



Synthesis and Characterization of Transition Metals Coordination Compounds Based on Bioactive Spatial Alicyclic Hydrazide-Hydrazones

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New coordination compounds of transition metals based on bioactive adamantane-containing hydrazide-hydrazones have been synthesized. By using of the data of IR and NMR spectral, thermal (TGA, DTA) and elemental analysis and by molar conductivity the structure of the obtained compounds have been established. By using model systems and semi empirical quantum-chemical AM1 method the electronic structure and complex forming capacity of obtained ligands have been established. It was shown that the organic ligand behaved as cyclic-bidentate (electron donor atoms -N and O) through the carbonyl oxygen and the NH₂- or azomethine nitrogen atoms. The bactericide activity of the initial ligands and obtained coordination compounds towards test objects has been studied.

Key Words: Adamantane, Hydrazide-hydrazones, Transition metal, Coordination compound, Bioactivity.

INTRODUCTION

Among ligand systems, hydrazide-hydrazones belong to a special place because of their vast variety of biological activities ranging from pharmacological, antitumor, fungicide, bactericide, antiinflammatory, antiviral, antioxidative and cytotoxic activities¹⁻⁴. By complex formation of hydrazide-hydrazones with transition metal sometimes, result in a several increase of this activity. Hydrazide-hydrazones and their metal complexes show varied applications in the fields such as fungicidal, bactericidal, antioxidative and cytotoxic studies^{5,6}. They used as potential chemotherapeutic agents⁷. Intensified interest in high biological active transition metal complexes with hydrazide-hydrazones^{8,9} developed because of their increasing application in medicine, analytical chemistry and synthesis of novel heterogeneous catalysts of oxidation-reduction processes, as well as in numerous fields of science and technology^{10,11}. For this purpose, we have decided to use spatial alicyclic adamantane as a polyfunctional component.

For the time being in the various spheres of science and technique are giving scientist's special attention to adamantane and its derivatives. The number of polymeric materials, bioactive compounds, adamantane-containing ligands and nano-materials in metal complexes is considerably increasing¹². The nitrogen-containing adamantane derivatives are known to have unique pharmacological activity, among them suppressive effect on rabies virus and human immune deficiency virus^{13,14}. Introduce of immunotropic and membrano-tropic

adamantane group in the molecule of bioactive compounds frequently provoke the shortening of preparation toxicity and reinforcement of pharmacological action. By using of adamantane-1-carboxylic acid successful were modified antibiotics, glycosides, steroids, *etc.*^{15,16}.

Following from the above mentioned we have decided prospectively for special purpose the synthesis of transition metal coordination compounds of adamantane-containing hydrazide-hydrazones from standpoint as theoretical and practical use. In addition, evaluation of influence of electron donor and pharmacophore adamantane radical on specific biological activity of obtained coordination compounds.

EXPERIMENTAL

Adamantane-1-carboxylic acid hydrazide

(a) **Adamantane-1-carboxylic acid ethyl ester:** to a mixture of 100 mL dry ethanol and 3 mL concentrated sulphuric acid at the permanent stirring condition were added 32 g (0.17 mol) adamantane-1-carboxylic acid and boiled during 7 h. A non reacted ethanol has been separated from the reaction mixture, then was added the mixture of benzene/diethyl ether for extraction of organic phase till neutral reaction, was dried on Na₂SO₄ and the residue was distilled under decreased pressure T_b 144-145 °C (12 mm), n_D²⁰ 1.4868, yield 80 %.

(b) The mixture of 33 mL (0.2 mmol) adamantane-1-carboxylic acid ethyl ester and 70 mL (80 %) hydrazine hydrate in 100 mL diethylene glycol was boiled during 36 h. To the obtained reaction mixture was added an ice-water at constant

stirring condition, then was filtered, the obtained white crystals was washed by water and dried. T_{melt} 153-154 °C, R_f 0.45 ($\text{CH}_3\text{OH}:\text{CHCl}_3/1:12$), yield 85 % (26 g).

Transition metals coordination compounds of adamantane-1-carboxylic acid hydrazide (I-XII): To a water-solution of corresponding transition metal salt was added adamantane-1-carboxylic acid hydrazide in dry ethanol [molar ratio $\text{MX}_n:L/1:3$]. The reaction mixture was stirred during 0.5-1 h and then boiled during 5-6 h. After 2-3 days, the separated crystals filtered, washed by ethanol and dried in vacuum over CaCl_2 .

Transition metals coordination compounds of 1-adamantoyl hydrazone of acetone (XIV-XVI): The solution of adamantane-1-carboxylic acid hydrazide in acetone was boiled at constant stirring condition during 1.5 h. Then was added corresponding transition metal salt in acetone [molar ratio $\text{MX}_n:L/1:3$]. The reaction mixture was stirred and boiled during 5-6 h. After 2-3 days, the separated crystals filtered, washed by ethanol and dried in vacuum over CaCl_2 .

Spectral analysis: IR spectra have obtained with a spectrophotometer FT-IR THERMO NICOLET in Ge plates and Spectrum BX FT-IR Perkin Elmer ($4000\text{-}400\text{ cm}^{-1}$) in liquid paraffin¹⁷. NMR spectra have obtained with an AM-400 (Brucker[®]) and Talsa BS-467 instrument at an operating frequency of 400 MHz using CDCl_3 as a solvent and tetramethylsilane as an internal standard. Thermo gravimetric analysis carried out by means of Paulik, Paulik & Erdey systems of Q 1500 thermal analyzer, heating rate 100/min, sensibility DTA 1/10¹⁸. Melting points were determined by apparatus melting point meter MPM-HV2, Germany; metal content was determined on atomic absorptive spectrophotometer Perkin Elmer 603; and molar conductivity in DMF at room temperature using a model Cond-720 conductometer.

Thin-layer chromatography: The reaction course and the purity of the obtained compounds have monitored by thin-layer chromatography on silufol UV-254 and alufol plates.

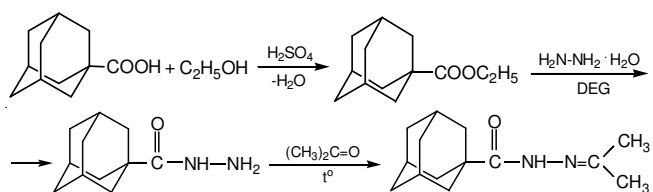
Quantum-chemical calculations carried out on PC with AMD processor with the built coprocessor by using Mopac 2000 and CS Chem3D Ultra, v8. We gave the following key words to guide each computation: EF GNORM = 0.100 MMOK GEO-OK AM1 MULLIK LET DDMIN = 0.0 GNORM = 0.1 GEO-OK.

Standard microbiological methods for study of bactericidal properties of synthesized adamantane-containing compounds have used.

RESULTS AND DISCUSSION

Synthesis and quantum-chemical investigation of adamantane-containing hydrazide-hydrazones: Adamantane-containing hydrazide was synthesized in two stages according to the **Scheme-I**. The esterification of adamantane-1-carboxylic acid was carried out in presence of concentrated sulphuric acid and then hydrazinolysis of the obtained adamantane-1-carboxylic acid ethyl ester in diethylene glycol. By boiling of adamantane-1-carboxylic acid hydrazide in acetone has been obtained the corresponding 1-adamantoyl hydrazone of acetone:

The composition and structure of the synthesized organic ligands we have established by IR and NMR spectral data. In the IR spectra of the obtained compounds we have observed



Scheme-I Synthesis of adamantane-containing hydrazide-hydrazone ligands

the characteristic absorption bands for the following groups: $\nu_{\text{as}}(\text{NH}_2)$ ($3595\text{-}3479\text{ cm}^{-1}$), $\nu(\text{NH})$ ($3332\text{-}3278\text{ cm}^{-1}$), $\nu_{\text{as}}(\text{C-H})$ of adamantyl group ($2910\text{-}2830\text{ cm}^{-1}$), $\nu_{\text{as}}(>\text{C}=\text{O})$ carbonyl group ($1640\text{-}1612\text{ cm}^{-1}$), $\nu_{\text{as}}(\text{CONH})$ ($1540\text{-}1520\text{ cm}^{-1}$), $\nu_{\text{as}}(\text{C-N})$ (1373 cm^{-1}), $\nu_{\text{def}}(\text{N-H, C-N})$ ($1558\text{-}1550\text{ cm}^{-1}$; $1360\text{-}1330\text{ cm}^{-1}$).

For preliminary estimation of complex forming capacity of used ligands and study of their electron structure we have carried out their quantum-chemical investigation [semi empirical method AM1 (Austin Model 1) CS MOPAC (Chem 3D Ultra-version 8.03)]¹⁹. We have calculated power and geometrical parameters, effective charges on atoms and electron occupation of atomic orbital (electronic density) in adamantane-containing hydrazide-hydrazone molecules.

Analysis of distances between atoms in the molecule of adamantane-1-carboxylic acid hydrazide (Fig. 1) shows that values of C-C bond lengths (R_{ij}) in adamantane nucleus ($\text{C}_{10}\text{H}_{15}$) is within limits 1.522-1.542 Å, what indicates on sp^3 hybridized position of carbon atoms ($\text{C}_1\text{-C}_{10}$). The bond lengths and valence bond angles of carbon atom C_{11} with neighbouring atoms ($\angle\text{C}_1\text{-C}_{11}\text{-O}_{12}=120.1^\circ$, $\angle\text{C}_1\text{-C}_{11}\text{-N}_{13}=118.6^\circ$ and $\angle\text{O}_{12}\text{-C}_{11}\text{-N}_{13}=121.4^\circ$) indicate mainly its sp^2 hybridized position.

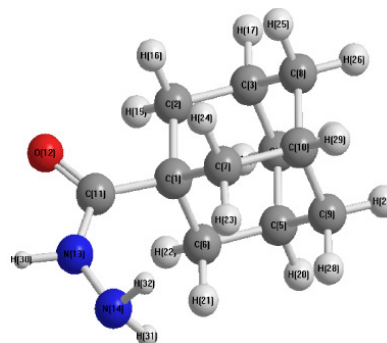


Fig. 1. 3D model of adamantane-1-carboxylic acid hydrazide

The values of valence bond angles of oxygen atom O_{12} shows on its sp^2 hybridized position. According to values of valence bond angles of nitrogen atoms ($\angle\text{C}_{11}\text{-N}_{13}\text{-N}_{14}=131.6^\circ$, $\angle\text{C}_{11}\text{-N}_{13}\text{-H}_{30}=116.1^\circ$, $\angle\text{N}_{14}\text{-N}_{13}\text{-H}_{30}=112.3^\circ$ da $\angle\text{N}_{13}\text{-N}_{14}\text{-H}_{31}=110.4^\circ$, $\angle\text{N}_{13}\text{-N}_{14}\text{-H}_{32}=110.0^\circ$, $\angle\text{H}_{31}\text{-N}_{14}\text{-H}_{32}=106.8^\circ$) they are in sp^2 (N_{13}) and sp^3 (N_{14}) hybridized position.

Analysis of values of effective charges on atoms (Table-1) shows that potentially electron donor atoms are O_{12} ($q_{12} = -0.3643$), N_{13} ($q_{13} = -0.3492$) and N_{14} ($q_{14} = -0.1787$).

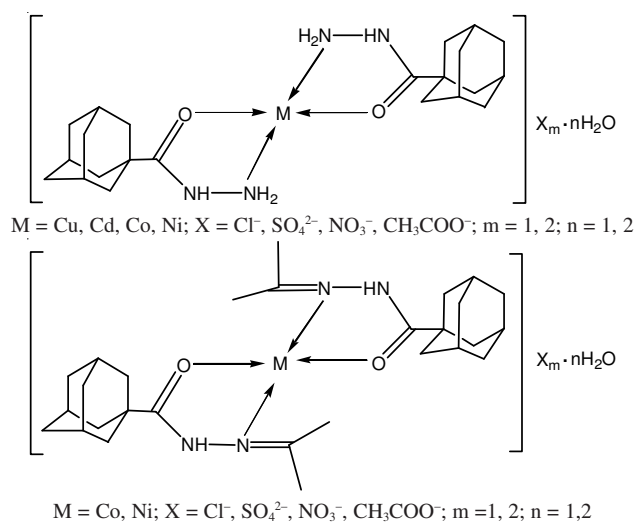
TABLE-1
EFFECTIVE CHARGES (q_i) AND ELECTRICAL DENSITY OF ATOMS [$q_i(d)$]

Atom (i)	Effective charges (q_i)	Electrical density, $q_i(d)$
O_{12}	-0.3643	6.3643
N_{13}	-0.3492	5.3492
N_{14}	-0.1787	5.1787

Electron occupation of atomic orbital's (Table-2) shows that one of electron pairs of oxygen atom is located on 2s orbital (electron occupation 1.91546) and has capacity to form σ -bond with metal atom by donor-acceptor mechanism. In spite of comparatively high negative relative charge of N₁₃ atom by comparison with N₁₄ atom, it is unable to form σ -bond with metal atom by donor-acceptor mechanism as an electron pair is located on nonhybridized 2p_z orbital (electron occupation 1.76977). As regards of N₁₄ atom, its electron pair is located one of hybridized sp³ orbital (electron occupation 1.62247) and in that way has inclination to form σ -bond with metal atom by donor-acceptor mechanism.

Atom (i)	2s	2p _x	2p _y	2p _z
O ₁₂	1.91695	1.51656	1.46034	1.47045
N ₁₃	1.47071	1.00026	1.10848	1.76977
N ₁₄	1.62247	1.18049	1.29435	1.08141

Thus the molecule contains two potentially electron donor atoms -O₁₂ and N₁₄ because of that represent a bidentate ligand and is capable to form coordination compounds with transition metals in the form of 5-membered cyclic compound (**Scheme-II**).



Scheme-II: Transition metals coordination compounds based on adamantane-containing hydrazide-hydrazones

In the molecule of 1-adamantoyl hydrazone of acetone (Fig. 2) by the values of valence bond angles ($\angle C_{11}-N_{13}-N_{14} = 125.2^\circ$, $\angle C_{11}-N_{13}-H_{33} = 114.6^\circ$, $\angle N_{14}-N_{13}-H_{33} = 120.2^\circ$, $\angle N_{13}-N_{14}-C_{15} = 121.7^\circ$) nitrogen atoms (N₁₃ and N₁₄) are in sp² hybridized position. In same position is carbon atom C₁₅ too ($\angle N_{14}-C_{15}-C_{16} = 126.8^\circ$, $\angle N_{14}-C_{15}-C_{17} = 118.9^\circ$, $\angle C_{16}-C_{15}-C_{17} = 114.3^\circ$), which formed double bond with nitrogen atom N₁₄. Analysis of the values of effective charges (Table-3) shows that potentially electron donor atoms in this case are also O₁₂ (q₁₂ = -0.3585), N₁₃ (q₁₃ = -0.3156) da N₁₄ (q₁₄ = -0.0374).

Electron occupation of atomic orbital's (Table-4) shows that one of the electron pairs of oxygen atom is located on 2s orbital (electron occupation 1.91635) and has capacity to form σ -bond with metal atom by donor-acceptor mechanism. In

spite of comparatively high negative relative charge of N₁₃ atom by comparison with N₁₄ atom, it is unable to form σ -bond with metal atom by donor-acceptor mechanism as an electron pair is located on nonhybridized 2p_z orbital (electron occupation 1.72317). As regards of N₁₄ atom, its electron pair is located one of hybridized sp² orbital (electron occupation 1.72500) and in that way has inclination to form σ -bond with metal atom by donor-acceptor mechanism.

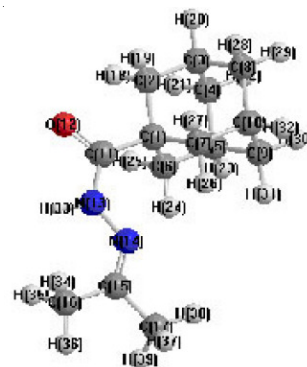


Fig. 2. 3D model of 1-adamantoyl hydrazone of acetone

Atom (i)	Effective charges (q _i)	Electrical density, q _i (d)
O ₁₂	-0.3585	6.3585
N ₁₃	-0.3156	5.3156
N ₁₄	-0.0374	5.0374

Atom (i)	2s	2p _x	2p _y	2p _z
O ₁₂	1.91635	1.53322	1.44607	1.46283
N ₁₃	1.47861	1.03813	1.07567	1.72317
N ₁₄	1.72500	0.94356	1.24480	1.12405

Synthesis and characterization of adamantane-containing coordination compounds of transition metals: Adamantane-containing hydrazide-hydrazone coordination compounds (**Scheme-II**) have been synthesized by interaction of organic ligands (L) with transition metal salts (MX_n) [molar ratio MX_n:L/1:3] in ethanol and acetone water-solution in stirring and boiling condition during 5-6 h. The most probable structures of obtained coordination compounds are given in **Scheme-II**.

The composition and structure of synthesized coordination compounds were established by using of IR and NMR spectral, thermal (TGA, DTA), elemental analysis methods and molar conductivity (Table-5).

Analysis of infrared spectra of the synthesized coordination compounds and adamantane-containing hydrazide-hydrazones has shown that the molecule of organic ligand behaved as cyclic-bidentate and is coordinated to the central metal atoms through the carbonyl oxygen and the -NH₂, also azomethine nitrogen atom. Particularly in the IR spectra of the coordination compounds the decrease of absorption band corresponding to valence oscillation of carbonyl group [$\Delta\nu$ (C=O) ca. 30-40 cm⁻¹] comparison with free ligand point at coordination of organic ligand to the central metal atom by

TABLE-5
SOME PHYSICAL-CHEMICAL CHARACTERISTICS OF TRANSITION METALS COORDINATION COMPOUNDS OF
ADAMANTANE-CONTAINING HYDRAZIDE-HYDRAZONES AND THE DATA OF THEIR IR SPECTRA

#	Compound*	m.p. (°C)	Yield (%)	λ_M^{**} (S cm ² mol ⁻¹)	Metal content (%)		IR spectrum (v, cm ⁻¹)
					Found	Calc.	
I	CoL ₂ Cl ₂ ·2H ₂ O	>260	84.4	87.6	10.04	10.63	3483.5 (NH ₂); 3142.4 (NH); 2972.1, 2884.3 (CH, Ad); 1653.8 (C=O); 1583.9, 1540.4 (CONH); 1344.1 (C-N); 1077.8 (Cl ⁻); 468.0, 450.4 (M-O, M-N)
II	NiL ₂ Cl ₂ ·2H ₂ O	>260	87.2	75.3	10.12	10.65	3483.5 (NH ₂); 3142.4 (NH); 2967.1, 2841.5 (CH, Ad); 1691.6 (C=O); 1536.4, 1512.4 (CONH); 1377.2 (C-N); 1131.5 (Cl ⁻); 491.4, 474.5 (M-O, M-N)
III	CdL ₂ Cl ₂ ·2H ₂ O	>230	84.6	68.4	17.93	18.40	3587.1, 3509.9, 3417.4 (NH ₂); 3340.2, 3293.9 (NH); 2923.7, 2854.2 (CH, Ad); 1635.4 (C=O); 1504.2 (CONH); 1373.1 (C-N); 1103.1 (Cl ⁻); 540.0 (M-O, M-N)
IV	CuL ₂ Cl ₂ ·H ₂ O	>260**	76.2	82.3	11.78	12.24	3483.5 (NH ₂); 3142.4 (NH); 2966.9, 2842.6 (CH, Ad); 1641.7 (C=O); 1586.2, 1512.7 (CONH); 1377.1 (C-N); 1073.4, 722.9 (Cl ⁻); 492.4, 455.5 (M-O, M-N)
V	CoL ₃ SO ₄ ·H ₂ O	>260	83.2	85.2	10.00	10.41	3417.4 (NH ₂); 3321.6 (NH); 2966.2, 2842.8 (CH, Ad); 1612.3 (C=O); 1551.8 (CONH); 1377.2 (C-N); 1170.7, 1056.3, 664.5 (SO ₄ ²⁻); 491.0, 460.5 (M-O, M-N)
VI	NiL ₃ SO ₄ ·H ₂ O	>230**	64.6	69.3	7.38	7.70	3401.9 (NH ₂); 3239.9 (NH); 2908.2, 2854.2 (CH, Ad); 1643.1 (C=O); 1535.1 (CONH); 1373.1 (C-N); 1187.9, 1079.9, 671.1 (SO ₄ ²⁻); 532.3, 447.4 (M-O, M-N)
VII	CdL ₂ SO ₄ ·H ₂ O	>300	78.4	73.5	17.87	18.24	3515.9 (NH ₂); 3340.2 (NH); 2972.1, 2839.4 (CH, Ad); 1620.5 (C=O); 1548.2 (CONH); 1377.6 (C-N); 1136.5, 1093.4, 723.9 (SO ₄ ²⁻); 491.4, 460.5 (M-O, M-N)
VIII	CoL ₂ (NO ₃) ₂ ·2H ₂ O	>300	96.2	76.6	9.18	9.71	3394.7 (NH ₂); 3321.6 (NH); 2914.0, 2853.5 (CH, Ad); 1653.5 (C=O); 1558.7 (CONH); 1397.0 (C-N); 1284.9, 669.3 (NO ₃ ⁻); 487.4, 456.1 (M-O, M-N)
IX	NiL ₂ (NO ₃) ₂ ·H ₂ O	>230	96.2	83.3	9.56	10.01	3594.8, 3540.8, 3479.0 (NH ₂); 3332.6, 3278.6 (NH); 2908.2, 2854.2 (CH, Ad); 1643.1 (C=O); 1535.1 (CONH); 1373.1 (CN); 1349.9, 1041.4, 825.4 (NO ₃ ⁻); 540.0 (M-O, M-N)
X	CoL ₂ (CH ₃ COO) ₂ ·H ₂ O	>230	87.8	83.9	9.25	10.10	3540.8, 3479.0 (NH ₂); 3278.5 (NH); 2918.9, 2871.1 (CH, Ad); 1630.9 (C=O); 1548.0 (CONH); 1373.1 (C-N); 1483.7 (COO); 1334.5 (CH ₃); 850.7 (C-C); 491.2, 455.5 (M-O, M-N)
XI	NiL ₂ (CH ₃ COO) ₂ ·H ₂ O	>230	92.0	64.7	9.64	10.11	3394.7 (NH ₂); 3255.1 (NH); 2920.9, 2853.5 (CH, Ad); 1653.6 (C=O); 1558.9 (CONH); 1397.0 (C-N); 1450.2, 1418.3 (COO); 1234.1, 668.7 (CH ₃); 918.0 (C-C); 486.3, 459.0 (MO, MN)
XII	CdL ₂ (CH ₃ COO) ₂ ·2H ₂ O	>360	93.0	77.6	16.25	17.09	3594.8, 3540.8, 3479.0 (NH ₂); 3332.6, 3278.6 (NH); 2908.2, 2854.2 (CH, Ad); 1643.1 (C=O); 1535.1 (CONH); 1373.1 (C-N); 1450.3, 1411.7 (COO); 1334.6 (CH ₃); 925.7, 918.0 (C-C); 540.0 (M-O, M-N)
XIII	CoL ₂ Cl ₂ ·2H ₂ O	>360**	69.4	64.6	8.93	9.29	3483.5 (NH ₂); 3147.4 (NH); 2923.7, 2854.3 (CH, Ad); 1604.6 (C=O); 1519.7 (CONH); 1457.9 (C=N); 1373.1, 725.1 [C-(CH ₃) ₂]; 1103.1 (Cl ⁻); 594.0, 509.1 (M-O, M-N)
XIV	NiL ₂ (NO ₃) ₂ ·2H ₂ O	>360**	55.1	66.9	8.50	8.58	3455.9 (NH ₂); 3355.7 (NH); 2923.7, 2854.3 (CH, Ad); 1612.3 (C=O); 1535.1 (CONH); 1457.9 (C=N); 1373.1, 725.1 [C-(CH ₃) ₂]; 1072.3, 825.4 (NO ₃ ⁻); 540.0 (M-O, M-N)
XV	CoL ₂ SO ₄ ·2H ₂ O	>360**	92.4	65.3	8.00	8.94	3417.4 (NH ₂); 3321.6 (NH); 2923.7, 2854.7 (CH, Ad); 1643.1 (C=O); 1519.7 (CONH); 1457.9 (C=N); 1373.1, 740.6 [C-(CH ₃) ₂]; 1104.0, 1079.9, 617.1 (SO ₄ ²⁻)
XVI	NiL ₂ (CH ₃ COO) ₂ ·2H ₂ O	>360**	49.4	68.4	8.,27	8.65	3394.7 (NH ₂); 3255.1 (NH); 2911.3, 2857.6 (CH, Ad); 1559.4 (CONH); 1350.6 (C-N); 1418.7, 668.8 (COO); 1350.6 (CH ₃); 498.2, 460.5 (M-O, M-N)

*L = AdCONHNH₂; L¹ = AdCONHNC(CH₃)₂; ** decomposition; *** λ_M determined in dimethylformamide, 25 °C, 0.001 M.

means of carbonyl oxygen $M \leftarrow O=C$. On the other hand, absorption band corresponding to NH_2 group comparison with non-coordinated ligand moved in high-frequency section off [$\Delta\nu(NH_2)$ ca. 120-200 cm^{-1}], characterising for valence oscillation of $NH_2 \rightarrow M$ bond.

In the IR spectra of the compounds **I-IV**, we observed the intensive absorption band characteristic for $\nu_e(Cl^-)$ group on ca. 1130-1070 cm^{-1} . In the IR spectra of the compounds **V-VII** on ca. 1110-1080 cm^{-1} observed the intensive, singlet absorption band characteristic for $\nu_e(SO_4^{2-})$ group. Coordination number of the central metal atom in complexes $ML_mSO_4 \cdot H_2O$ ($M=Co, Ni, Zn$) are 6 and correspondingly, in these complexes SO_4^{2-} groups are inside spherical groups. In the complex $CdL_2SO_4 \cdot H_2O$ absorption band corresponding to SO_4^{2-} groups is breaking on some component up from this, it is concluded that they directly connected with cadmium central atom. In the IR spectra of the compounds **VIII-IX** on ca. 1538-1380 cm^{-1} observed the intensive, divided on two component absorption band characteristic for $\nu_e(NO_3^-)$ group and we have made a supposition that group is directly connected with central metal atoms and corresponding compound have octahedral structure. In the IR spectra of the compounds **X-XII** we observed the intensive absorption bands characteristic for CH_3COO^- group: $\nu_e(COO^-)$ ca. 1450-1410 cm^{-1} , $\nu_e(CH_3)$ ca. 1335-1235 cm^{-1} , $\nu_e(C-C)$ ca. 960-900 cm^{-1} .

In the 1H NMR spectra of the synthesized compounds one can observe signals with chemical shifts at 1.57-2.01 ppm related to the 15 protons in adamantyl groups. In transition metals coordination compounds of adamantane-1-carboxylic acid hydrazide, we found also a singlet signal with chemical shifts within the range 7.01-8.03 ppm for the protons in the NH groups and singlet signal with chemical shifts within the range 2.01-2.05 ppm, for the protons in the NH_2 groups. In transition metals coordination compounds of 1-adamantoyl hydrazone of acetone singlet signal with chemical shifts within the range 7.01-7.03 ppm belongs to the protons of NH groups. Singlet signal with chemical shifts within the range 2.06-2.50 ppm belongs to the protons of the NH_2 groups. Singlet signal with chemical shifts within the range 3.09-3.83 ppm corresponds to three protons of methyl groups.

In ^{13}C NMR spectra, a signal is observed with four chemical shifts within the range 27.6-40.7 ppm typical for adamantyl group and the chemical shift 16.4 ppm related to the carbon atom of CH_3 groups in transition metals coordination compounds of 1-adamantoyl hydrazone of acetone. In the ^{13}C NMR spectra we also observed chemical shifts within the range 151.5-162.8 ppm and chemical shifts within the range 165.1-181.7 ppm related to carbon atoms of imines ($N=C$) and carbonyl ($C=O$) groups, correspondingly.

Thermogravimetric analysis showed that thermolysis of obtained compounds is a complicated process. After losing of water molecules (ca. 100-105 $^{\circ}C$), takes place gradual removal of molecules of organic ligands (ca. 400-560 $^{\circ}C$). A final product of thermolysis is oxide or salt of corresponding transition metal (≥ 800 $^{\circ}C$).

Curves of differential-thermal analysis (Fig. 3) of coordination compound **IX** (Table-5) show that the first weakly expressed endothermic effect takes place at 105 $^{\circ}C$, decrease of mass is 3.0 % (theor. 3.0 %), what corresponds to cleaving

of water molecules from the coordination compound. During the following increase of the temperature at 500 $^{\circ}C$ takes place the second endothermic effect, decrease of mass is 86.5 % (theor. 87.0 %), which is provoked from step-wise cleaving of organic molecules. At the 900 $^{\circ}C$, the mass decreased by 12.5 % and the final product of thermolysis is NiO (theor. 12.56 %).

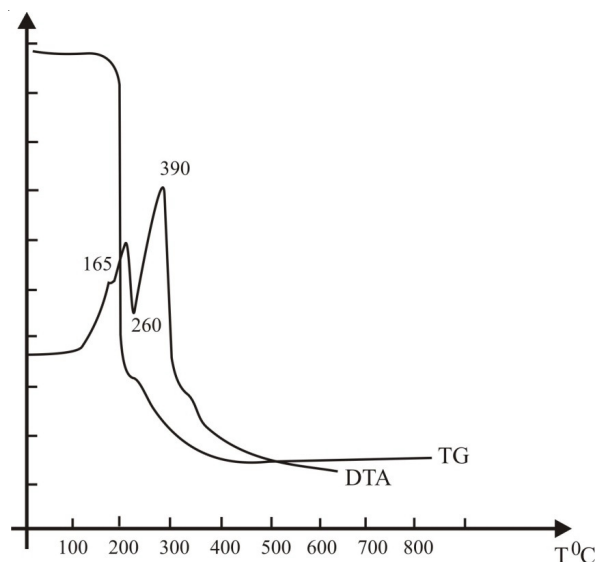


Fig. 3. DTA and TGA curves of coordination compounds $NiL_2(NO_3)_2 \cdot H_2O$

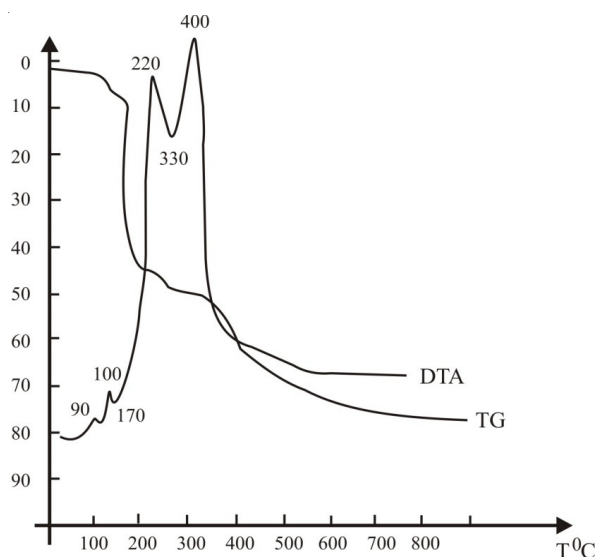


Fig. 4. DTA and TGA curves of coordination compounds $NiL_2(NO_3)_2 \cdot 2H_2O$

By determination of metal content in obtained compounds **I-XVI** (Table-5), we established that mainly formed bi(ligand) (aqua) and bi(ligand)bi(aqua) complexes. Their molar electric conductivity in DMFA changes within the range of 64-87 $S\ cm^2\ mol^{-1}$ (Table-5), which corresponds with 1:1 type electrolyte^{20,21}.

Roentgenographic (X-ray) analysis of synthesized coordination compounds confirms that the obtained coordination compounds did not contain impurity of the initial substances.

The results of microbiological investigation (*in vitro*) shows that the synthesized coordination compound (concentration of test-solution 0.01-0.1 g/L) have selective specific bactericide properties. They have toxic action and by different

activity suppress growth and development of researched cultures (*Agrobacterium tumefaciens*, *Esherichia coli*, *Pectobacterium aroideac*, *Xanthomonas campestris*). Herewith bactericidal properties of adamantane-containing hydrazide-hydrazones are expressed weakly comparatively with corresponding coordination compounds.

The preliminary investigation have shown, that the obtained coordination compounds may be recommended for preparing:

(a) Protective covers with multivectorial application (film materials and impregnating compositions) stable to biocorrosion.

(b) Materials with antimycotic properties for prophylaxis and treatment of mycosis.

(c) Biologically active polymer materials for protection of museum exhibits.

(d) For human protection during its contact with microorganisms²².

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