$Zn(NioxH)_2(An)_2$]·$4H_2O$ (**11**) complexes including 1,2-cyclohexanedionedioxime ($NioxH_2$) in neutral or monodeprotonated form [8].

In the complex $[Cd(HCOO)_2(NioxH_2)_2]$ (**8**) the cadmium ion has a N_4O_2 octahedral geometry sphere generated by the four nitrogen atoms which belong to the two $NioxH_2$ molecules and two carboxylic oxygen atoms which belong to the two formiate anions in *cis* positions. A pair of intramolecular hydrogen bonds formed between the OH-oxime groups and the non-coordinating oxygen atom of the formiate anion, strengthens the coordination polyhedron. The other two oxime groups are involved in the intermolecular hydrogen bonds which bind the molecules in an infinite chain (Fig.4).

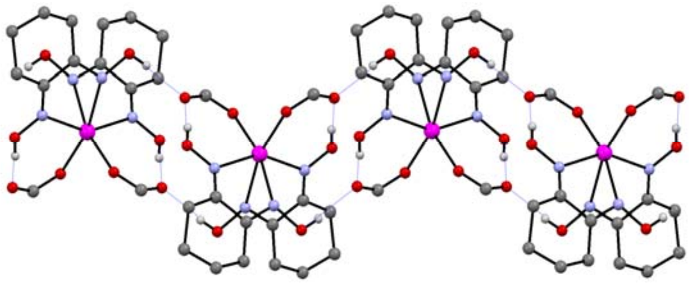


Fig.4. Chain built on the basis of the hydrogen bonds between the $[Cd(HCOO)_2(NioxH_2)_2]$ molecules.

In the $[Zn(SO_4)(NioxH_2)_2(H_2O)]{\cdot}DMF{\cdot}2H_2O$ complex the geometric sphere of zinc ion is formed by a set of N_4O_2 donor atoms (the nitrogen atoms belong to the two $NioxH_2$ neutral molecules in a *cis* arrangement, an oxygen atom of the monodentate coordinated sulphate anion and an oxygen atom of a water molecule). Each sulphate anion is involved in OH···O (SO_4^{2-}) hydrogen bonds with water molecules and the hydroxyl oxime groups of the neighbor complexes.

During the interaction of cadmium acetate, $NioxH_2$ and N,N'-carbonyldiimidazole, the latter was decomposed with the formation of the imidazole (Im) molecules which coordinated to the central atom forming the $[Cd(CH_3COO)_2(NioxH_2)(Im)_2]{\cdot}H_2O$ compound. The cadmium atom adopts the N_4O_2 distorted octahedral configuration, the basal plane of the metal is formed of $NioxH_2$ chelate molecule and two monodentate acetate anions which coordinate in *cis*- positions, while two *trans*-apical positions are occupied by two Im ligands. The rigidity of the base platform is provided additionally by the OH···O hydrogen bonds between the hydroxyl oxime groups and the oxygen atoms of the acetate anions. At the end of the study it has been stated that in the central atom coordination competition between $NioxH_2$ and imidazole, the last ligand causes the substitution of a dioxime molecule and the reorganization of the coordination polyhedron.

The $[Zn(NioxH)_2(An)_2]{\cdot}4H_2O$ complex is the first zinc bis-dioxime mononuclear compound which has in the coordination sphere two monodeprotonated NioxH residues (Fig.5). The octahedral coordination polyhedron of the zinc atom is filled up to the N_6 by the nitrogen atoms of the amine group of two aniline (An) molecules. The oxygen atoms of the oxime residues are linked by intramolecular hydrogen bonds of OH···O type. The aniline molecules in the complex are arranged above and below the basal plane of the complex. The self-assembly of the complexes in this structure takes place *via* the NH_2 group of the aniline molecule which is involved in hydrogen bonds with the oxygen atoms of the oxime group.

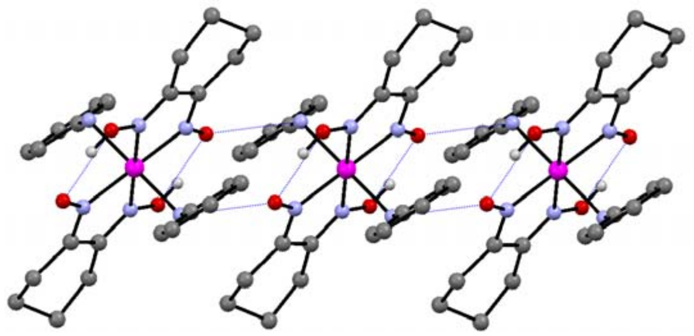


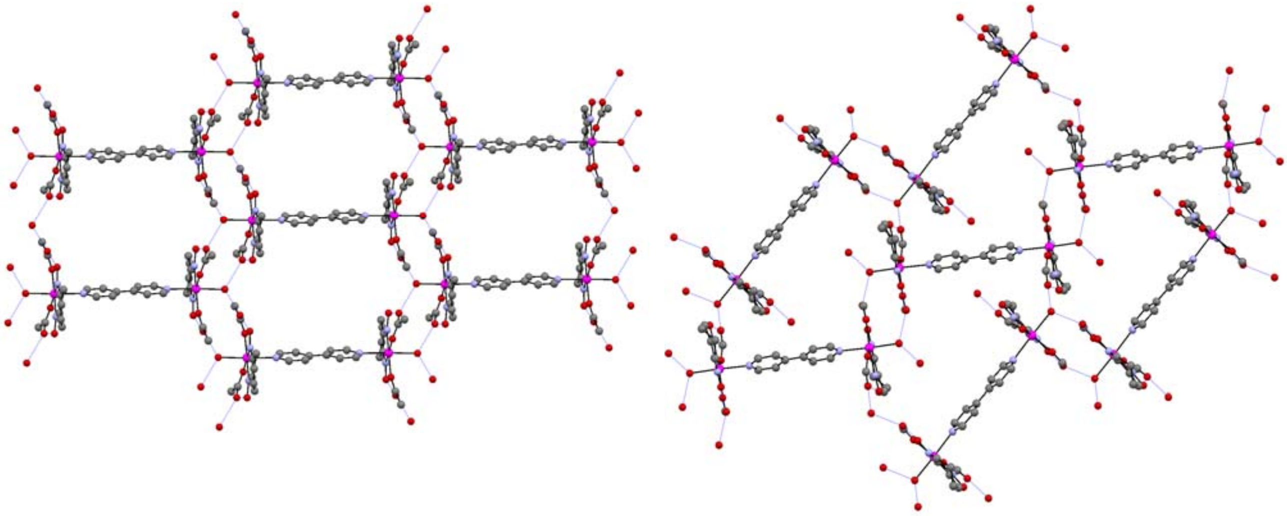
Fig.5. Chain fragment formed on the basis of hydrogen bonds in $[Zn(NioxH)_2(An)_2]{\cdot}4H_2O$.

The use of aniline molecules which contain amino group and can change the reaction medium allowed us to deprotonate the $NioxH_2$ molecule, fact which leads to the formation of intramolecular hydrogen bonds and to the arrangement of 1,2-cyclohexanedionedioxime monoanions in *trans* position.

One of the objectives was to vary the apical ligands. The strategy for the synthesis of zinc and cadmium compounds with oximes has evolved from the production of mononuclear compounds to bi- and polynuclear ones on the basis of some bridging ligands (inorganic anions, bidentate organic molecules, etc.).

As a result of the interaction in the $Zn(CH_3COO)_2/Cd(CH_3COO)_2/Cd(HCOO)_2$ – $NioxH_2$ – bpy/bpe (bpy – 4,4-bipyridyl; bpe – 1,2-bis(4-pyridyl)-ethane) system have been obtained $[Zn_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2(bpy)]$ (**12**), $[Cd_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2(bpy)]$ (**13**), $[Cd_2(HCOO)_4(NioxH_2)_2(H_2O)_2(bpy)]$ (**14**), $[Cd_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2(bpe)]$ (**15**) binuclear compounds. In compounds (**12-15**) the two metal atoms are bound by the bridging ligand (bpy/bpe). The basal plane of the coordination polyhedron is formed by the $NioxH_2$ molecule and two monodentate acetate/ formate anions. The neutral $NioxH_2$ coordinates in a bidentate typical way, through the oxime nitrogen atoms, forming a five-membered chelate ring with a complex generator. The apical positions are occupied by the oxygen atoms of water molecules.

The compounds (**12**) and (**13**) are isostructural. Between the non-coordinating oxygen atom of the acetate radical and the hydrogen atom of the oxime group are formed hydrogen bonds which strengthen the structure of the complex. Although the organization of the binuclear unit may not differ, the molecular packing in the crystal lattice in (**13**) and (**14**) is different (Fig.6). In water molecule (**13**) from the apical position of the metal polyhedron, being involved in hydrogen bonds with the oxygen atoms of the acetate anions, there are formed two cycles which give rise to an ordered layer, wherein each binuclear unit is engaged in eight OH···O hydrogen bonds and is connected with four neighbors symmetrically linked (Fig.6a). In binuclear molecules (**14**) linked by hydrogen bonds it is formed a 3D chain (Fig.6b).



a b

Fig.6. Components in crystal packing **13** (a) and **14** (b).

The IR spectra of the compounds (**12-14**) contain bands characteristic for the oxime group: ν(C=N) at 1600 cm^{-1}, ν(N–OH) in the range of 950-980 cm^{-1}. The bands in the region 1533-1606 cm^{-1} are attributed to the valence oscillations υ (C=N) of the oxime and partially overlap the sharp bands of medium intensity in the range of 1600–1200 cm^{-1} corresponding to the valence oscillations ν(C=C) and ν(C=N) of the bpy coordinated ligand. To this ligand it is also attributed the valence oscillation υ_s(C=C) to ~ 1491 cm^{-1}. The bands characteristic for the aromatic rings are seen in the region 820-600 cm^{-1}. The presence of acetate ions, evidenced by vibrations δ(CH_3) at 1431, 1335 cm^{-1} for **12**; 1342, 1320 cm^{-1} for **13**, as well as ρ_r(CH_3) 1040 (**12**), and 1035 cm^{-1} (**13**). In addition, there have been detected bands υ(COO) at 1537 (**14**), 1550 (**12**), and 1533 cm^{-1} (**13**), and also, π(COO) at 615-613 cm^{-1} for all three compounds. The M-O-C metal-ligand oscillations were recorded at ~ 1980 cm^{-1}, υ(M-O) + υ(C-C) at ~ 518 cm^{-1}, and υ(M-N) at ~ 420 cm^{-1}.

In the molecule of compound (**15**) the bridging role is played by the bpe bidentate ligand, which, due to the two CH_2 groups adopts the *trans* conformation with the C–CH_2–CH_2–C torsion angle of 180º and a parallel arrangement of the pyridine rings. The Cd…Cd distance along the bpe molecule is equal to 13.863 Å. Each cadmium cation is hexacoordinated, having the octahedral coordination polyhedron formed by the set of N_3O_3 atoms. The basal plane of the metal is defined by the $NioxH_2$ bidentate coordinated molecule and two monodentate coordinated acetate anions. The neutral $NioxH_2$ coordinates *via* its nitrogen oxime atoms, leading to the formation of the five-membered metal chelate ring in the metal coordination sphere.

The water molecules occupy the sixth position in the coordination polyhedron of the central atom. The Cd…Cd distance along the bpe molecule is equal to 13.863 Å.

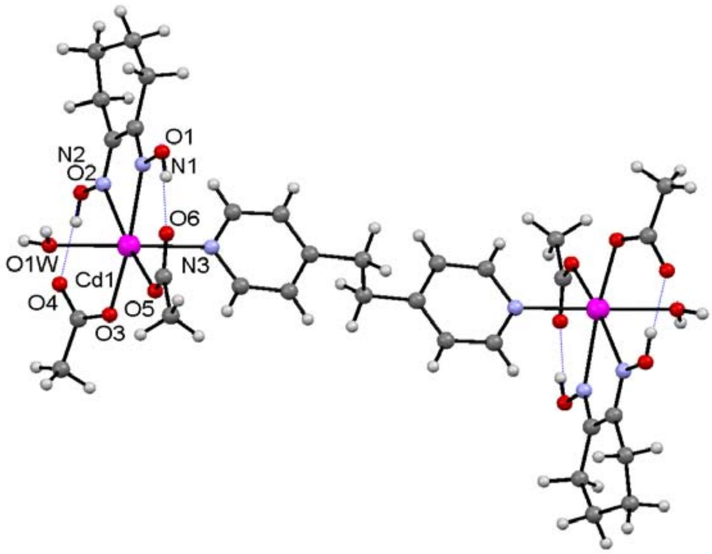


Fig.7. Structure of the $[Cd_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2(bpe)]$ binuclear molecule.

Each water molecule from the apical position acts as a double donor being involved in the hydrogen bonds with the oxygen atoms of the acetate anions *via* the two R_2^2 rings (**15**) joined by hydrogen. As a result it forms a chain bridged by hydrogen bonds, which is extended in the ab plane, wherein each binuclear molecule is involved in eight O–H···O hydrogen bonds and is connected to six neighbors symmetrically linked. The size of the cavities in the two-dimensional chain is 9.9 × 17.6Å. The layers are self-sealed so that each molecule may include its $NioxH_2$ fragment in the "pocket" of another layer.

Thus, the accumulated material allows us to make conclusions on modelling synthesis conditions for the oriented assembly of complexes with the required nuclearity degree.

Conclusions

In the interaction of the 3- and 4-pyridinealdoxime ligands with zinc and cadmium the coordination is carried out through the nitrogen atom of the pyridine fragment, but in the case of 2-pyridinealdoxime coordination the nitrogen atom of the oxime group participates as well. The vic-dioxime bidentate ligands coordinate through the nitrogen atoms of the oxime groups; however, for the substitution of the acetate or formiate ions it is required to create a basic environment in order to cause the deprotonation of the oxime groups. As a result, can be formed intramolecular hydrogen bonds between two dioxime monoanions with the formation of bis-dioximates. The use of bipyridine molecules and ions (acetate, formiate, and sulfate) allowed the development of the assembly strategy of the zinc and cadmium coordination compounds, evolving from the mononuclear to the binuclear complexes, but the exclusion of water molecules that block the chain extension creates favorable conditions for obtaining polymeric compounds. The $NioxH_2$ molecules coordinated in a chelate way stabilize the metal geometric area due to the participation of the hydroxyl groups to the formation of OH···O hydrogen bonds with the anions which hold non-coordinating oxygen atoms to metal, imposing to carboxylates the monodentate coordination mode. The bulky $NioxH_2$ molecule coordination refines the crystal structure, resulting in forming intermolecular cavities that can be embedded with small molecules.

Bibliography:

1. ALEXIOU, M., DENDRINOU-SAMARA, C., RAPTOPOULOU, C., TERZIS, A., KESSISSOGLOU, P. In: *Inorg. Chem*., 2002, 41, p.4732-4738. ISSN 0020-1669
2. ANGELOFF, A., DARAN, J.-C., BERNADOU, J., MEUNIER, B. The Ligand 1,10-Phenanthroline-2,9-dicarbaldehyde Dioxime can Act Both as a Tridentate and as a Tetradentate Ligand − Synthesis, Characterization and Crystal Structures of its Transition Metal Complexes. In: *Eur. J. Inorg. Chem.*, 2000, 9, p.1985-1996. ISSN 1099-0682

3. BIRKELBACH, F., WEYHERMULLER, T., LENGEN, M., GERDAN, M.,TRAUTWEIN, A., WIEGHARDT, K., CHAUDHURI, P. Linear trinuclear oximato-bridged complexes $Mn^{III,IV}M^{II}Mn^{III,IV}$ (M = Zn, Cu or Mn): synthesis, structure, redox behaviour and magnetism. In: *J. Chem. Soc., Dalton Trans.*, 1997, p.4529-4537. ISSN 1477-9226
4. BURDINSKI, D., BILL, E., BIRKELBACH, F., WIEGHARDT, K., CHAUDHURI, P. Long-Range Exchange Interactions and Integer-Spin S_t= 2 EPR Spectra of a $Cr^{III}Zn^{II}Cr^{III}$ Species with Multiplet Mixing. In: *Inorg. Chem.*, 2001, 40, p.1160-1166. ISSN 0020-1669
5. CHAUDHURI, P., WINTER, M., BIRKELBACH, F., FLEISCHHAUER, P., HAASE, W., FLOERKE, U., HAUPT, H. Long-range magnetic interactions between manganese centers separated by 7 A in $Mn^{III}Zn^{II}Mn^{III}$ and $Mn^{IV}Zn^{II}Mn^{IV}$ complexes. In: *Inorg. Chem*., 1991, 30, p.4291-4293. ISSN 0020-1669
6. COROPCEANU, E., CROITOR, L., FONARI, M. Mononuclear Cd(II) and Zn(II) complexes with 1,2-cyclohexane-dionedioxime ligand: preparation and structural characterization. In: *Polyhedron*., 2012, 38, p.68-74. ISSN 0277-5387
7. COROPCEANU, E., CROITOR, L., SIMINEL, A., FONARI, M. Preparation, structural characterization and luminescence studies of mono- and binuclear Zn(II) and Cd(II) acetates with pyridine-4-aldoxime and pyridine-4-amidoxime ligands. In: *Polyhedron*., 2014, 75, p.73-80. ISSN 0277-5387
8. CROITOR, L., COROPCEANU, E., JEANNEAU, E., DEMENTIEV, I., GOGLIDZE, T., CHUMAKOV, Y., FONARI, M. Anion-induced generation of binuclear and polymeric Cd(II) and Zn(II) coordination compounds with 4,4-bipyridine and dioxime ligands. In: *Crystal Growth & Design*, 2009, 9, p.5233-5243.
9. GOLDCAMP, M., KRAUSE BAUER, J., BALDWIN, M. Structural characterization of a zinc(II) complex of a tris(oxime)amine ligand. In: *J. Chem. Cryst.*, 2005, 35, p.77-83. ISSN 1074-1542
10. KATSOULAKOU, E., BEKIARI, V., RAPTOPOULOU, C., TERZIS, A., LIANOS, P., MANESSI-ZOUPA, E., PERLEPES, S. Dinuclear versus tetranuclear cluster formation in zinc(II) nitrate/di-2-pyridyl ketone chemistry: synthetic, structural and spectroscopic studies. In: *Spectrochim. Acta A Mol. Biomol. Spectrosc*., 2005, 61, 7, p.1627-38. ISSN 1386-1425
11. KONIDARIS, K., KAPLANIS, M., RAPTOPOULOU, C., PERLEPES, S., MANESSI-ZOUPA, E., KATSOU-LAKOU, E. Dinuclear versus trinuclear complex formation in zinc(II) benzoate/pyridyl oxime chemistry depending on the position of the oxime group. In: *Polyhedron*., 2009, 28, 15, p.3243-3250. ISSN 0277-5387
12. KONIDARIS, K., PAPI, R., KATSOULAKOU, E., RAPTOPOULOU, C., KYRIAKIDIS, D., MANESSI-ZOUPA, E. Synthesis, Crystal Structures, and DNA Binding Properties of Zinc(II) Complexes with 3-Pyridine Aldoxime. In: *Bioinorg. Chem. Appl*., 2010, p.803424-803431. ISSN 1565-3633
13. KRENO, L., LEONG, K., FAHRA, O. ALLENDORF, M., VAN DUYNE, R., HUPP, J. Metal-organic framework materials as chemical sensors. In: *Chem. Rev.*, 2012, 112, 2, p.1105-25. ISSN 0009-2665
14. LUO, Q.-Y., LI, M.-L., ZHONG, H., ZENG, X.-R.; YANG, X.-M. (Dimethylglyoxime-κ^2-N,N′)bis(1,10-phenanthroline-κ^2-N,N′)zinc(II) dinitrate dihydrate. In: *Acta Crystallogr.*, 2007, E63, m642-m644. ISSN 1600-5368
15. NANDY, M., BANERJEE, S., RIZZOLI, C., ZANGRANDO E., NONAT, A., CHARBONNIERE, L., MITRA S. Syntheses, structural diversity and photo-physical properties of copper(I) and silver(I) coordination polymers based on the pyridine-4-amidoxime ligand. In: *Polyhedron*., 2013, 65, p.252-261. ISSN 0277-538.
16. NICHOLSON, G., PETERSEN, J., McCORMICK, B. Comparison of the molecular structures of five-coordinate copper(II) and zinc(II) complexes of 2,6-diacetylpyridine dioxime. In: *Inorg. Chem.*, 1982, 21, p.3274-3280. ISSN 0020-1669
17. PAPATRIANTAFYLLOPOULOU, C., KOSTAKIS, G., RAPTOPOULOU, C., TERZIS, A., PERLEPES, S., PLAKATOURAS, J. Investigation of the $MSO_4 \cdot xH_2O$ (M=Zn, x=7; M=Cd, x=8/3)/methyl 2-pyridyl ketone oxime reaction system: A novel Cd(II) coordination polymer versus mononuclear and dinuclear Zn(II) complexes. In: *Inorg. Chem. Acta*, 2009, 362, p.2361-2370. ISSN 0020-1693
18. RUIZ, R., JULVE, M., FAUS, J., LLORET, F., MUNOZ, M., JOURNAUX, Y., BOIS, C. Ferromagnetic Coupling between Copper(II) Centers through the Diamagnetic Zinc(II) Ion: Crystal Structure and Magnetic Properties of $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]\cdot 0.5H_2dmg\cdot H_2O$ (H_2dmg = Dimethylglyoxime). In: *Inorg. Chem.*, 1997, 36, 16, p.3434-3439. ISSN 0020-1669
19. SHELDRICK, G. A short history of *SHELX*. In: *Acta Crystallogr.*, 2008, *A64*, 112-122.
20. SONG, J.-L., MAO, J., ZENG, H., KREMER, R., DONG, Z.-C. Synthesis, crystal structures and properties of two new metal complexes of syn-2-pyridinealdoxime with a "metallocrown" unit and a 1D double chain structure. In: *Inorg. Chem. Commun*., 2003, 6, p.891-895. ISSN 1387-7003

Prezentat la 04.06.2014