Coordination Compounds of 3*d*-Metal Phthalates with Semicarbazide

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Abstract—Complexes of cobalt(II), nickel(II), copper(II), and zinc phthalates with semicarbazide were synthesized. The obtained compounds were characterized by the methods of chemical analysis, IR spectroscopy, diffusion reflection spectroscopy, and thermogravimetry.

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Coordination compounds containing residues of phthalic acid H₂Pht are interesting from both theoretical and practical points of view. They are capable to catalyze various reactions, whereas non-coordinated carboxy group residues Pht²⁻ and HPht⁻ can be important in various catalytic processes [1]. Earlier we have prepared coordination compounds of phthalates of 3*d*-metals with nicotinamide and have determined structures of copper and cobalt compounds by the XRD method [2, 3]. The copper(II) phthalate complex with nicotinamide (NA) has the composition $[Cu(NA)_2Pht(H_2O)]$ ·0.5H₂O, the phthalate anion being a bridging ligand. The composition of the cobalt(II) phthalate coordination compound with nicotinamide corresponds to the formula [Co(NA)₂(H₂O)₄]Pht·2H₂O, the phthalate anion being in the outer sphere.

To study variations of the phthalate anion function in coordination compounds upon replacement of one molecular ligand by another, with a potentially greater denticity, we have chosen semicarbazide NH₂NHC· (=O)NH₂ (L) as such a ligand. Semicarbazide contains the same donor atoms as nicotinamide (oxygen and nitrogen), however nicotinamide in complexes is preferably coordinated in a monodentate mode through the nitrogen atom of the pyridine cycle, whereas semicarbazide is capable to be both mono- and bidentate. We have obtained blue and pink isomers of the coordination compounds of cobalt(II) benzoate with semicarbazide of the compositions 1:3 and 1:4. In the 1:4 complex semicarbazide is monodentate and is coordinated through oxygen, whereas the isomers are of the ionization type: in the pink complex benzoateanions are present into the inner sphere, and in the blue complex, in the outer sphere. In the 1:3 complex the bond isomerism is added to the ionization isomerism: in the pink isomer only bidentate semicarbazide molecules enter into the inner sphere, whereas in the blue isomer a tetrahedral coordination unit is formed by three monodentate semicarbazides and one monodentate benzoate anion [4].

The aim of the present work was to isolate products of reactions of cobalt(II), nickel(II), copper(II), and zinc(II) phthalates with semicarbazide in a solid state and to study their structure and properties.

The complexes were prepared by the action of dry phthalates of the corresponding 3*d*-metals on aqueous solutions of preliminarily neutralized semicarbazide, in the ratios metal–semicarbazide 1:2 and 1:4.

The chemical analysis (Table 1) shows that the composition of isolated solid compounds is constant irrespective of the taken ratio of reagents. Coordination compounds of cobalt(II) and zinc(II) are similar in composition: the metal-semicarbazide ratio 1:3, and the phthalate anion is twice deprotonated. Copper(II) and nickel(II) phthalates are monodeprotonated, and the metal-semicarbazide ratio is 1:2 in the copper(II) complex and 1:4 in the nickel(II) complex. The comparison with analogous data for nicotinamide complexes of phthalates of 3*d*-metals [2, 3] shows that semicarbazide increases the tendency to the phthalate anion protonation: among the nicotinamide complexes of phthalates, the anion HPht⁻ was present only in the nickel(II) complex, whereas in the copper complexes

Comp. no.	Color	Found, %		Formula	Calculated, %	
		М	Ν	Foimula	М	Ν
Ι	Pink	13.4	28.3	C ₁₁ H ₁₉ CoN ₉ O ₇ ([CoL ₃]Pht)	13.2	28.1
п	Colorless	14.7	28.1	C ₁₁ H ₁₉ N ₉ O ₇ Zn ([ZnL ₃]Pht)	14.3	27.8
Ш	Blue	8.6	24.2	C ₂₀ H ₃₀ N ₁₂ NiO ₁₂ ([NiL ₄](HPht) ₂)	8.6	24.4
IV	Dark brown	12.2	15.8	C ₁₈ H ₂₀ CuN ₆ O ₁₀ ([CuL ₂](HPht) ₂)	11.8	15.4

Table 1. Elemental analysis data for the products I-IV of reactions of 3d-metals phthalates with semicarbazide

(1:2 and 1:4) the anion Pht^{2-} was retained. The majority of phthalate complexes with nicotinamide includes bound water, whereas water is absent from the analogous semicarbazide compounds. In the complexes of all studied metals, except for copper(II), the number of coordinated semicarbazide molecules is greater than the number of coordinated nicotinamide molecules.

If we compare these products with complexes of the same metals with semicarbazide synthesized earlier, in which valerate and benzoate were taken as anions of a salt, it is possible to assume that the phthalate anion allows only one complex with the most stable inner sphere to be isolated. So, for cobalt(II) valerate the compounds 1:2 and 1:3 with semicarbazide were isolated, and analogous compounds were isolated for cobalt(II) benzoate (1:3 and 1:4), i.e. the complex with the metal-L ratio of 1:3 is characteristic for both anions [4]. This is the ratio, which is also realized in the semicarbazide complex of cobalt(II) phthalate. For other studied complexforming agents the composition of the complexes of phthalates with semicarbazide was the same as in the complexes of valerates and benzoates.

The assignment of bands in the IR spectra of semicarbazide hydrochloride and of semicarbazide complexes of 3*d*-metals phthalates based on the data [5–7] is given in Table 2. Initial semicarbazide hydrochloride contains a protonated amino group, and its IR spectrum includes the v_s and $v_{as}(NH_3^+)$ bands at 2911, 2670, 1946 cm⁻¹, which are absent from the IR spectra of the synthesized complexes. As a result of the complex formation the difference between frequencies of the symmetric and antisymmetric stretching vibrations of the amino group substantially increases (from 54 up to 74–113 cm⁻¹).

Frequencies of the absorption bands involving contributions of CO groups vibrations decrease as a result of the complex formation: v(C=O) reduces its

frequency by 30-44 cm⁻¹ and the decrease in the frequency of $\delta(O=C-N)$ is even more essential, 50-79 cm⁻¹. The v(C–N) band is shifted to the highfrequency region, the value of this shift being about 40 cm⁻¹ for complexes with M:L ratios of 1:2 [copper(II) complex] and 1:3 [cobalt(II) and zinc(II) complexes], whereas it does not exceed 30 cm^{-1} for the nickel(II) complex, in which four coordinated ligands belong to one metal atom. There are differences also in shifts of the band $v(C-N) + \delta(N-H) + \delta(N-N)$: for the nickel complex, despite of the equal direction of the shift (in all cases to the low-frequency region), its value is slightly less than for all the rest synthesized compounds. Thus, taking into account a stoichiometry of the complexes and certain differences in the values of shifts of absorption bands in the IR spectra, we should assume that semicarbazide is coordinated variously: at the M:L ratios 1:2 (the copper complex) and 1:3 (the cobalt and zinc complexes) it is bidentate and coordinated to the metals through the oxygen atom and the nitrogen atom of the hydrazine fragment to form a five-membered chelate cycle, whereas in the nickel complex (1:4) it is monodentate and is coordinated only through the oxygen atom.

Comparative analysis of the positions and shapes of absorption bands in the IR spectra of synthesized coordination compounds shows that the spectra of CoL_3Pht and ZnL_3Pht are very similar, in some regions these spectra are almost identical (Table 2). The spectra of copper and nickel compounds are more specific. It holds true for vibrational frequencies of both semicarbazide and phthalate anions.

To make a diagnosis of a coordination model of carboxylate groups, a value of $\Delta v(v_{as} - v_s)$, i.e. the distance between v_{as} and v_s is often used [8]. We think that the value of $\Delta \Delta v(COO^-)$, i.e. the difference of $\Delta v(COO^-)$ values for a mix-ligand complex and the initial carboxylate, but not $\Delta v(v_{as} - v_s)$, is more convenient for the interpretation of the IR spectra of

COORDINATION COMPOUNDS OF 3d-METAL PHTHALATES

G 1		Absorption bands (cm ⁻¹) of COO ⁻ group			
Compound	Absorption bands (cm ⁻⁺) of semicarbazide and phthalate anion		$\nu_s(COO^-)$	$\Delta v(COO^{-})$	$\Delta\Delta\nu(COO^{-})$
L·HCl	3425 [v(NH)], 3314 [v _{as} (NH ₂)], 3260 [v _s (NH ₂)], 2911, 2670, 1946 [v _s , v _{as} (NH ₃ ⁺)], 1687 [v(C=O)], 1585 [v(CO) + δ (NH ₂)], 1524 [v(C–N)], 1478 [v(C–N) + δ (NH) + δ (N–N)], 1385 [v(C–N) + δ (NH ₂)], 1213, 1182, 1090 [δ (NH ₂)], 935 [δ (O=C–N)], 770 [π (O=C–N ₂)], 721 [w(NH ₂)] or <i>r</i> (NH ₂)], 562, 512 [v(C–N) + δ (HNN) + δ (NNC) + δ (OCN) + δ (NCN)]				
$CoPht{\cdot}2H_2O$		1558	1398	160	
I	3451 [v(NH)], 3286 [v _{as} (NH ₂)], 3212 [v _s (NH ₂)], 1645 [v(C=O)], 1563 ^a [v(C-N)], 1444 [v(C-N) + δ (N-H) + δ (N-N)], 1312 [v(C-N) + δ (NH ₂)], 1124, 1154, 1117, 1087, 964 [δ (NH ₂)], 876 [δ (O=C-N)], 763 [π (O=C-N ₂)], 722 [w(NH ₂) or <i>r</i> (NH ₂)], 529 [v(C-N) + δ (HNN) + δ (NNC) + δ (OCN) + δ (NCN)]	1563 ^ª	1383	180	-20
ZnPht·2H ₂ O		1616	1394	222	
Π	3453 [v(N–H)], 3285 [v _{as} (NH ₂)], 3192 [v _s (NH ₂)], 1647 [v(C=O)], 1563 ^a [v(C–N)], 1445 [v(C–N) + δ (N–H) + δ (N–N)], 1312 [v(C–N) + δ (NH ₂)], 1123, 1153, 1117, 1087, 1038, 964 [δ (NH ₂)], 885 [δ (O=C–N)], 771 [π (O=C–N ₂)], 721 [w(NH ₂) or <i>r</i> (NH ₂)], 514 [v(CN) + δ (HNN) + δ (NNC) + δ (OCN) + δ (NCN)]	1563 ^a	1383	180	-42
NiPht·2H ₂ O		1560	1405	155	
ш	3402 [v(N–H)], 3275 [v _{as} (NH ₂)], 3162 [v _s (NH ₂)], 1643 ^a [v(C=O)], 1553 [v(C–N)], 1452 [v(C–N) + δ (N–H) + δ (N–N)], 1300 [v(C–N) + δ (NH ₂)], 1222, 1124, 1025, 965 [δ (NH ₂)], 856 [δ (O=C–N)], 756 [π (O=C–N ₂)], 722 [w(NH ₂) or <i>r</i> (NH ₂)], 554 [v(C–N) + δ (HNN) + δ (NNC) + δ (OCN) + δ (NCN)]	1582	1403	179	24
CuPht·H ₂ O		1530	1410, 1350	120, 180	
IV	3400 [v(N–H)], 3290 [v _{as} (NH ₂)], 3204 [v _s (NH ₂)], 1657 [v(C=O)], 1565 [v(C–N)], 1444 [v(C–N) + δ (N–H) + δ (N–N)], 1300 [v(C–N) + δ (NH ₂)], 1214, 1150, 1123, 1087, 1000 [δ (NH ₂)], 864 [δ (O=C–N)], 762 [π (O=C–N ₂)], 704 [w(NH ₂) or <i>r</i> (NH ₂)], 565 [v(C–N) + δ (HNN) + δ (NNC) + δ (OCN) + δ (NCN)]	1594	1391	203	83, 23

Table 2. IR spectra of semicarbazide (L), phtha	ates of 3d-metals, and products I-IV of their reactions
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^a Both semicarbazide and the phthalate anion make contributions to the absorption band.

the carboxylate complexes. The values of $\Delta\Delta\nu(\text{COO}^-)$ for the synthesized CoL₃Pht and ZnL₃Pht compounds have appeared negative, i.e. the difference between frequencies of antisymmetric and symmetric vibrations has decreased as a result of the complex formation. Obviously, it is connected with a certain equalization of bonds in the phthalate anion. The most probable reason for such changes can be the displacement of the phthalate anion into the outer sphere of the complexes. The negative $\Delta\Delta\nu(\text{COO}^-)$ value was observed also in the IR spectrum of cobalt(II) phthalate with nicotinamide, for which outer-sphere position of the phthalate anion was confirmed by the XRSA method [3]. The IR spectra of copper(II) and nickel(II) complexes confirm the presence of the monoprotonated outer-sphere phthalate anion. Coordination compounds of nickel(II), cobalt(II), copper(II), and zinc(II) phthalates with 1-methyl-imidazole were studied by the XRSA and IRS methods [1]. In the IR spectra of the complexes [M(1-MeIm)₆](HPht)₂·2H₂O (M = Co, Ni) v(COOH) absorption bands at 1634 cm⁻¹ are present. In the spectra of the CuL₂(HPht)₂ and NiL₄(HPht)₂ complexes similar bands were also recorded: in the copper(II) spectrum a separate absorption band at 1640 cm⁻¹ is observed, whereas in the case of the nickel compound NiL₄(HPht)₂ the v(COOH) absorp-

Comp. no.	λ_{max}, nm	Assignment		
I	495	${}^4T_{1g}(\mathbf{F}) \to {}^4T_{1g}(\mathbf{P})$		
	1188	${}^{4}T_{1g}(\mathbf{F}) \to {}^{4}T_{2g}$		
III	580	${}^{3}T_{1} \rightarrow {}^{3}T_{1}(\mathbf{P})$		
	895	${}^{3}T_{1} \rightarrow {}^{1}E$		
	2067	${}^{3}T_{1} \rightarrow {}^{3}A_{2}$		
IV	1665			
	2153			

Table 3. Diffusion reflection spectra of semicarbazide complexes of 3d-metals phthalates I, III, IV

tion band is imposed on the v(C=O) band of semicarbazide at 1643 cm⁻¹, therefore its intensity is increased and this band becomes the most intensive in the whole spectrum, whereas it is weaker than other absorption bands in the spectra of the other compounds: for CoL₃Pht and ZnL₃Pht the band at 1563 cm⁻¹ has the greatest intensity and for CuL₂(HPht)₂ it is the band at 1391 cm⁻¹. For the copper(II) compound $\Delta\Delta v$ (COO⁻) has two values due to differently bound groups in the initial complex CuPht·H₂O, which was confirmed by the XRD data [9]. To determine the geometry of coordination units, we have fulfilled the study of the synthesized complexes by the diffusion reflection spectroscopy (Table 3). The examination of bands positions suggests that the cobalt(II) complex has the octahedral structure, the nickel(II) complex, the tetrahedral structure, and the copper (II), the pseudo-tetrahedral structure [10].

The results of the thermogravimetric study of the synthesized compounds (Table 4) have shown that the thermal stability of the synthesized semicarbazide complexes of phthalates of various 3d-metals decreases in the sequence: $Zn^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+}$.

For cobalt(II), nickel(II), and copper(II) compounds the first two effects in the thermograms are endothermic, a similar pattern was observed also for semicarbazide complexes of these metals with the valerate anion [4]. For the zinc compound the first three effects are endothermic. All effects at higher temperatures are exothermic. Obviously, the endoeffects correspond to the destruction of chemical bonds of metals with semicarbazide and acido ligands, and exoeffects, to burning-out organic fragments.

Comp. no.	Endoeffects		Exoeffects		Total weight
	t, °C	$\Delta m, \%$	t, °C	$\Delta m, \%$	loss, %
Ι	92–155 (118)	8.2	255-300 (290)	6.6	70.0
	177–237 (195)	8.2	300-350 (340)	8.2	
			350-408 (390)	16.7	
			408–460 (450)	10.5	
			460-500 (490)	7.9	
П	122–202 (152)	12.2	320-350 (335)	8.7	77.1
	220-281 (260)	11.0	350-400 (390)	13.3	
	281-320 (300)	3.8	400-450 (435)	8.4	
			450–500 (470)	5.3	
III	110–183 (133)	6.2	283-340 (330)	17.1	56.2
	210-270 (225)	21.5	340-400 (360)	10.5	
IV	90–110 (103)	8.0	216–270 (252)	24.7	74.2
	110–190 (150)	5.5	270-320 (300)	10.6	
			320-350 (340)	8.5	
			350-438 (400)	8.0	
			438–460 (450)	7.5	

Table 4. Thermogravimetric data on the thermal stability of semicarbazide complexes of 3d-metals phthalates I-IV

The data obtained allow us to assign the following structure to the synthesized compounds of 3*d*-metals phthalates with semicarbazide.



Thus, the replacement of monodentate nicotinamide by potentially bidentate semicarbazide in the complexes of phthalates of 3d-metals increases the tendency of the phthalate anion to protonation and decreases its ability to take a position in the inner sphere of a complex.

EXPERIMENTAL

The IR spectra were taken on a Perkin–Elmer SPECTRUM BX II FT-IR instrument in tablets with

KBr. Diffusion reflection spectra (DRS) were recorded on a Perkin–Elmer Lambda-9 spectrophotometer with MgO (β_{MgO} 100%) as a standard. The thermogravigrams were taken on a Paulik-Paulik-Erdey derivatograph in air at a heating rate of 10 deg min⁻¹.

Analytical-grade cobalt(II), nickel(II), copper(II), and zinc chlorides, phthalic acid, and semicarbazide hydrochloride were used in the work.

Content of metals in the isolated compounds was determined by the chelatometry method [11] and those of nitrogen by the Dumas method [12].

Neutralization of semicarbazide hydrochloride [13]. A weighted sample of semicarbazide hydrochloride L·HCl was dissolved in a minimal quantity of distilled water. The solution was neutralized by adding one after the other granules of dry KOH. After addition of each granule pH was checked by means of the universal indicator. As soon as pH exceeded seven, the addition of KOH was stopped. The resulting solution was evaporated to dryness on a water bath, and hot anhydrous ethanol was added in portions to the solid residue. The precipitate of potassium chloride was separated by filtering off the alcohol solution of semicarbazide.

Complexes (I, II, IV). The alcohol solution obtained after neutralization of 0.56 g of semicarbazide hydrochloride was evaporated to a volume of 1.5 ml, 10 ml of water was added, and 0.0025 mol of a dry 3*d*-metal phthalate was added in portions with stirring. The mixture was stirred up to the formation of a precipitate, which was filtered off, washed by a minimal quantity of water, and dried in an desiccator above $CaCl_2$ to a constant weight.

Complex (III). An initial solution of semicarbazide hydrochloride (0.56 g) was neutralized, the base being prepared similarly. Dry nickel(II) phthalate (0.0025 mol) was added to the resulting solution in portions with stirring and heated up to the full dissolution. A blue solution was transferred to a porcelain cup and evaporated at room temperature till the formation of a precipitate, which was washed out by a minimal quantity of water, and dried in an desiccator above $CaCl_2$ to a constant weight.

Complexes with the molar ratio semicarbazide–3*d*-metal phthalate of 0.01:0.0025 were obtained similarly.

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