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Coordinational Compounds of 3*d*-Metal Phthalates with Nicotinamide

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Abstract—Complexes of iron(II), cobalt(II), nickel(II), copper(II), and zinc with nicotinamide were synthesized. The compounds obtained were characterized by means of chemical analysis, conductometry, thermogravimetry, and by means of the IR and the diffuse reflection spectroscopy.

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Anions of *o*-phthalic acid, H_2Pht, are interesting objects from the point of view of complex formation. Phthalate ligand exhibits broad variety in the structure of H_2Pht-containing complexes existing either as polymeric or monomeric compounds with different functions of two chemically equivalent carboxylic groups [1]. Structural function of acid, and of its monoation $HPht^-$ and dianion Pht^{2-} is determined by compromise between the steric hindrances determined by two carboxylic groups in *o*-position and their tendency to form the maximum number of the metal-oxygen bonds while complex formation [2]. On the basis of analysis of the great array of experimental and reported data the workers [3] have distinguished 26 ways of coordination of *o*-phthalate anion with the dentity varying from 1 to 7. The way of coordination of phthalate anion in complexes with different ligands is effected by sterical characteristics of co-ligands. The Complexes, formed by the molecular nitrogen-containing ligands, in detail, by pyridine and methylpyridines and the phthalate anions are reported about [1, 2, 4]. But no data on the products of the reaction of metal phthalates with another organic molecules containing the pyridine fragment were found by us. Due to that we have chosen nicotinamide with the purpose of synthesis and investigation of structure and properties of its coordinational com-pounds with iron(II), cobalt(II), nickel(II), copper(II), and zinc phthalates.

The complexes were synthesized by addition of crystalline 3*d*-metal phthalate to the nicotinamide aqueous solution in the 1:2 and 1:4 metal–nicotinamide ratio. The composition of complexes appeared to be independent of the reagent ratio for all the metals under study. Results of chemical analysis (Table 1) show that all the complex formers under study give the compounds of the 1:2 metal–nicotinamide composition. In the case of copper(II) the compound of the 1:4 composition was also obtained. Reaction of nickel(II) with nicotinamide is accompanied by partial protonation of the phthalate residue, and it enters the complex as monoanion. Complexes of 3*d*-metal phthalates with nicotinamide dissolve in water and DMF, and to some extent lower in ethanol. For the compound with sufficient solubility in water (above 0.01 mol l^{-1}) the values of molar electroconductivities were measured, what permitted to establish the type of their ionic decay (Table 1).

Structure of the compounds **II**, **IV** was evaluated by means of the X-ray analysis [5, 6]. It was found that structural units of compound **II** are $[CoL_2(H_2O)_4]^{2+}$ cations and the Pht^{2-} anions. The Co atom is located in the sufficiently regular octahedral surrounding of two pyridine nitrogen atoms, two nicotinamide ligands, and four oxygen atoms belonging to water molecules. Structural units of the compound **IV** are linear chains formed by means of the bridge phthalate anions and the molecules of crystallization water.

Each copper atom is coordinated by two pyridine nitrogen atoms of two nicotinamide ligands, by two oxygen atoms of different phthalate anions, and the oxygen atom of water molecule. Coordination number

Table 1. Elemental analysis, molar electroconductivity in water, and coloration of products **I–VI** of the reaction of 3*d*-metal phthalates with nicotinamide

Comp. no.	Color	Found, %		Formula	Calculated, %		Λ_m, Ω^{-1} cm^2 mol^{-1}
		M	N		M	N	
I	Brown	12.4	12.2	$C_{20}H_{16}FeN_4O_6$ [FeL_2Pht]	12.1	12.1	Poorly soluble
II	Reddish pink	10.2	9.4	$C_{20}H_{16}CoN_4O_6\cdot 6H_2O$ [$CoL_2Pht\cdot 6H_2O$]	10.3	9.7	91
III	Greenish light blue	8.8	8.1	$C_{28}H_{22}N_4NiO_{10}\cdot 2H_2O$ [$NiL_2(HPht)_2\cdot 2H_2O$]	8.8	8.4	253
IV	Blue	13.2	11.1	$C_{20}H_{16}CuN_4O_6\cdot 1.5H_2O$ [$CuL_2Pht\cdot 1.5H_2O$]	12.8	11.2	Poorly soluble
V	Light blue	8.9	15.2	$C_{32}H_{28}CuN_8O_8$ [CuL_4Pht]	8.9	15.6	Poorly soluble
VI	White	12.6	11.2	$C_{20}H_{16}N_4O_6Zn\cdot 2H_2O$ [$ZnL_2Pht\cdot 2H_2O$]	12.8	11.0	74

is completed to six by the second (chelating) distant atom of carboxy group. Coordinational polyhedron of copper atom is the elongated tetragonal bipyramide.

Conclusions concerning the character of ligand coordination and the coordination polyhedrons of the rest substances **I**, **III**, **V**, and **VI** were made on the basis of spectral data. Attribution of frequencies of the main absorption bands in the IR spectra of nicotinamide and the complexes synthesized was carried out on the basis of the reported data [7–9] and presented in Table 2. Frequencies of some bands in the IR spectrum of nicotinamide are significantly influenced by the association of its molecules in the solid state due to formation of H-bonds. This effect is more significant for the spectra of crystalline amides, while in the spectra of crystalline complexes of metals with amides the effect of H-bonding is insignificant if the amino group nitrogen atom of nicotinamide does not take part in bonding. Spectral and X-ray data of the large number of complexes tell in favor of this fact [8]. That is why for the correct attribution of shifts of the absorption bands of nicotinamide while complex formation we suggested it necessary to obtain IR spectra of the ligand in KBr pellets as well as in the suspension in vaseline oil. In the case of metal phthalates and complexes the IR spectra of samples in vaseline oil are not informative because the absorption bands of oil overlap partially with the absorption bands of carboxylic group. Hence, comparison of the absorption bands of nicotinamide in vaseline oil and of metal phthalates and complexes synthesized in KBr pellets was most convenient for interpretation of the IR spectra.

Comparison of the absorption bands of nicotinamide on the one hand, and of the complexes obtained on the other showed that in all the cases the frequency of $\nu(C{=}O)$ (“amide **I**”) absorption band increases in complexes what is caused by the absence of bonding between the oxygen atom of the amide group and the central atom. Absorption bands ν_{ring} at 1600 and at 1000 cm^{-1} in the IR spectra of complexes undergo the high frequency shift as compared to the spectrum of free nicotinamide what corresponds to coordination of nicotinamide with the central atom through the nitrogen atom of the pyridine ring. Such character of shifts of the above-mentioned absorption bands is observed also for the complexes characterized by the X-ray data what shows that the proposals concerning the type of coordination are true.

It is established that IR spectroscopy is the reliable method for identification of the mode of coordination of carboxylate ligands, in detail of dicarboxylates [10]. For the diagnostics of the coordination model of carboxylic group $\Delta\nu(COO^-)$ ($\nu_{as} - \nu_s$) value, that is the difference between ν_{as} and ν_s frequencies is used [11]. The workers [10] showed that $\Delta\nu$ value about 200 cm^{-1} for the phthalate anion in copper(II) complexes with nitrogen-containing ligands is the bordering between the monodentate and the bidentate–chelate coordination. One of the oxygen atoms of COO^- forms strong coordination bond with the complex-forming ion while the second one takes part in the considerably weaker binding with the same ion or the adjacent one to form the linear polymeric chain. Just the same picture is observed in our case for the $CuL_2PHt\cdot 1.5H_2O$ complex **IV**: $\Delta\nu$ for this compound is just equal to 200 cm^{-1}, and the X-ray analysis showed that Cu–O distances are 1.964 and 2.235 Å for two oxygen atoms of different phthalate anions bound with one atom of copper, and 2.587 Å for another (chelating) oxygen atom of one of the carboxy groups [5]. We consider that more convenient for the interpretation of the IR spectra of carboxylate complexes is not the $\Delta\nu = \nu_{as} - \nu_s$ value, but $\Delta\nu(COO^-)$, the difference between $\Delta\nu(COO^-)$ values of the mixed-ligand complex and starting carboxylate. According to the reported data on the X-

Table 2. IR spectral data for nicotinamide L, 3*d*-metal phtalates and the reaction products **I**–**VI**

Compound	Absorption bands of nicotinamide and phthalate anion (cm^{-1})	Absorption bands (cm^{-1}) of COO^- group			
		$\nu_{as}(COO^-)$	$\nu(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
L (KBr pellets)	3376, 3300, 3170 [ν(NH)], 3090, 3035, 2970, 2960, 2910, 2890, 2820 [ν(CH)], 1687 [ν(C=O)], 1627 [δ(NH_2)], 1580 (ν_{ring}), 1380, 1360, 1340 [δ(CCH)], 1290, 1250, 1205 [δ(CCH), δ(CCC)], 1160, 1134 [δ(NH_2), δ(CCH)], 1030, 1005 (ν_{ring}), 890, 835, 760 [ν(CC), δ(CCC)], 702 [δ$(CCN)_{ring}$], 635, 610 [δ$(CNC)_{ring}$], 550 [δ(CCN), δ(CCC)]				
L (suspension in vaseline oil)	3350, 3145 [ν(NH)], 1665 [ν(C=O)], 1610 [δ(NH_2)], 1585, 1560 (ν_{ring}), 1365, 1330 [δ(CCH)], 1295, 1195 [δ(CCH), δ(CCC)], 1145, 1120 [δ(NH_2), δ(CCH)], 1020, 965 (ν_{ring}), 880, 820, 765 [ν(CC), δ(CCC)], 710 [δ$(CCN)_{ring}$], 635, 615 [δ $(CNC)_{ring}$], 595, 500 [δ(CCN), δ(CCC)]				
$FePht\cdot 2H_2O$		1570	1408	162	
I	3368, 3180 [ν(NH)], 3064 [ν(CH) (L)], 1672 [ν(C=O)], 1611 [δ(NH_2)], 1575 (ν_{ring}), 1491 [δ(CCH)], 1298 [δ(CCH), δ(CCC)], 1150 [δ(NH_2), δ(CCH)], 1090, 1043 (ν_{ring}), 863, 830, 792 [ν(CC), δ(CCC)], 754 [δ(OCO)], 698 [δ$(CCN)_{ring}$], 669, 652 [δ$(CNC)_{ring}$], 586 [δ(CCN), δ(CCC)]	1569	1409	160	–2
$CoPht\cdot 2H_2O$		1558	1398	160	
II	3340 [ν(OH)], 3175 [ν(NH)], 3005, 2820, 2795 [ν(CH) (L)], 1705 [ν(C=O)], 1660 [δ(NH_2)], 1620 [ν_{ring} (L)], 1435 [δ(CCH)], 1305 [δ(CCH), δ(CCC)], 1150 [δ(NH_2), δ(CCH)], 1080, 1065 [ν_{ring}(L)], 890, 830 [ν(CC), δ(CCC)], 765 [δ (OCO)], 690 [δ$(CCN)_{ring}$(L)], 635 [δ$(CNC)_{ring}$(L)], 550 [δ(CCN), δ(CCC)]	1535	1385	150	–10
$NiPht\cdot 2H_2O$		1560	1405	155	
III	3365, 3159 [ν(NH)], 1699 [ν(C=O)], 1630 [ν(COOH)], 1615 [δ(NH_2)], 1604 [a] (ν_{ring}), 1436 [δ(CCH)], 1320 (δOH), 1285 [a] (δOH), 1255, 1198 [δ(CCH), δ(CCC)], 1136 [δ(NH_2), δ(CCH)], 1054, 1036 (ν_{ring}), 946 (γOH), 850, 830, 811, 762 [ν(CC), δ(CCC)], 730 [δ(OCO)], 696 [δ$(CCN)_{ring}$], 668, 654 [δ$(CNC)_{ring}$], 584 [δ(CCN), δ(CCC)]	1604 [a]	1393	211	56
$CuPht\cdot H_2O$		1530	1410, 1350	120, 180	
IV	3445, 3425 [ν(OH)], 3370, 3350, 3320, 3290 [ν(NH)], 3065, 3050, 3030 [ν(CH) (L)], 1705 [ν(C=O)], 1650 [δ(NH_2)], 1605 [ν_{ring}(L)], 1440, 1425 [δ(CCH)], 1280 [δ(CCH), δ(CCC)], 1180 [δ(NH_2), δ(CCH)], 1060, 1045 [ν_{ring}(L)], 870, 845, 810 [ν(CC), δ(CCC)], 745 [δ(OCO)], 710 [δ$(CCN)_{ring}$(L)], 680, 635 [δ$(CNC)_{ring}$(L)], 515 [δ(CCN), δ(CCC)]	1560	1360	200	80, 20
V	3346, 3180, 3114 [ν(NH)], 3073 [ν(CH) (L)], 1695 [ν(C=O)], 1632 [δ(NH_2)], 1604 (ν_{ring}), 1326 [δ(CCH)], 1297, 1251, 1203 [δ(CCH), δ(CCC)], 1148 [δ(NH_2), δ(CCH)], 1085, 1060, 1035 (ν_{ring}), 853, 841, 792, 775 [ν(CC), δ(CCC)], 724 [δ(OCO)], 700 [δ$(CCN)_{ring}$], 690, 650 [δ$(CNC)_{ring}$]	1557	1383	174	54, –6
$ZnPht\cdot 2H_2O$		1616	1394	222	
VI	3342, 3226, 3123 [ν(NH)], 3070 [ν(CH) (L)], 1694 [ν(C=O)], 1671 [δ(NH_2)], 1629 (ν_{ring}), 1436 [δ(CCH)], 1202 [δ(CCH), δ(CCC)], 1146 [δ(NH_2), δ(CCH)], 1086, 1054, 975 (ν_{ring}), 842, 824 [ν(CC), δ(CCC)], 770 [δ(OCO)], 708 [δ$(CCN)_{ring}$], 656, 646 [δ$(CNC)_{ring}$], 550 [δ(CCN), δ(CCC)]	1541	1395	146	–76

[a] Absorption band is contributed by nicotinamide and the phthalate anion.

ray analysis of copper(II) phthalate monohydrate [12] carboxy groups of the phthalate ion are bound with copper in different manner. One of them forms a bridge connecting two atoms of copper while another one in fact occupies one coordination site, but it is bound with two metal atoms through one atom of oxygen in its turn bound with the bridge molecule of water. Evidently due to that the IR spectrum of CuPht·H_2O contains one band $\nu_{as}(COO^-)$ at 1530 cm^{-1} and two $\nu_s(COO^-)$ bands at 1410 and 1350 cm^{-1}. Hence in the case of starting copper(II) phthalate $\Delta\nu(COO^-)$ has two values, 120 and 180 cm^{-1}. From that it follows that $\Delta\Delta\nu(COO^-)$ also acquires two meanings. The largest one, 80 cm^{-1}, relates to the transformation of the bidentate bridge carboxy group to that occupy-ing one coordination place. Smaller value, 20 cm^{-1}, corresponds to the carboxylic group occupying one coordination site in the starting phthalate as well. Presence of one more distant bond between copper and the carboxylic group oxygen is not reflected in the IR spectrum. For the compounds **II**, **V**, and **VI** (COO^-) values acquire negative meanings. For the compound $CoL_2Pht{\cdot}6H_2O$ **II** it was established by means of the X-ray studies that phthalate ion is located in the outer sphere, and under these conditions not an increase but a decrease in difference between $\nu_{as}(COO^-)$ and $\nu_{as}(COO^-)$ by 10 cm^{-1} takes place. That means that $\Delta\nu(COO^-)$ for the complex obtained by us is negative. Hence, it can be proposed that some equalization of bonds in the phthalate anion takes place. Such picture is most probably caused by the fact that due to the interaction of starting salt with nicotinamide phthalate anion is not bound with cobalt what relates to its displacement in the outer sphere of complex. Negative $\Delta\Delta\nu(COO^-)$ value for the copper(II) compound of the 1:4 com-position also permits to propose that phthalate anion is located in the outer sphere though this compound as well as copper(II) complex of the 1:2 composition has two $\Delta\Delta\nu(COO^-)$ meanings. As it was shown above, that means that starting copper(II) phthalate contains differently bound groups. The outer sphere location of phthalate anion is confirmed by molar electrocon-ductivity measurements in water (Table 1). According to [13] compounds $CoL_2Pht{\cdot}6H_2O$ **II** and $ZnL_2Pht{\cdot}2H_2O$ **VI** can be regarded as electrolytes of the 1:1 type while the compound $NiL_2(HPht)_2{\cdot}2H_2O$ **III** is a three-ionic electrolyte. For the latter one specific features in the IR spectrum are also observed. The workers [3] have described complexes with 1-methyl-imidazole of the composition M(1-MeIm)$_6$(HPht)$_2$· $2H_2O$ (M = Co, Ni). IR spectra of these compounds contain absorption bands at 1634 cm^{-1} [ν(COOH)], at 1290 cm^{-1} [ν(OH)], and at 939–937 cm^{-1} [γ(OH)]. That means that *o*-phthalic acid presents here in a form of monoanion. IR spectra of $NiL_2(HPht)_2{\cdot}2H_2O$ ob-tained by us contain analogous bands at 1630 (shoulder), 1285, and 946 cm^{-1} what also tells in favor of presence of the monoprotonated phthalate anion. Hence, conductometric as well as spectroscopic data confirm that nickel complex contains monoanions of phthalic acid in the outer sphere. For the iron(II) complex (compound **I**) $\nu(COO^-)$ shows no alterations after the reaction with nicotin-amide. It permits to propose that phthalate anion does not change its symmetry in the course of complex formation, but remains the bidentate ligand in the com-position of the inner sphere of the iron(II) complex.

Table 3. Diffuse reflection spectra of complexes of 3*d*-metal phthalates with nicotinamide **I**–**VI**

Comp. no.	λ_{max}, nm	Assignment
I	2471.8	$^5E \rightarrow {}^5T_2$
II	479	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	1120.2	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$
	1968	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
III	592.8	$^3T_1 \rightarrow {}^3T_1(P)$
	1224	$^3T_1 \rightarrow {}^3A_2$
IV	740.5	
V	736.4	
	1981.6	

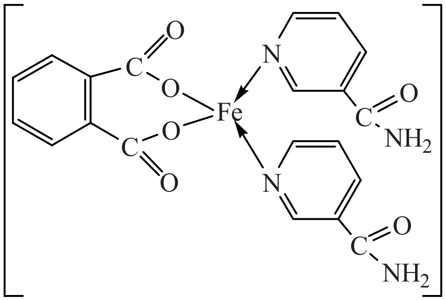
Data of the diffuse reflection spectroscopy are listed in Table 3. Analysis of the band location permits to propose that the compounds **I** and **III** have tetrahedral structure, while the compound **V** is pseudo-tetrahedral [14].

Table 4 presents the data concerning thermogravimetric studies of the compounds synthesized. Thermal stab-ility of analogous comlexes depending on the complex forming metal decreases in the following series:

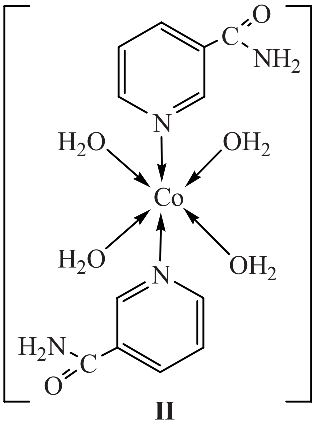
$$Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}.$$

This series of thermal stability of d-metal phthalate complexes with nicotinamide is analogous to the series obtained for metal valerates and benzoates [15]. Note that the compounds **IV** and **V** having the same complex former copper(II), but differing in the metal:nicotinamide stoichiometric ratio exhibit large difference of the decomposition temperatures. In this case higher thermal stability of $CuL_2Pht{\cdot}1.5H_2O$ **IV** as compared to CuL_4Pht **V** arises evidently from the polymeric structure of the compound having 1:2 ratio of metal to ligand. The same reason explains lower solubility of compound **IV** as compared to **V**, because crystallization of the first product and its isolation from the solution in the course of synthesis proceeds much easier.

For the compound $CoL_2Pht{\cdot}6H_2O$ (**II**) first two endoeffects are connected evidently with the loss of the crystallization water. First endoeffect is accompanied by the 6% loss of mass, while for the second one this value is 13.6%. Theoretical calculations show that loss of two molecules of water gives the value of 6.26%, while four water molecules give 12.52%. These data are in good agreement with the experimental results. Hence, at lower temperature the liberation of two molecules from the outer sphere water takes place, while further heating leads to the liberation of four intraspheric water molecules. On the basis of the results obtained following structures can be offered for the compounds **I–IV**.

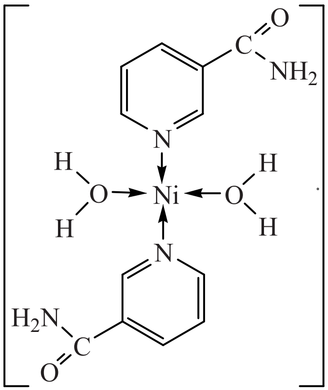


I



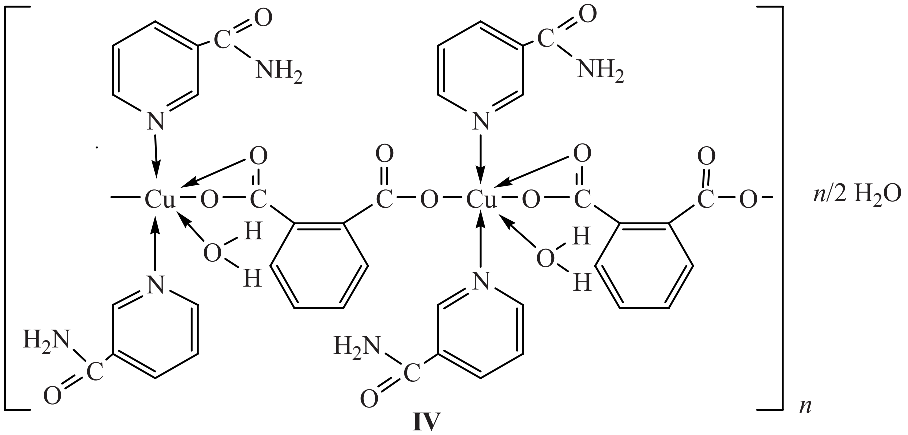
II

$C_6H_4(COO)_2{\cdot}2\ H_2O$

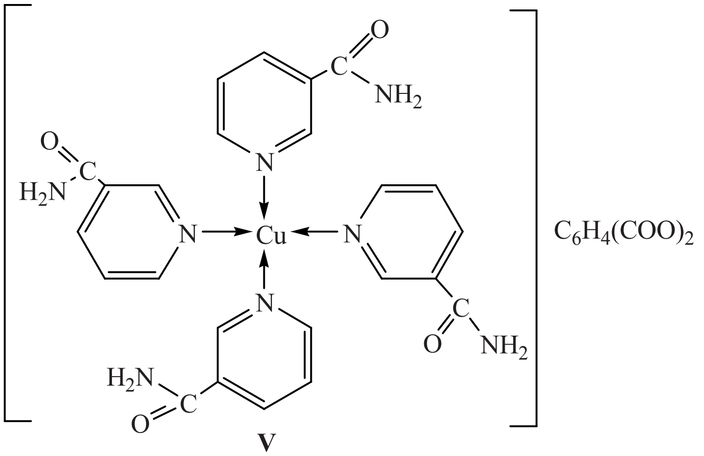


III

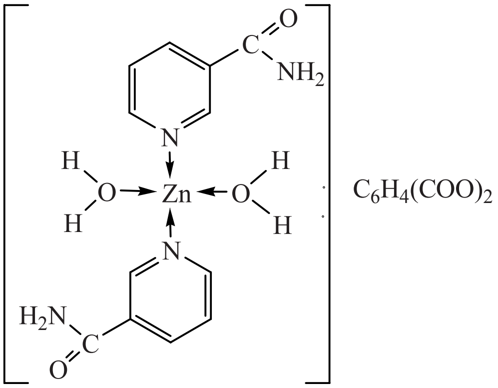
$\cdot\ [C_6H_4(COO)(COOH)]_2$



IV



V



VI

Table 4. Results of derivatographic studies of thermal stability of the 3*d*-metal phthalate complexes with nicotinamide **I**–**VI**

Comp. no.	Endoeffects		Exoeffects		General loss of mass, %
	T, °C	Δm, %	*T*, °C	Δm, %	
I			285–450(385)	70.0	80.5
II	70–112(100)	6.0	150–287(242)	33.4	52.9
	112–150(130)	13.6			
III	93–178(112)	13.5	225–292(260)	22.2	75.4
			292–450(428)	31.7	
IV			225–350(300)	53.8	76.0
			350–445(418)	17.3	
V	150–190(170)	4.6	190–280(230)	56.9	84.4
			280–455(385)	10.8	
			455–500(480)	10.8	
VI	100–180(150)	8.9	180–290(228)	67.4	80.3
			380–475(442)	4.0	

Comparison of the results presented in this work with the previously reported data on the analogous complexes of 3*d*-metal valerates and benzoates with nicotinamide [15–19] shows that phthalate anion as compared to the above-mentioned monocarboxylate ones is more inclined to driving in the outer sphere. In some cases it leads to decrease in the coordination number of the central ion.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer SPECTRUM BX II FT-IR spectrometer in KBr pellets. Diffuse reflection spectra were obtained on a Perkin-Elmer Lambda-9 spectrophotometer against MgO (β_{MgO} 100%). Thermogravigrams were measured on a Paulik–Paulik–Erdey derivatograph in air, heating rate 10 deg min^{-1}.

Iron(II), cobalt(II), nickel(II), copper(II) and zinc chlorides, phthalic acid, and nicotinamide of the "pure for analysis" grade were used.

Metal content in the compounds obtained was measured complexonometrically [20], nitrogen content was evaluated by means of the Dumas method [21].

Complex I. Nicotinamide, 0.005 mol, was dissolved in 5 ml of water, and 0.0025 mol of dry metal phthalate was added in portions under constant stirring. After the addition was complete, the mixture obtained was heated to boil and then stirred with a magnetic stirrer until the alteration in the coloration of precipitate. The crystals formed were filtered off on a Schott filter, washed with small amont of water and dried in a dessicator over $CaCl_2$ until the constant mass.

Complex II. Nicotinamide, 0.61 g, was dissolved in 5 ml of water, and 0.65 g of crystalline $CoPht{\cdot}2H_2O$ was added in portions under permanent stirring. Obtained pink solution was left on cold, and after 3 h pink crystals were formed. The precipitate was filtered from the mother liquor and dried in a dessicator over $CaCl_2$ until the constant mass.

Complex III. Nicotinamide, 0.61 g, was dissolved in 5 ml of water, and 0.65 g of the crystalline $NiPht{\cdot}2H_2O$ was added in portions under permanent stirring. After the addition was complete resulting mixture was stirred with a magnetic stirrer until the complete dissolution of crystals. The emerald-colored solution obtained was placed in the porcelain cup for the partial evaporation of solvent. After some time green precipitate was formed. It was filtered off on a Schott filter, washed with small amount of water, and dried in a dessicator over $CaCl_2$ until the constant mass.

Complexes IV, V. Nicotinamide, 0.61 g, was dissolved in 5 ml of water, and 0.00125 mol of crystalline $CuPht{\cdot}H_2O$ was added in portions with stirring. Resulting mixture was heated to boil. Dissolution of starting phthalate was accompanied by formation of new precipitate. After stirring for an hour, light blue precipitate of compound **IV** was separated on a Schott filter and crystallized from water. After some time the crystals of compound **V** precipitated from the filtrate.

Complex VI. Nicotinamide, 0.61 g, was dissolved in 5 ml of water, and 0.66 g of crystalline $ZnPht{\cdot}2H_2O$ was added in portions under permanent stirring. Resulting mixture was heated to boil until the complete dissolution of precipitate of the starting salt. The mixture obtained was stirred on a magnetic stirrer until the formation of white precipitate. The crystals obtained were filtered off on a Schott filter, washed with small amount of water, and dried in a dessicator over $CaCl_2$ until the constant mass.

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