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Coordination Compounds of *p*-Hydroxybenzoates and *p*-Aminobenzoates of 3*d* Metals with Thiosemicarbazide

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Abstract—Complexes of *p*-hydroxybenzoates and *p*-aminobenzoates of copper(II), nickel(II), and cobalt(III) with thiosemicarbazide have been prepared. The products have been studied by means of elemental analysis, IR spectroscopy, diffuse reflection spectroscopy, and thermogravimetry.

Keywords: thiosemicarbazide, *p*-hydroxybenzoate, *p*-aminobenzoate, 3*d* metal, coordination compound

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Bidentate coordination via nitrogen and sulfur atoms occurs with thiosemicarbazide (HL) in practically all its complex compounds. The composition and structure of its complexes with 3*d* metals depends on the anion of the salt of the complex forming metal. The interaction of thiosemicarbazide with glycinates, glycylglycinates [1], nicotinates, isonicotinates [2], and salicylates [3] of certain 3*d* metals is accompanied with thiosemicarbazide deprotonation. Moreover, anions of the interacting salts mainly determine the geometry parameters of the corresponding coordination polyhedrons of thiosemicarbazide complexes. In the cases of anions of substituted arylcarboxylates, the nature and position of the substituent may affect the formation of the structure of the coordination node. Using the complexes with well known chelating ligand ethylenediamine (en) it has been demonstrated [4] that the $[Cu(en)_2(OH_2)_2](p\text{-}AB)_2\cdot 3H_2O$, $[Cu(en)_2(OH_2)_2](o\text{-}AB)_2\cdot 2H_2O$, and $[Ni(en)_2(OH_2)_2](p\text{-}AB)_2$ are octahedral, whereas the $[Cu(en)_2](o\text{-}OB)_2\cdot H_2O$ is square-planar (AB stands for a single-charged anion of aminobenzoic acid, OB is a single-charged anion of hydroxybenzoic acid).

In this work we have prepared and studied coordination compounds of *p*-hydroxybenzoates and *p*-aminobenzoates of copper(II), nickel(II), and cobalt(III) with thiosemicarbazide. The complexes were prepared via interaction of aqueous solution of thiosemicarbazide with solid *p*-hydroxybenzoate or *p*-aminobenzoate of the corresponding 3*d* metal, the metal to thiosemicarbazide ratio being 1 : 2 in the cases of copper(II) and nickel(II) and 1 : 3 in the case of cobalt(II). The starting *p*-hydroxybenzoates and *p*-aminobenzoates were prepared by addition of the 3*d* metal chloride to the separately synthesized sodium *p*-hydroxybenzoate or *p*-aminobenzoate.

The elemental analysis data (Table 1) showed that the metal:thiosemicarbazide : carboxylate ratio was 1 : 1 : 1 in the case of copper(II) (the interaction was accompanied with thiosemicarbazide deprotonation), 1 : 2 : 2 in the case of nickel(II), and 1 : 3 : 3 in the case of cobalt(II) [the metal was oxidized into Co(III) in the course of the interaction]. We failed to prepare the corresponding zinc complexes via the same procedure.

Analysis of IR spectra of thiosemicarbazide and the prepared complexes (Table 2) showed that in the cases of all complexes the “thioamide I” band was shifted towards higher frequency, the band intensity being simultaneously decreased. In the spectra of copper and nickel complexes with *o*-oxybenzoate anions (**I** and **II**) that band was not observed. The “thioamide II” band was shifted towards higher frequency as well, but the band intensity remained unchanged. The “thioamide III” band was substantially weakened due to the complex formation, and the frequency of “thioamide IV” band was lowered. The similar pattern of thioamide bands changes is known to correspond to bidentate coordination of the ligand involving sulfur and nitrogen atoms [5], being in line with the earlier reported data for thiosemicarbazide complexes of 3*d*

Table 1. Elemental analysis data and color of coordination compounds **I–VI** of 3*d* metals *p*-hydroxybenzoates and *p*-aminobenzoates with thiosemicarbazide[a]

Complex	Color	Found, %			Formula	Calculated, %		
		M	N	S		M	N	S
[CuL(X)] (**I**)	Grey	21.6	14.3	11.1	$C_8H_9CuN_3O_3S$	22.0	14.4	11.0
$[Ni(HL)_2]X_2$ (**II**)	Grey-green	11.9	16.2	12.7	$C_{16}H_{20}N_6NiO_6S_2$	11.5	16.3	12.4
$[Co(HL)_3]X_3$ (**III**)	Brown	8.3	17.2	12.8	$C_{24}H_{30}CoN_9O_9S_3$	7.9	17.0	12.9
[CuL(Y)] (**IV**)	Light-grey	21.7	18.9	11.1	$C_8H_{10}CuN_4O_2S$	22.1	19.3	11.0
$[Ni(HL)_2]Y_2$ (**V**)	Grey-green	11.9	21.7	12.2	$C_{16}H_{22}N_8NiO_4S_2$	11.5	21.8	12.5
$[Co(HL)_3]Y_3$ (**VI**)	Dark-red	8.0	22.8	13.1	$C_{24}H_{33}CoN_{12}O_6S_3$	8.0	22.7	13.0

[a] Hereinafter: X is *p*-hydroxybenzoate, Y is *p*-aminobenzoate, HL is thiosemicarbazide.

Table 2. Features of IR spectra (cm^{-1}) of thiosemicarbazide (HL), 3*d* metals *p*-hydroxybenzoates and *p*-aminobenzoates and their complexes **I–VI** with thiosemicarbazide

Compound	Thioamide bands				ν(NH) [ν(NCS)]	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
	I	**II**	**III**	**IV**					
HL	1530	1315	1000	800	3370, 3260, 3170				
$CuX_2·2H_2O$						1608	1385	223	
I	–	1360	–	791	3408, 3303, 3262, 3085 [2082]	1607	1392	215	–8
$NiX_2·2H_2O$						1603	1402	201	
II	–	1360	–	790	3416, 3314, 3203, 3008	1597	1392	205	4
$CoX_2·2H_2O$						1610	1400	210	
III	1595	1383[a]	–	770	3331, 3168, 3079	1608	1383[a]	225	15
$CuY_2·2H_2O$						1611	1390	221	
IV	1575	1323	1010	793	3461, 3382, 3365, 3290 [2174, 2109]	1602	1422	180	–41
$NiY_2·2H_2O$						1605	1382	223	
V	1580	1377[a]	–	790	3416, 3314, 3203, 3008	1602	1377[a]	225	2
$CoY_2·2H_2O$						1610	1384	226	
VI	1575	1344	1010	772	3459, 3363, 3176	1602	1384	218	–8

[a] Both thiosemicarbazide and carboxylate anion contribute to the absorption band.

metals with inorganic anions or carboxylate anions [6, 7].

The spectrum of complex **I** contained a very strong absorption band at 2082 cm^{-1}, and the spectrum of compound **IV** had a doublet of very strong bands at 2174 and 2109 cm^{-1}. As was demonstrated earlier [1–3], those bands were assigned to the formation of four-membered cycle involving nitrogen and sulfur atoms of deprotonated thiosemicarbazide.

The testing of the coordination model of carboxylate groups is conveniently done by using $\Delta\Delta\nu(COO^-)$ value, the difference between the $\Delta\nu(COO^-)$ values for the mixed complex and the starting carboxylate [$\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-)$]. The $\Delta\Delta\nu(COO^-)$

Table 3. Parameters of diffuse reflection spectra of complexes **I–VI**

Comp. no.	λ, nm	Assignment
I	649	
	1680	
II	423	$^3T_1 \rightarrow {}^1T_2$
	597	$^3T_1 \rightarrow {}^3T_1(P)$
	2132	$^3T_1 \rightarrow {}^3A_2$
III	540	$^1A_{1g} \rightarrow {}^1A_2$
IV	1680	
V	627	$^3T_1 \rightarrow {}^3T_1(P)$
	2215	$^3T_1 \rightarrow {}^3A_2$
VI	900	$^1A_{1g} \rightarrow {}^1A_2$

values (Table 2) between the starting carboxylates and their complexes with thiosemicarbazide were low, being negative in the cases of the complexes **I**, **IV**, and **VI** . Hence, the symmetry of carboxylate anions in the prepared coordination compounds suffered minor changes as compared to that of the starting carboxylates. In the complexes of cobalt(III) and nickel(II) the substituted benzoate ions were displaced to the outer sphere, and in the copper complexes they remained bidentate and located in the inner sphere.

The bands position in the diffuse reflection spectra of the prepared compounds (Table 3) corresponded to pseudotetrahedral structure of copper complexes **I** and **IV**, tetrahedral structure of nickel complexes **II** and **V**, and octahedral structure of cobalt complexes **III** and **VI** [8].

Thermogravigrams of all studied compounds (Table 4) were similar. The first effect was in all cases endothermic. For some of the complexes the second effect was endothermic as well. In all cases the highest mass loss corresponded to either the first or the second endothermic effect. One or two endo-thermic effect(s) were followed by one or two exo-thermic effect(s) corresponding to burning out of the organic part of the molecules. Those processes were complete at 570–650°C. At even higher temperature, endothermic effects were observed (exothermic effect was observed in the case of complex **II**), accompanied by a slight mass increase. That possibly resulted from the formation of intermediate nitrides or carbides of the

Table 4. Derivatography studies of thermal stability of complexes **I–VI**

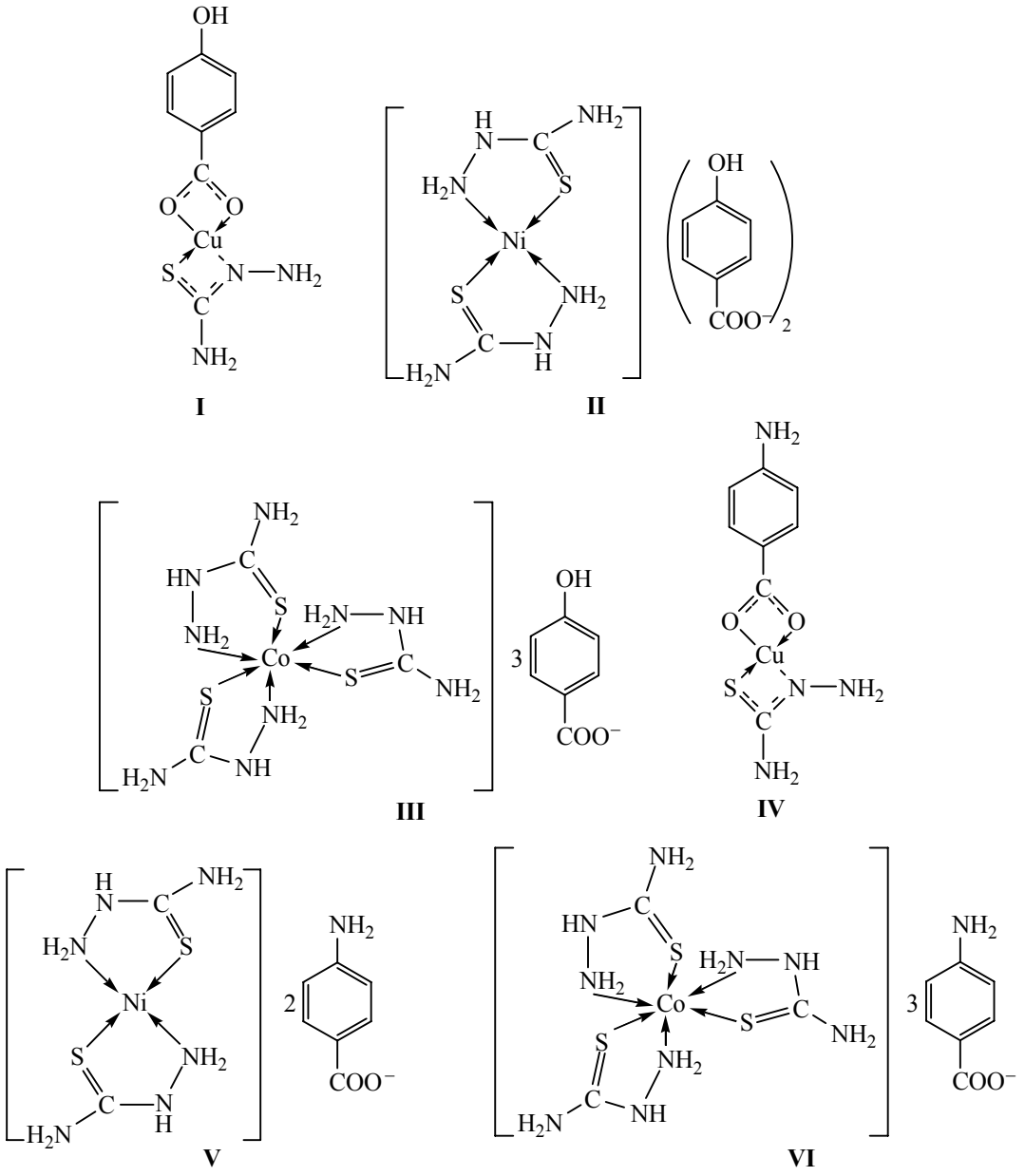
Comp. no.	Endothermic effects		Exothermic effects		Total weight loss, %
	t, °C	Δ*m*, %	*t*, °C	Δ*m*, %	
I	200–270(240)	45.1	390–450(420)	7.2	71.3
	610–800(700)	+4.7	450–610(530)	10.9	
II	120–190(150)	6.9	440–570(550)	12.4	84.5
	230–270(250)	52.9	570–610(600)	+2.0	
	610–900(800)	6.9			
III	200–260(250)	33.5	400–460(430)	5.6	68.8
	630–950(700)	+1.7	520–630(600)	12.0	
IV	190–250(210)	31.3	400–460(420)	7.2	67.5
	650–820(730)	+3.4	460–650(570)	16.9	
V	200–250(230)	46.5	400–540(460)	7.8	77.5
	620–820(695)	+3.4	540–620(590)	13.4	
VI	90–110(100)	5.1	540–630(600)	13.8	84.0
	190–230(220)	36.9			
	630–870(680)	+1.0			

corresponding metal that were further transformed into oxides.

The collected data allow ascribing the following structures to the prepared coordination compounds **I–VI** (Scheme 1).

The comparison of the prepared complexes with thiosemicarbazide complexes based on other carboxylates revealed that in the case of the cobalt(III) complex the stoichiometry and the geometry of the coordination node were similar to those of the sulfosalicylate; the copper complex showed the stoichiometry and coordination number identical to those of the glycine complex [1]; and the nickel(II) complex was similar to the corresponding salicylate [3] and sulfosalicylate [9]. However, glycine–thiosemicarbazide complex of copper(II) and salicylate-thiosemicarbazide complex of nickel(II) were square-planar, and sulfosalicylate-thiosemicarbazide complex of nickel(II) existed in the form of two isomers (square-planar and tetrahedral). The complexes of copper(II)

Scheme 1.



and nickel(II) prepared in this work were tetrahedral. Seemingly, *p*-substituted benzoate anions increased the probability of tetrahedral coordination of copper(II) and nickel(II).

EXPERIMENTAL

IR spectra (KBr pellets) were recorded using a FTIR-8400S (Shimadzu) instrument. Diffuse reflection spectra were obtained using a Lambda-9 spectrophotometer (Perkin Elmer) with MgO as reference (β_{MgO} 100%). Thermograms of mass loss were recorded using a Paulik–Paulik–Erdey derivatograph in air at heating rate of 10 deg/min. Elemental analysis of the isolated complexes was performed as follows: the metals content by complexonometry [10], nitrogen content by the Dumas method [11], and sulfur content by the Schoeniger method [11].

Cobalt(II), nickel(II), and copper(II) chlorides, *p*-hydroxybenzoic and *p*-aminobenzoic acids, and thiosemicarbazide (all of "analytically pure" grade) were used as received.

Complexes I, II, IV, and V. Thiosemicarbazide (1.365 g, 15 mmol) was dissolved in 150 mL of water at heating. The solution was cooled to ambient temperature, and 7.5 mmol of crystalline copper(II) or nickel(II) *p*-hydroxybenzoate or *p*-aminobenzoate was added by portions. The mixture was stirred till complete homogenization. The formed precipitate was filtered off, washed with small amount of water, and dried to constant mass at 60°C.

Complexes III and VI. Thiosemicarbazide (2.05 g, 22.5 mmol) was dissolved in 200 mL of water at heating. The solution was cooled down to ambient temperature, and 7.5 mmol of crystalline cobalt(II) *p*-hydroxybenzoate or *p*-aminobenzoate was added by portions. The mixture was stirred till complete dissolution. The solution was evaporated to form a precipitate that was filtered off, washed with small amount of water, and dried to constant mass at 60°C.

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