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**SYNTHESIS AND CHARACTERIZATION  
OF COORDINATION COMPOUNDS OF 3d-METAL  
MALEATES WITH THIOSEMICARBAZIDE**

Complexes of copper(II), nickel(II), cobalt(III), and zinc(II) maleates with thiosemicarbazide were synthesized. The resulting compounds were characterized by the elemental analysis data, infrared spectroscopy, diffuse reflectance spectroscopy, and thermogravimetry.

**Keywords:** coordination compounds, 3d-metals, thiosemicarbazide

Thiosemicarbazide is an interesting ambidentate ligand able to form five-membered chelate rings or monodentately coordinate by sulfur. It is interesting to trace the mutual effect and competition for the inner-sphere sites in coordination compounds with different inorganic and organic anions. We have previously obtained thiosemicarbazide (HL) complexes with inorganic salts [1], carboxylates [2-4], naphthalenesulfonates [5]. Depending on the central atom and salt anion, compounds with different metal:HL ratios are realized, and the ligand can act in a molecular or deprotonated form.

Thiosemicarbazide coordination compounds where anions of unsaturated carboxylic acids, in particular maleic ( $H_2Mal$ ), act as counterions, have been studied relatively little. The structure was described only for the complex  $[Ni(HL)_2(H_2O)_2](HMal)_2 \cdot 2H_2O$  [6].

The aim of this work was studying the products of reaction of copper(II), nickel(II), cobalt(II), and zinc(II) maleates with thiosemicarbazide.

**EXPERIMENTAL SECTION**

Copper(II), nickel(II), cobalt(II), and zinc(II) nitrates, maleic acid and thiosemicarbazide were of analytical grade.

The metal content in the isolated compounds was determined by atomic absorption spectrometry on a Shimadzu 7000AA instrument, the nitrogen content, according to the Dumas method [7], the sulfur content, by the Schoeniger method [7].

The IR spectra were taken on a Perkin-Elmer SPECTRUM BX II FT-IR SYSTEM instrument, samples were prepared in the form of tablets with KBr. The diffuse reflection spectra were recorded on a Lambda-9 (Perkin-Elmer) spectrophotometer with MgO (100βMgO) as the standard. Thermogravigrams were taken in air on a Paulic-Paulic-Erdei derivatograph at the heating rate of 10 deg/min.

The synthesis was carried out according to the methods developed earlier [2-4].

**Synthesis of  $[Cu(HL)L](HMal)$ .** 0.01 mol of  $Cu(NO_3)_2 \cdot 3H_2O$  was dissolved in water, to the resulting solution was added 8 g of NaOH. The precipitated hydroxide was filtered through a paper filter on a Buchner funnel and washed with water, transferred

to a beaker with a portion of 2.38 g of maleic acid. The mixture of hydroxide with acid was thoroughly mixed adding drops of water. When the precipitate was completely dissolved, the solution was added in small portions to a solution of 1.82 g (0.02 mol) of thiosemicarbazide in 100 ml of water. The precipitate formed was separated, washed with water and air dried to constant weight.

**Synthesis of  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$ .** 0.01 mol of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in water, to the resulting solution was added 8 g of NaOH. The precipitated hydroxide was filtered through a paper filter on a Buchner funnel and washed with water, transferred to a beaker with a portion of 2.38 g of maleic acid. The mixture of hydroxide with acid was thoroughly mixed adding drops of water. When the precipitate was completely dissolved, the solution was added in small portions to a solution of 1.82 g (0.02 mol) of thiosemicarbazide in 100 ml of water. The precipitate formed was separated, washed with water and air dried to constant weight.

**Synthesis of  $[\text{Ni}(\text{HL})_4](\text{HMal})_2$ .** 0.005 mol of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in water, to the resulting solution was added 4 g of NaOH. The precipitated hydroxide was filtered through a paper filter on a Buchner funnel and washed with water, transferred to a beaker with a portion of 1.18 g of maleic acid. The mixture of hydroxide with acid was thoroughly mixed adding drops of water. When the precipitate was completely dissolved, the solution was added in small portions to a solution of 1.82 g (0.02 mol) of thiosemicarbazide in 100 ml of water. The precipitate formed was separated, washed with water and air dried to constant weight.

**Synthesis of  $[\text{Co}(\text{HL})_2\text{L}](\text{HMal})_2$ .** 0.01 mol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in water, to the resulting solution was added 8 g of NaOH. The precipitated hydroxide was filtered through a paper filter on a Buchner funnel and washed with water, transferred to a beaker with a portion of 2.38 g of maleic acid. The mixture of hydroxide with acid was thoroughly mixed adding drops of water. When the precipitate was completely dissolved, the solution was added in small portions to a solution of 2.73 g (0.03 mol) of thiosemicarbazide in 150 ml of water. The mixture was allowed to stand until complete homogeneity of the precipitate, which was separated, washed with water and air dried to constant weight.

**Synthesis of  $[\text{Zn}(\text{HL})_4](\text{HMal})_2$ .** 0.005 mol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in water, to the resulting solution was added 4 g of NaOH. The precipitated hydroxide was filtered through a paper filter on a Buchner funnel and washed with water, transferred to a beaker with a portion of 1.18 g of maleic acid. The mixture of hydroxide with acid was thoroughly mixed adding drops of water. When the precipitate was completely dissolved, the solution was added in small portions to a solution of 1.82 g (0.02 mol) of thiosemicarbazide in 100 ml of water. The precipitate formed was separated, washed with water and air dried to constant weight.

## RESULTS AND DISCUSSION

As can be seen from the results of chemical analysis (Table 1), for copper (II) is realized a complex with a ratio of metal: thiosemicarbazide 1:2, for zinc – 1:4, for cobalt (III) – 1:3, with cobalt (II) is oxidized by air oxygen to cobalt (III). For nickel (II), depending on the ratio of reagents, two compounds are formed – 1:2, which was described by the authors [6] and not described in the literature a compound 1:4. The ratio of metal: maleate in all complexes corresponds to a single-charged anion.

Table 1

The elemental analysis data and colors of complexes

No	Compound	M,%		N,%		S,%		Color
		Found	Calculated	Found	Calculated	Found	Calculated	
I	[Cu(HL)L](HMal)	18.0	17.8	23.2	23.3	18.1	17.8	Brown
II	[Ni(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (HMal) <sub>2</sub> ·2H <sub>2</sub> O	10.5	10.9	15.8	15.5	11.4	11.8	Blue
III	[Ni(HL) <sub>4</sub> ](HMal) <sub>2</sub>	9.2	9.0	25.4	25.7	19.2	19.6	Green
IV	[Co(HL) <sub>2</sub> L](HMal) <sub>2</sub>	10.2	10.5	22.9	22.5	17.3	17.1	Dark-pink
V	[Zn(HL) <sub>4</sub> ](HMal) <sub>2</sub>	10.3	9.9	25.1	25.5	19.8	19.4	White

Analysis of the IR spectra of thiosemicarbazide, 3d-metal maleates, and complexes (Table 2) shows that for complexes with a composition of 1: 4 they are practically identical regardless of the central atom (green Ni(HL)<sub>4</sub>(HMal)<sub>2</sub> and Zn(HL)<sub>4</sub>(HMal)<sub>2</sub>).

At the same time, some common features are observed in the spectra of cobalt (III) and copper (II) complexes.

The thioamide I band behaves similarly for each group of complexes with similar stoichiometry. For complexes with a composition of 1: 4, the band frequency increases by about 40 cm<sup>-1</sup>. For the rest of the complexes, it splits into a doublet, while for the complexes of cobalt (III) and copper (II) the difference in the frequencies of the bands of the doublet is much larger (68 and 82 cm<sup>-1</sup>, respectively) than for the nickel complex with the composition Ni(HL)<sub>2</sub>(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (25 cm<sup>-1</sup>). The thioamide II band shifts towards higher frequencies and splits into a doublet for all complexes except the last one. Wherein the frequency differences of the doublet bands for the 1: 4 complexes slightly exceed those for the cobalt (III) and copper (II) complexes. In all cases, the thioamide III band does not undergo noticeable changes, while the thioamide IV band decreases.

For complexes of cobalt (III) and copper (II), very intense absorption bands appear in the IR spectra in the region of about 2000-2100 cm<sup>-1</sup>. For copper (II), the frequencies of the bands of the doublet (2173, 2102 cm<sup>-1</sup>) for the complex of maleate with thiosemicarbazide [Cu(HL)L](HMal) obtained in this work practically coincide with the bands in the spectra of previously obtained thiosemicarbazide complexes with similar stoichiometry: glycinate with the composition Cu(L)(Gly) (2174 and 2100 cm<sup>-1</sup>) and glycyglycinate with the composition Cu(HL)L(HGG) (2174 and 2082 cm<sup>-1</sup>) [2]. Previously, the interaction of a number of aliphatic copper (II) carboxylates Cu(C<sub>n</sub>H<sub>2n+1</sub>COO)<sub>2</sub> with thiosemicarbazide was studied and it was found that at n≥4 the carboxylate anion is not included in the reaction products, while thiosemicarbazide appears in a deprotonated form and forms the compound CuL<sub>2</sub> [1]. In the spectrum of this compound, absorption bands in the region of about 2100 cm<sup>-1</sup> were also found. The region 2200-1900 cm<sup>-1</sup> is characteristic of stretching vibrations of cumulated double bonds [8], in particular, for thiocyanate ions. The NCS group, similar to the thiocyanate group, in our case can arise only when the metal is bonded to the nitrogen atom adjacent to the carbon atom. Consequently, for deprotonated thiosemicarbazide, it is necessary to sug-

Table 2  
The IR spectroscopy data (cm<sup>-1</sup>) of complexes, maleates and ligand HL

Compound	ν(NH) <sup>+</sup> ν(OH)	Thioamide bands				ν(NCS)	ν <sub>as</sub> (COO <sup>-</sup> )	ν <sub>s</sub> (COO <sup>-</sup> )	Δν(COO <sup>-</sup> )	ΔΔ ν(COO <sup>-</sup> )
		I	II	III	IV					
HL	3370, 3260, 3170	1530	1315	1000	800					
Cu(Mal)H <sub>2</sub> O							1578	1385	193	
[Cu(HL)L](HMal)	3164	1585, 1502	1385, 1360	1000	763	2173, 2102	1585	1360	225	32
Ni(Mal)·3H <sub>2</sub> O							1551	1418	133	
[Ni(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (HMal) <sub>2</sub> ·2H <sub>2</sub> O	3564, 3390, 3330, 3202, 3154, 3099, 2990, 2881	1559, 1534	1382	1009	736	-	1534	1427	107	-26
[Ni(HL) <sub>4</sub> ](HMal) <sub>2</sub>	3414, 3261, 3187, 2890	1571	1385, 1352	1003	731	-	1571	1385	186	53
Co(Mal)·3H <sub>2</sub> O							1579	1440	139	
[Co(HL) <sub>2</sub> L](HMal) <sub>2</sub>	3326, 3206, 3162	1589, 1521	1395, 1365	1003	736	2055	1521	1395	126	-13
Zn(Mal)·2H <sub>2</sub> O							1575	1432	143	
[Zn(HL) <sub>4</sub> ](HMal) <sub>2</sub>	3408, 3263, 3190, 2885	1572	1385, 3152	1003	731	-	1572	1385	187	44

gest the formation of a four-membered ring, where the metal is covalently bonded to nitrogen and coordinated to sulfur. Thus, for the obtained compounds of cobalt (III) and copper (II), taking into account the analysis data, it should be supposed the complex contains two forms of thiosemicarbazide: molecular and deprotonated. For the complex  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$ , the formation of a chelate also occurs, but the cycle is five-membered with the participation of sulfur and nitrogen of the amino group, which coincides with the X-ray diffraction data of [6]. In coordination compounds with a composition of 1: 4, thiosemicarbazide is obviously monodentate with coordination only through sulfur. It is necessary to pay attention to the presence of a much larger number of absorption bands in the region of about  $3000 \text{ cm}^{-1}$  in the spectrum of the  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$  complex in comparison with the spectra of all other complexes. This can be explained by the presence of bound water in the composition of this compound; separate identification of the N-H and O-H bands is not possible due to the presence of numerous hydrogen bonds.

The values of  $\Delta\Delta \nu(\text{COO}^-)$  for all synthesized complexes are small, and for  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Co}(\text{HL})_2\text{L}](\text{HMal})_2$  are negative at all, that allows to suppose in all cases the outer-sphere character of maleate ions.

In the IR spectra of all synthesized complexes of maleates with thiosemicarbazide, except for the cobalt (III) complex, there is a shoulder at about  $1700 \text{ cm}^{-1}$ . There are no such bands in the spectra of nickel (II) maleate complexes with phenylacetylhydrazide and cobalt (II) maleate with benzhydrazide, for which the presence of the  $\text{Mal}^{2-}$  anion in the compounds was established by X-ray diffraction analysis [9]. The presence of bands around  $1700 \text{ cm}^{-1}$  is related with the presence in the composition of thiosemicarbazide complexes of one COOH group from monodeprotonated maleic acid, for which absorption bands of COOH appear at  $1707 \text{ cm}^{-1}$  [10].

Diffuse reflection spectra (Table 3) indicate the octahedral structure of the nickel complex of composition 1: 2 and the cobalt (III) complex, the tetrahedral structure of the nickel (II) complex of composition 1: 4 and the pseudotetrahedral structure of the copper (II) complex.

Table 3

The diffusion reflectance spectroscopy data of complexes

Compound	$\nu, \text{cm}^{-1}$	Assignment
$[\text{Cu}(\text{HL})\text{L}](\text{HMal})$	18230	
	15060	
	4830	
$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$	17210	${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$
	13110	${}^3\text{T}_1 \rightarrow {}^1\text{E}$
	4450	${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$
$[\text{Ni}(\text{HL})_4](\text{HMal})_2$	17180	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$
$[\text{Co}(\text{HL})_2\text{L}](\text{HMal})_2$	18150	${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_1$

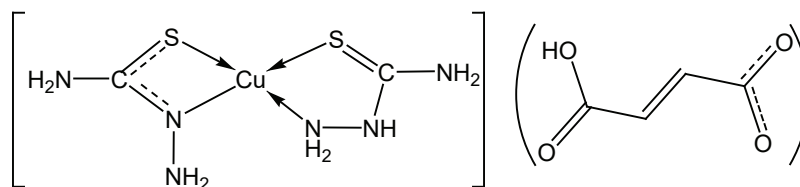
Thermal analysis data (Table 4) show that the highest thermal stability has the complex  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$ , the other complexes decompose at fairly close temperatures. For all synthesized compounds on thermogravigrams the first few effects are endothermic, exoeffects are observed above 500 °C, and about 700 °C there are effects (exothermic for Co(III) and endothermic for other complexes), accompanied by a small increase in mass. Similar increases were also in thiosemicarbazide complexes with malonates, glutarates [3], p-hydroxybenzoates and p-aminobenzoates [4].

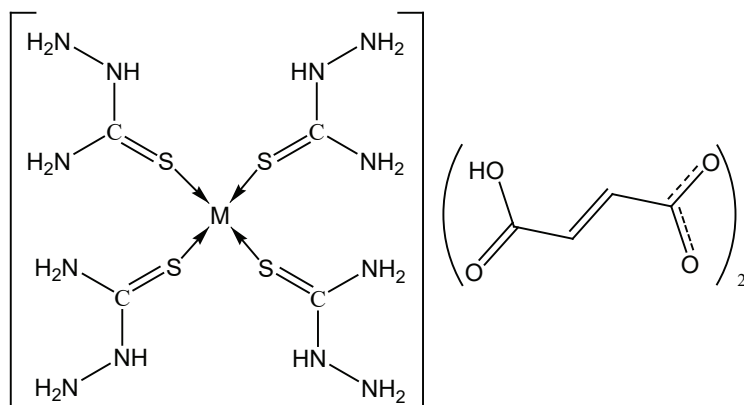
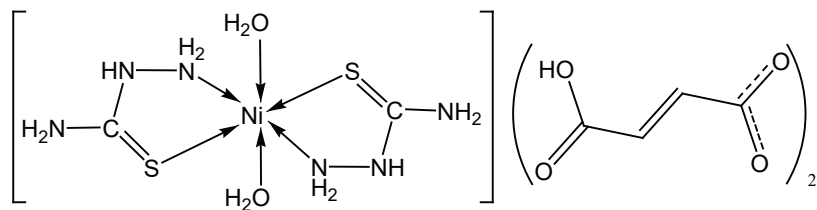
Table 4

The TG analysis data of complexes

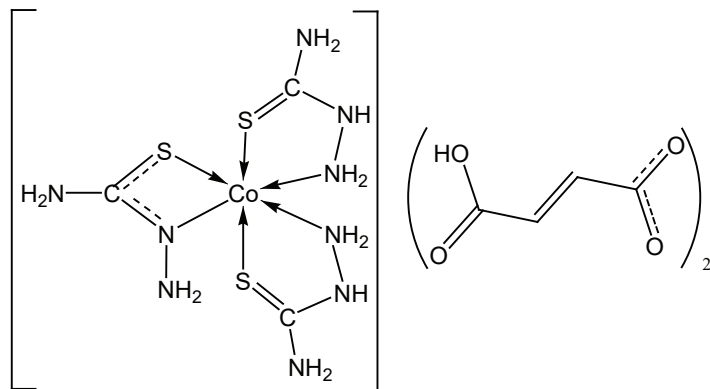
Compound	Endo-effects		Exo-effects		Total mass loss, %
	t, °C	Δm, %	t, °C	Δm, %	
[Cu(HL)L](HMal)	90-110(100)	4.4	500-700(620)	23.0	67.5
	170-190(180)	7.8			
	260-330(270)	14.2			
	700-820(750)	+2.5			
[Ni(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](HMal) <sub>2</sub> ·2H <sub>2</sub> O	170-220 (180)	6.4	570-660 (620)	23.7	80.0
	220-260 (230)	20.7			
	660-800(690)	+1.0			
[Ni(HL) <sub>4</sub> ](HMal) <sub>2</sub>	100-130 (110)	14.3	500-630 (560)	24.0	85.0
	200-240(220)	19.7			
	630-800(750)	+3.0			
[Co(HL) <sub>2</sub> L](HMal) <sub>2</sub>	100-120 (110)	7.2	550-670(580)	23.6	82.5
	180-280(240)	28.7	670-830 (690)	+2.6	
[Zn(HL) <sub>4</sub> ](HMal) <sub>2</sub>	90-110(100)	10.7	600-730(700)	17.8	81.3
	150-200(180)	6.1			
	730-880(770)	+3.1			

The studies carried out suggest the following structures of the synthesized compounds:





M = Ni, Zn



Thus, coordination compounds of copper(II), nickel(II), cobalt(III), and zinc(II) maleates with thiosemicarbazide were synthesized. Their structure was studied by the IR and diffuse reflection spectroscopy methods. In coordination compounds with a composition of 1: 4, thiosemicarbazide is monodentate with coordination only through sulfur. There is five-membered cycle with the participation of sulfur and nitrogen of the amino group for the complex  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$ . For the obtained compounds of cobalt (III) and copper (II), it should be supposed the complex contains two forms of thiosemicarbazide: molecular and deprotonated.

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## СИНТЕЗ І ХАРАКТЕРИСТИКА КООРДИНАЦІЙНИХ СПОЛУК МАЛЕАТІВ 3d-МЕТАЛІВ З ТІОСЕМІКАРБАЗИДОМ

Реакцію водного розчину нітрату двовалентного металу (Cu, Ni, Co, Zn) з гідроксидом натрію добували гідроксид 3d-металу, до нього додавали малеїнову кислоту. Суміш ретельно перемішували, додаючи краплями воду до повного розчинення відповідного малеату металу. Утворений розчин додавали малими порціями до водного розчину тиосемикарбазиду. Осад, що випадав, виділяли, промивали водою та сушили на повітрі. Було синтезовано 5 координаційних сполук: [Cu(HL)L](HMal) (I), [Ni(HL)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](HMal)<sub>2</sub>·2H<sub>2</sub>O (II), [Ni(HL)<sub>4</sub>](HMal)<sub>2</sub> (III), [Co(HL)<sub>2</sub>L](HMal)<sub>2</sub> (IV), [Zn(HL)<sub>4</sub>](HMal)<sub>2</sub> (V). Для кобальту реакція комплексоутворення супроводжується переходом Co(II) у Co(III). Для Cu, Co, Zn склад утворених комплексів сталий незалежно від співвідношення вихідних реагентів, для Ni при співвідношенні метал: тиосемикарбазид 1: 2 утворюється блакитний [Ni(HL)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](HMal)<sub>2</sub>·2H<sub>2</sub>O, а при 1: 4 – зелений [Ni(HL)<sub>4</sub>](HMal)<sub>2</sub>. Для добутих сполук [Co(HL)<sub>2</sub>L](HMal)<sub>2</sub> і [Cu(HL)L](HMal), з урахуванням даних аналізу і ІЧ спектроскопії слід припустити присутність у складі комплексу двох форм тиосемикарбазиду: молекулярної і депротонованої. Для депротонованого тиосемикарбазиду припускається утворення чотиричленного циклу, де метал зв'язаний



ковалентним зв'язком з азотом і координаційним зв'язком із сіркою. Тіосемікарбазид у молекулярній формі в комплексах складу 1:2 і 1:3 координований з утворенням п'ятичленного циклу за участю сірки і азоту аміногрупи. У координаційних сполуках складу 1:4 тіосемікарбазид монодентатний з координацією лише через сірку. Малєат-іони у всіх випадках є зовнішньосферними. При цьому в ІЧ спектрах присутні смуги близько  $1700\text{ см}^{-1}$ , що підтверджує наявність однієї протонованої карбоксильної групи і узгоджується з тим, що малєат-іон однозарядний.

Спектри дифузного відбиття вказують на октаедричну структуру  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$  і  $[\text{Co}(\text{HL})_2\text{L}](\text{HMal})_2$ , тетраедричну структуру  $[\text{Ni}(\text{HL})_4](\text{HMal})_2$  і псевдотетраедричну структуру  $[\text{Cu}(\text{HL})\text{L}](\text{HMal})$ .

Дані термічного аналізу показують, що найбільшу термічну стабільність має комплекс  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2](\text{HMal})_2 \cdot 2\text{H}_2\text{O}$ , інші комплекси розкладаються при досить близьких температурах. Перші ефекти на термогравіграмах є ендотермічними, екзоэффекти спостерігаються вище  $500^\circ\text{C}$ , а близько  $700^\circ\text{C}$  присутні ефекти, що супроводжуються невеликим збільшенням маси.

**Ключові слова:** координаційні сполуки, 3d-метали, тіосемікарбазид

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## СИНТЕЗ И ХАРАКТЕРИСТИКА КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ МАЛЕАТОВ 3d-МЕТАЛЛОВ С ТИОСЕМИКАРБАЗИДОМ

Синтезированы комплексы малєатов меди(II), никеля(II), кобальта(III) и цинка(II) с тіосемікарбазидом. Полученные соединения охарактеризованы методами элементного анализа, инфракрасной спектроскопии, спектроскопии диффузного отражения и термогравиметрии.

**Ключевые слова:** координационные соединения, 3d-металлы, тіосемікарбазид.

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