Vol. 8, No. 2, 2014

Chemistry

Ljudmyla Roman and Stepan Chundak

SYNTHESIS, STRUCTURE, AND CHARACTERISTIC OF Zn(II) AND Cd(II) COORDINATION COMPOUNDS WITH 3-METHOXYBENZENE ACID HYDRAZIDE AND THEIR BIOLOGICAL ACTIVITY

State Higher Educational Institution "Uzhhorod National University", 46, Pidhirna str., 88000 Uzhhorod, Ukraine; Iukachinec@ukr.net

Received: February 05, 2014 / Revised: February 11, 2014 / Accepted: March 26, 2014

© Roman L., Chundak S., 2014

Abstract. Zinc(II) and cadmium(II) coordination compounds with 3-methoxybenzene acid hydrazide have been received from the hot ethanol or hydra-ethanol solutions in slightly acidic environment. Composition of the synthesized complexes is suggested on the basis of chemical analysis and the study of electrical conductivity of their solutions. The structure of the coordination compounds is established with the help of ¹H NMR and IR-spectroscopy and thermogravimetry as well as quantum-chemical calculations in the approximation of PM3. Two molecules of organic ligand in amidohydrazonic form take part in the building of strong Zn(II) and Cd(II) coordination compounds with 3-methoxybenzene acid hydrazide. In this process their coordination with the central metal ion proceeds chelate-bidentately with the formation of C=O \rightarrow Me and Me \leftarrow NH₂ bonds. Octahedral surrounding of the central atom is added with anions of $(NO_3^- \text{ or } CI^-, \text{ respectively})$ acidic remains or with water molecule. The synthesized coordination compounds show antibacterial properties against microorganisms of the following strains: Acinetobacter baumanni, Sarcina flava, Pseudomonas aeruginosa, Streptococcus pneumoniae, and *Bacillus subtilis* as well as bacteriostatic properties against Escherichia coli, Salmonella typhimurium, Klebsiella pneumoniae, MRSA, Enterobacter cloaceae, and Klebsiella oxytoca.

Keywords: 3-methoxybenzene acid hydrazide, zinc coordination compounds, cadmium coordination compounds, structure of synthesized substances, biological activity.

1. Introduction

Due to their multifunctional characteristics carboxylic acids hydrazides are used in different fields of science. Firstly, these compounds are used as organic ligands for the synthesis of new coordination compounds [1-8] and as analytic form while analyzing some elements in the environmental objects [9, 10]. Secondly, hydrazides and their derivatives are well known biologically active substances used in medicine as therapeutic drugs [11, 12].

Despite the great number of literature data on the biological activity of carboxylic acids hydrazides, it should be noted that most of the works are dedicated to the investigation of composition, structure, and bioactivity of coordination compounds of 3d-metals with these organic ligands. Scientific publications on the research of the structure and biological activity of coordination compounds of carboxylic acids hydrazides with *p*-elements are found in a limited number.

The purpose of this work is the synthesis and identification of coordination compounds of zinc(II) and cadmium(II) with 3-methoxybenzene acid hydrazide, study of their chemical composition, structure, coordination of donor atoms to the central metal ion and tautomeric form of the ligand, and study of biological activity of synthesized coordination compounds.

2. Experimental

Chlorides and nitrates of zinc(II) and cadmium(II) (ZnCl₂, CdCl₂·2,5H₂O, Zn(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O) "chemically pure" type are used in the work. 3-Methoxybenzene acid hydrazide (L-C₈H₁₀N₂O₂) is synthesized by the action of 3-methoxybenzene ethyl ester ("chemically pure" type) on the hydrazine-hydrate ("chemically pure" type) by the method [13]. The resulting products are identified by the results of ¹H NMR, IR-spectroscopic methods.

Synthesized compounds brought to the air-dry state were subjected to the analysis of the nitrogen, carbon, hydrogen, and chlorine metal content. While determining the metal, the sample of the complex was discomposed when heated with a mixture of concentrated nitric and sulfuric acids, after which the metal content was defined according to the known method of complexometric titration [14]. Nitrogen was defined according to the Dumas method [15], carbon and hydrogen – by the Pregl method [15], and chlorine – by the volume method with the previous burning of the sample in oxygen [15].

[Zn(L)₂NO₃H₂O]NO₃ (I). The complex was received when combining 1.5 g of Zn(NO₃)₂·6H₂O hot ethanol solution and 1.7 g of 3-methoxybenzene acid hydrazide (molar ratio M:L=1:2). After 24 h white needle-shaped crystals were educed, which were filtered on the Schott filter, washed with alcohol, diethyl ether and dried in the air. The yield is 65 % of the theoretical one. The compound is well-soluble in DMF and DMSO, poorly in water, acetone and ethanol, and insoluble in benzene, toluene, and chloroform $T_m = 393$ K.

[Zn(L)₂Cl₂]H₂O (II). To hot aqueous solution containing 1.5 g of zinc dichloride hot alcohol solution of 3.4 g 3-methoxybenzene hydrazide was added. After cooling for 24 h transparent small crystals of white color were educed, which were filtered on the Schott filter, washed with ethanol and diethyl ether and dried in the air. The yield is 74 % of the theoretical one. The precipitate is well soluble in DMF and DMSO, poorly soluble in water and ethanol, and insoluble in benzene, acetone, and chloroform. T_m = 408 K.

[Cd(L)₂NO₃H₂O]NO₃ (III). The complex is synthesized when combining 3.1 g of Cd(NO₃)₂·4H₂O heated ethanol solutions and 1.7 g of 3-methoxybenzene hydrazide (molar ratio of reacting substances is 1:1). The total volume of the solution is 10.0 cm³. After 24 h needleshaped crystals of white color were educed, which were filtered on the Schott filter, washed with ethanol and diethyl ether and dried in the air. The yield is 66 % of the theoretical one. The precipitate is well soluble in DMF and DMSO, poorly soluble in water and ethanol, and insoluble in acetone, benzene, and toluene. T_m = 493 K (flash).

[Cd(L)₂Cl₂]H₂O (IV). The compound is received when combining 2.3 g of heated water-ethanol solutions CdCl₂·2.5H₂O (in 3 cm³ of water) and 1.7 g of 3-methoxybenzene hydrazide (in 5.0 cm³ of ethanol). Molar ratio of the reacting substances is 1:1. The total volume of the solution is about 10.0 cm³. After 24 h white needle-shaped crystals were educed, which were filtered on the Schott filter, washed with ethanol and diethyl ether and dried in the air. The yield is 73 % of the theoretical one. The precipitate is well soluble in DMF and DMSO, poorly soluble in water, ethanol, and acetone, and insoluble in benzene, toluene, and chloroform. T_m .= 383 K.

It should be noted that when the ratio of the reactants is 1:1 or 1:2 we have coordination compounds of the same composition.

The electrical conductivity of solutions of the investigated complexes is defined by the mobility of ions (at the concentration of $(1 \cdot 10^{-3})$ – $(1 \cdot 10^{-7})$ M), included in the compound [16]. When defining the electrical conductivity weak alternating currents of high frequency were used.

The structure of coordination compounds is suggested on the basis of comparison of the IR spectra of non-coordinated ligand and synthesized compounds, which were registered in KBr pellets on the UR-20 device, and the comparison of the ¹H NMR spectra registered in DMSO-D6 by Bruker spectrometer (200 MHz) with the TMS internal standard.

The thermal stability of the synthesized coordination compounds is studied with the help of the "Q-1500D" derivatograph of the Paulik-Paulik-Erdei system with the registration of the analytical signal of weight loss and thermal effects by the computer. Thermogram images are taken in dynamic mode with the heating rate of 5°/min in argon atmosphere. Its weight is 100 mg.

Taking into consideration the amorphism of the synthesized coordination compounds, the study of their spatial structure was conducted with the help of semiempirical (PM3) method [17] using a range of quantum chemical programs "HyperChem-8.0.8.". Semi-empirical calculations were carried out with complete optimization of geometrical parameters (the norm of the gradient does not exceed 4.19 J/mol) in the approximation to the limited Hartree-Fock method (excluding electronic correlation) [18]. The probability of correctness of results of quantum-chemical calculations is carried out by the comparison of the obtained numbers with experimental ones.

3. Results and Discussion

Table 1 presents the results of the chemical analysis of the studied coordination compounds and proposes empirical formula complexes.

The research of molar electrical conductivity of the synthesized compounds showed that the substances $(\lambda = 41.8 \text{ ohm}^{-1} \cdot \text{cm}^2)$ $[Zn(L)_2Cl_2]H_2O$ (II) and $[Cd(L)_2Cl_2]H_2O$ (IV) ($\lambda = 57.4$ ohm⁻¹·cm²) are nonelectrolytes and $[Zn(L)_2NO_3H_2O]NO_3$ $(\lambda =$ $ohm^{-1} \cdot cm^2$ = 152.0and $[Cd(L)_2NO_3H_2O]NO_3$ $(\lambda = 138.5 \text{ ohm}^{-1} \cdot \text{cm}^2)$ are two-ion electrolytes [19].

It should be noted that interaction of argentums nitrate $(AgNO_3)$ with solutions of $[Zn(L)_2Cl_2]H_2O$ and $[Cd(L)_2Cl_2]H_2O$ does not lead to AgCl precipitation. Based on the results of the chemical analysis of molar electrical conductivity of the studied compounds one can conclude that chlorine atom in chloride complexes (II) and (IV) is included in the internal coordination sphere.

| М, | Content of elements, % | | | | | | | | | |
|--|------------------------|--------|------------|--------|------------|--------|------------|--------|------------------|--------|
| g/mol | М | | С | | Н | | N | | Cl | |
| | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. |
| | | | | | | | | | | |
| 166.18 | 57.67±0.02 | 57.82 | 5.96±0.02 | 6.07 | 16.72±0.03 | 16.86 | - | - | 57.67±0.02 | 57.82 |
| $[Zn(L)_2NO_3H_2O]NO_3$ | | | | | | | | | | |
| 539.76 | 12.04±0.02 | 12.11 | 35.43±0.02 | 35.60 | 3.97±0.01 | 4.11 | 15.41±0.03 | 15.57 | - | - |
| $[Zn(L)_2Cl_2]H_2O$ | | | | | | | | | | |
| 486.75 | 13.31±0.02 | 13.43 | 39.27±0.03 | 39.48 | 4.39±0.03 | 4.56 | 11.43±0.02 | 11.51 | 14.46 ± 0.02 | 11.51 |
| [Cd(L) ₂ NO ₃ H ₂ O]NO ₃ | | | | | | | | | | |
| 586.8 | 19.11±0.04 | 19.15 | 32.70±0.03 | 32.75 | 3.74±0.02 | 3.78 | 14.27±0.04 | 14.32 | - | - |
| $[Cd(L)_2Cl_2]H_2O$ | | | | | | | | | | |
| 533.78 | 20.92±0.03 | 21.06 | 35.87±0.02 | 36.00 | 3.96±0.02 | 4.15 | 13.18±0.02 | 13.30 | 10.39 ± 0.01 | 10.50 |

The results of the chemical analysis of complex compounds of 3-methoxybenzene hydrazide with nitrates and chlorides of zinc(II) and cadmium(II)

Table 2

Characteristic frequencies of stretching vibrations of groups of atoms of zinc(II) and cadmium(II) with 3-methoxybenzene hydrazide studied compounds

| v(NH) | $v_{as}(NH_2)$ | $v_s(NH_2)$ | $v(H_2O)$ | v(C=O) | $v(NO_3)$ | v(Me-O) | v(Me-N) | |
|-------------------------|--|-------------|------------|--------|------------------|---------|---------|--|
| | L | | | | | | | |
| 3350 | 3250 | 3155 | - | 1670 | - | - | — | |
| | [Zn(L) ₂ NO ₃ H ₂ O]NO ₃ | | | | | | | |
| 3256 | 3200 | 3072 | 3604, 3410 | 1632 | 1388, 1356, 1320 | 492 | 588 | |
| $[Zn(L)_2Cl_2]H_2O$ | | | | | | | | |
| 3264 | 3176 | 3064 | 3610 | 1628 | - | 484 | 624 | |
| $[Cd(L)_2NO_3H_2O]NO_3$ | | | | | | | | |
| 3232 | 3140 | 3046 | 3604, 3404 | 1636 | 1380, 1340, 1305 | 528 | 604 | |
| | $[Cd(L)_2Cl_2]H_2O$ | | | | | | | |
| 3272 | 3202 | 3060 | 3612 | 1632 | _ | 484 | 596 | |

Table 3

The data of ¹H NMR spectroscopy of 3-methoxybenzene hydrazide acid and Zn²⁺ and Cd²⁺ complexes

| Compound | δ , m.f., J, Hz |
|-------------------------|--|
| L | 4.503 m (2H,NH ₂); 7.061, 7.382 m (1H,C ₆ H ₄ OCH ₃); 9.776 m (1H,NH) |
| $[Zn(L)_2NO_3H_2O]NO_3$ | 6.075 m (2H,NH ₂); 7.215, 7.474 m (1H,C ₆ H ₄ OCH ₃); 11.212 m (1H,NH) |
| $[Zn(L)_2Cl_2]H_2O$ | 5.456 m (2H,NH ₂); 7.181, 7.437 m (1H,C ₆ H ₄ OCH ₃); 10.540 m (1H,NH) |
| $[Cd(L)_2NO_3H_2O]NO_3$ | 5.407 m (2H,NH ₂); 7.181, 7.420 m (1H,C ₆ H ₄ OCH ₃); 10.583 m (1H,NH) |
| $[Cd(L)_2Cl_2]H_2O$ | 4.831 m (2H,NH ₂); 7.097, 7.388 m (1H,C ₆ H ₄ OCH ₃); 10.052 m (1H,NH) |

Peculiarities of the structure of zinc(II) and cadmium(II) coordination compounds with 3-methoxybenzene hydrazide are grounded on results of the methods of ¹H NMR, IR-spectroscopy, gravimetry, X-ray diffraction, and quantum-chemical calculations.

IR-spectra of the organic part of the investigated complexes and non-coordinated ligand have a significant number of intense absorption bands. Some important from the point of view of coordination of the ligand to the central ion, characteristic frequencies of stretching vibrations of the investigated compounds, as well as of non-coordinated organic ligand are presented in Table 2. The study of IR-spectra of the free ligand and synthesized coordination compounds has shown that in the area of $3000-3400 \text{ cm}^{-1}$ in IR-spectra of the complexes a complex of absorption bands is shown, which are strongly shifted (to 36–83 cm⁻¹) toward the low-frequency region in comparison with the spectrum of non-coordinated ligand [20] due to the participation of amino group in complex-forming.

In the area of 1500–1700 cm⁻¹ the high frequency bands around 1610–1636 cm⁻¹ corresponds to the socalled "amide-I" band. In the spectra of the free noncoordinated organic ligand this band corresponds to the

125

Table 1

frequency of 1670 cm⁻¹. The amide-I band shifts to the region of low frequencies in the case of the investigated complexes is 34-42 cm⁻¹, which may be explained by participation of the carbonyl group C=O in the coordination of the central atom.

In the area of 3600 cm^{-1} absorption bands are observed, which are characteristic of water molecules vibrations, which is a part of the internal sphere of the complex, at frequencies of about $3404-3410 \text{ cm}^{-1}$ – the characteristic vibrations of interior-sphere water molecules.

The position of the nitrate-anion (NO₃⁻) in IR-spectra of $[Zn(L)_2NO_3H_2O]NO_3$ and $[Cd(L)_2NO_3H_2O]NO_3$ coordination compounds is observed in the form of intensive split lines into two components at 1400, 1380, and 1330 cm⁻¹ to indicate the interior-sphere coordination of the anion to the central atom [20]. The monodentate coordination is the most likely.

In IR-spectra of coordination compounds in the area of 480–600 cm⁻¹ the intensive bands of stretching vibrations of Me-N and Me-O bonds (where Me is Zn or Cd) appear on the background of skeletal vibrations of organic ligand. The stretching vibrations of phenolic groups were not considered because they are not informative in terms of complex-forming.

For studying of the structure of the synthesized coordination compounds the ¹H NMR spectra of coordination compounds and non-coordinated organic ligand have been studied and compared [21], because they can be used to characterize the position of the hydrogen atoms in the molecules of substances, as well as their number. Some of the bands in the ¹H NMR spectra characteristic from the complex-forming point of view are presented in Table 3.

Analysis of ¹H NMR spectra confirms the results of IR-spectroscopy. The displacement of absorption of the NH-protons (for 0.33–1.57 m.f.) and NH₂-groups (for 0.28–1.23 m.f.) in the ¹H NMR spectra of the studied coordination compounds in the region of strong field compared with the absorption bands of the same groups in ¹H NMR spectrum of non-coordinated ligand is noted, which testifies to the participation of 3-methoxybenzene hydrazide acid in complex-forming through the NH₂-group and the central metal ion in complexes is formed without the replacement of hydrogen atoms as the number of protons of free ligand and organic part of the synthesized coordination compounds is the same.

The study of coordination compounds in the field of gravimetry is conducted in the argon atmosphere using "Q-1500D" derivatograph with the registration of an analytical signal of weight loss and thermal effects by computer. According to the results of thermogravimetric studies (on the example of $[Zn(L)_2NO_3H_2O]NO_3$ complex) compounds have a high thermal stability [22]. Thermal decomposition of the investigated compound (Fig. 1) starts at 433 K, then there is a gradual weight loss, which is accompanied by endothermic effects at 433, 538, 693, 903 and 1113 K.

The process of the studied substance decomposition is preceded by the sample melting (endothermic effect on the DTA curve with the minimum at 333 K respectively, without weight loss). Dehydration of the complex takes place in the temperature range of 373–433 K, with the substance weight loss by 3.33 %. Final weight of the investigated compounds is 15.06 %, which corresponds to the percentage of zinc oxide (ZnO). One can make the assumption that $[Zn(L)_2NO_3H_2O]NO_3$ complex decomposition is a thermo-oxidative destruction of ligand with the participation of nitrate-group (NO₃⁻).

For the objective establishing of the structure of the studied coordination compounds X-ray structural analysis of complex cadmium isosorbide with 3-methoxybenzene hydrazide acid was performed, the results of which were described earlier in [23]. It is established that the compound consists of complex cation $[Cd(L)_2NO_3H_2O]^+$ and nitrate-ion in the external coordination sphere. Cadmium coordination polyhedron has the geometry of a deformed octahedron and includes two hydrazide ligands connected chelately with the central atom through the nitrogen atom of amino group and the oxygen atom of carbonyl group. The fifth coordination place is taken by water molecule, the sixth –by oxygen atom of nitrate group, which is part of the internal sphere of the complex.



Fig. 1. Derivatogram of [Zn(L)₂NO₃H₂O]NO₃ coordination compound

Unfortunately, due to their amorphous state, for some coordination compounds synthesized from the solution it is not possible to work out the X-ray study. Therefore, using quantum-chemical calculations in the approximation of PM3 we conducted calculations of parameters of coordination compounds and prognosticated the number of the dipole moments, entropy (Table 4), and the effective charge of the nuclei of the coordinationrelated atoms and central metal ion (Table 5).

| Table | 4 |
|-------|---|
|-------|---|

The results of quantum-chemical calculations of the parameters of coordination compounds of Zn²⁺ and Cd²⁺ with 3-methoxybenzene acid hydrazide and their stability constants

| | Calculated theoretically | | | | | | Established experimentally | | |
|-------------------------|--------------------------|------|-------|-------------------------|-------------|-------|----------------------------|--------------------|--|
| Coordination compound | Lattice parameters Å | | | <i>V</i> Å ³ | S. I/mol·K | ΡD | $c \cdot 10^2$ | $\beta \cdot 10^4$ | |
| | а | b | С | <i>v</i> , A | 5, J/1101 K | 1, D | 6 10 | p 10 | |
| $[Zn(L)_2NO_3H_2O]NO_3$ | 5.95 | 4.62 | 16.92 | 465.11 | 991.6 | 8.92 | 68.92±0.4 | 4.3±0.4 | |
| $[Zn(L)_2Cl_2]H_2O$ | 7.99 | 5.17 | 16.89 | 697.70 | 966.6 | 8.13 | 68.63±0.4 | 2.4±0.3 | |
| $[Cd(L)_2NO_3H_2O]NO_3$ | 8.07 | 5.71 | 14.00 | 645.12 | 1153.5 | 10.65 | 72.31±0.3 | 8.6±0.4 | |
| $[Cd(L)_2Cl_2]H_2O$ | 9.70 | 5.64 | 14.36 | 785.61 | 959.3 | 10.21 | 75.42±0.3 | 1.5±0.4 | |

Note: pH = 4-5; $C(M^{2+}) = 10^{-3}$ mol/cm³ (where $M^{2+} = Zn^{2+}$, Cd^{2+}), (L) = 10^{-2} mol/cm³; I = 380 nm; l = 1 cm.

Table 5

The results of quantum-chemical calculations of charges of nuclei of coordination compounds of Zn²⁺ and Cd²⁺ with 3-methoxybenzene acid hydrazide

| Coordination compound | Nuclei charge |
|-------------------------|---|
| $[Zn(L)_2NO_3H_2O]NO_3$ | Zn +0.071; O1A -0.341; N2A -0.385; O1B -0.298; N2B -0.326; O1 -0.608; OW -0.387 |
| $[Zn(L)_2Cl_2]H_2O$ | Zn +0.036; O1A -0.305; N2A +0.333; O1B -0.348; N2B +0.314; Cl1 -0.455; Cl2 -0.670 |
| $[Cd(L)_2NO_3H_2O]NO_3$ | Cd +1.374; O1A -0.378; N2A -0.380; O1B -0.591; N2B -0.037; O1 -0.890; OW -0.402 |
| $[Cd(L)_2Cl_2]H_2O$ | Cd +1.368; O1A -0.308; N2A -0.015; O1B -0.386; N2B -0.063; Cl1 -0.678; Cl2 -0.670 |

For the calculation of the sustainability of coordination compounds of metal with 3-methoxybenzene hydrazide the absorption spectra of solutions of complexes in the UV-region (I = 380 nm) were studied. Constants of stability of coordination compounds calculated by the Komar method [24] and the results are presented in Table 4.

According to the results of quantum-chemical calculations one can conclude that the studied coordination compounds are symmetric with perpendicular arrangement of ligands and have high numbers of dipole moments with a different type of coordination of bond. Thus, for complexes $[Zn(L)_2NO_3H_2O]NO_3$ and $[Zn(L)_2Cl_2]H_2O$ covalent-ionic type of bonds and for cadmium coordination compounds ($[Cd(L)_2NO_3H_2O]NO_3$ and $[Cd(L)_2Cl_2]H_2O$ – ionic-covalent one is observed.

Fig. 2 presents the optimized structures of the studied coordination compounds that are consistent with the crystal structure of $[Cd(L)_2NO_3H_2O]NO_3$ compound that we described earlier in the literature [23] on the basis of X-ray diffraction studies.

Synthesized coordination compounds were investigated for their biological activity. The study was conducted in relation to the strains of the following microorganisms: Acinetobacter baumanni, Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Klebsiella oxytoca, MRSA, Enterobacter cloaceae, Proteus mirabilis, Sarcina flava, Streptococcus pneumoniae, Bacillus subtilis, and Salmonella typhimurium. Antibacterial characteristics have been established by paper disks on firm nutrient environments, measuring areas of growth delay of test cultures of bacteria [25].



Fig. 2. Optimized geometry of coordination polyhedron of the compounds: [Zn(L)₂NO₃H₂O]NO₃ (I); [Zn(L)₂Cl₂]H₂O (II); [Cd(L)₂NO₃H₂O]NO₃ (III) and [Cd(L)₂Cl₂]H₂O (IV)

It was found out that these compounds show bactericidal characteristics with relation to the strains of the following microorganisms: *Acinetobacter baumanni*, *Sarcina flava, Pseudomonas aeruginosa, Streptococcus* pneumoniae, Bacillus subtilis (zone of growth delay is more than 20 mm), Staphylococcus aureus, and Proteus mirabilis (only cadmium compounds), as well as bacteriostatic effect against Escherichia coli, Salmonella typhimurium, Klebsiella pneumoniae, MRSA, Enterobacter cloaceae, Klebsiella oxytoca, and zinc compounds to Staphylococcus aureus and Proteus mirabilis.

4. Conclusions

Based on the above results of the studies on the composition and structures of coordination compounds of zinc and cadmium with 3-methoxybenzene acid hydrazide one can make the conclusion that two molecules of organic ligand in the amide-hydrazone form take part in the formation of strong complex. Their coordination to the central metal ion proceeds chelate-bidentately with the formation of C=O→Me and Me←NH₂ bonds. Nitrate-group and molecule of water add to the octahedral environment of the central atom.

References

[1] Harikumaran N. and Thankamani D.: Koord. Khimiya, 2010, **36**, 261.

[2] Gusev V., Radushev A., Slepukhin P. and Vnutskikh Zh.: Zh. Neorg. Khim., 2008, **53**, 83.

[3] Chundak S., Leovac V., Obadovic D. and Petrovic D.: Transition Met. Chem., 1986, **11**, 308.

[4] Shulgin V., Kopnik O. and Seredyuk N.: Zh. Neorg. Khim., 1993, **38**, 637.

[5] Shulgin V., Konnik O. and Chirva V.: Zh. Neorg. Khim., 1991, 26, 960.

[6] Kharitonov Yu. and Machkhoshvili R.: Zh. Neorg. Khim., 1972, 17, 3268.

[7] Yaul A., Dhande V., Bhadange S. and Aswar A.: Zh. Neorg. Khim., 2011, **56**, 589.

[8] Gerbeleu N., Chundak S., Manole S. and Butsko S.: Zh. Neorg. Khim., 1975, **20**, 1632.

[9] Sukharev S.: Doct. thesis, Physico-Khim. Inst., Odesa 2012.

[10] Delegan-Kokayko S.: PhD thesis, Uzhgorod Nats. Univ., Uzhgorod 2013.

[11] Dzharadat N.: PhD thesis, Nats. Pharmavc. Avad., Kharkiv 2000.

[12] Xue L., Zhao G., Han Y. and Feng Y.: Coordin. Khim., 2011, **37**, 261.

[13] Veygand-Khilgetag N.: Metody Eksperimenta v Organicheskoi Khimii. Khimiya, Moskwa 1969.

[14] Shvartsenbakh G. and Flashka G.: Kompleksonometricheskoe Titrovanie. Khimiya, Moskwa 1970.

[15] Klimova V.: Osnovnye Micrometody Analiza Organicheskikh Soedineniy. Khimiya, Moskwa 1975.

[16] Uendland U.: Termicheskie Metody Analiza. Mir, Moskwa 1978.

[17] Orozco M., Bachs M. and Luque F.: J. Comp. Chem., 1995, 16, 563.

[18] Zagradnik R. and Polak R.: Osnovy Kvantovoi Khimii. Mir, Moskwa 1979.

[19] Glikina F. and Klyuchnikov N.: Khimiya Kompleksnykh Soedineniy. Prosveshchenie, Moskwa 1972.

[20] Nakamoto K.: IK-spectry i Spectry KR Neorganicheskikh i Koordinatsyonnykh Soedineniy. Mir, Moskwa 1991.

[21] Prech E., Byulmann F. and Affolter K.: Opredelenie Stroeniya Organicheskikh Soedineniy. Mir, Moskwa 2006.

[22] Kostrzhitskiy A.: Fizichna ta Koloidna Khimiya. Centre uchb. liter., Kyiv 2007.

[23] Roman L., Chundak S., Dashkevich M. and Mariychuk R.: Nauk. Visnik Uzhg. Nats. Univ., 2011, **26**, 60.

[24] Bulatov M. and Kalinkin I.: Prakticheskoe Rukovodstvo po Fotometricheskim Metodam Analiza. Khimiya, Leningrad 1986.

[25] Bean D., Krahe D. and Wareham D.: Ann. Clin. Microbiol. Antimicrob., 2008, **7**, 13.

СИНТЕЗ, БУДОВА, ВЛАСТИВОСТІ КООРДИНАЦІЙНИХ СПОЛУК Zn(II) І Cd(II) З ГІДРАЗИДОМ З-МЕТОКСИБЕНЗЕНОВОЇ КИСЛОТИ ТА ЇХ БІОЛОГІЧНА АКТИВНІСТЬ

Анотація. З використанням гарячих етанольних або водно-етанольних розчинів у слабо кислому середовиші (pH = 4, 0-5, 0) отримано координаційні сполуки Zn(II) і Cd(II) з гідразидом 3-метоксибензенової кислоти. На основі хімічного аналізу та вивчення електропровідності розчинів запропоновано склад синтезованих комплексів. За допомогою методів ¹Н ЯМР та ІЧ-спектроскопії, термогравіметрії та квантово-хімічних розрахунків у наближенні РМЗ встановлено будову координаційних сполук. Показано, що в утворенні міцних координаційних сполук Zn(II) і Cd(II) з гідразидом 3-метоксибензенової кислоти беруть участь дві молекули органічного ліганду у амідогідразоновій формі. Встановлено, що координація сполук до центрального йону металу проходить хелатно бідентатно з утворенням зв'язків $C=O \rightarrow Me \ i \ Me \leftarrow NH_2$ з доповненням октаедричного оточення центрального атому аніонами кислотних залишків (NO₃⁻ чи Cl⁻ відповідно) або молекулами води. Синтезовані координаційні сполуки проявляють бактерицидні властивості по відношенню до мікроорганізмів штаму Acinetobacter baumanni, Sarcina flava, Pseudomonas aeruginosa, Streptococcus pneumoniae, Bacillus subtilis, а також бактеріостатичні – по відношенню Escherichia coli, Salmonella typhimurium, Klebsiella <u>до</u> pneumoniae, MRSA, Enterobacter cloaceae, Klebsiella oxytoca.

Ключові слова: гідразид 3-метоксибензенової кислоти, координаційні сполуки цинку, координаційні сполуки кадмію, будова синтезованих речовин, біологічна активність.