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Coordination Compounds of Cobalt(II), Nickel(II), and Zinc(II) Valerates and Benzoates with Isonicotinic Acid Hydrazide

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Abstract—Complexes of cobalt(II), nickel(II), and zinc(II) valerates and benzoates with isonicotinic acid hydrazide (isonicotinic hydrazide) have been synthesized. The prepared compounds have been characterized by means of elemental analysis, thermogravimetry, and IR and diffuse reflectance spectroscopy.

Keywords: isonicotinic (acid) hydrazide, valerate, benzoate, coordination compound

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Carboxylic acids hydrazides including isonicotinic hydrazide (L) are intensively studied objects of comprehensive coordination chemistry of *d*-metals due to their special complex formation properties and biological activity. The complex formation properties of isonicotinic hydrazide are owing to the presence of several potential donor atoms in the molecule and are governed by the nature of the coordination centre and the solvent as well as possibility of hydrogen bonding and stacking interaction [1]. The ability to inhibit reproduction of *Mycobacterium tuberculosis* makes isonicotinic hydrazide one of the most efficient antituberculosis drugs [2]. Copper complexes of isonicotinic hydrazide possess activity against Rous sarcoma virus of chicken [3, 4].

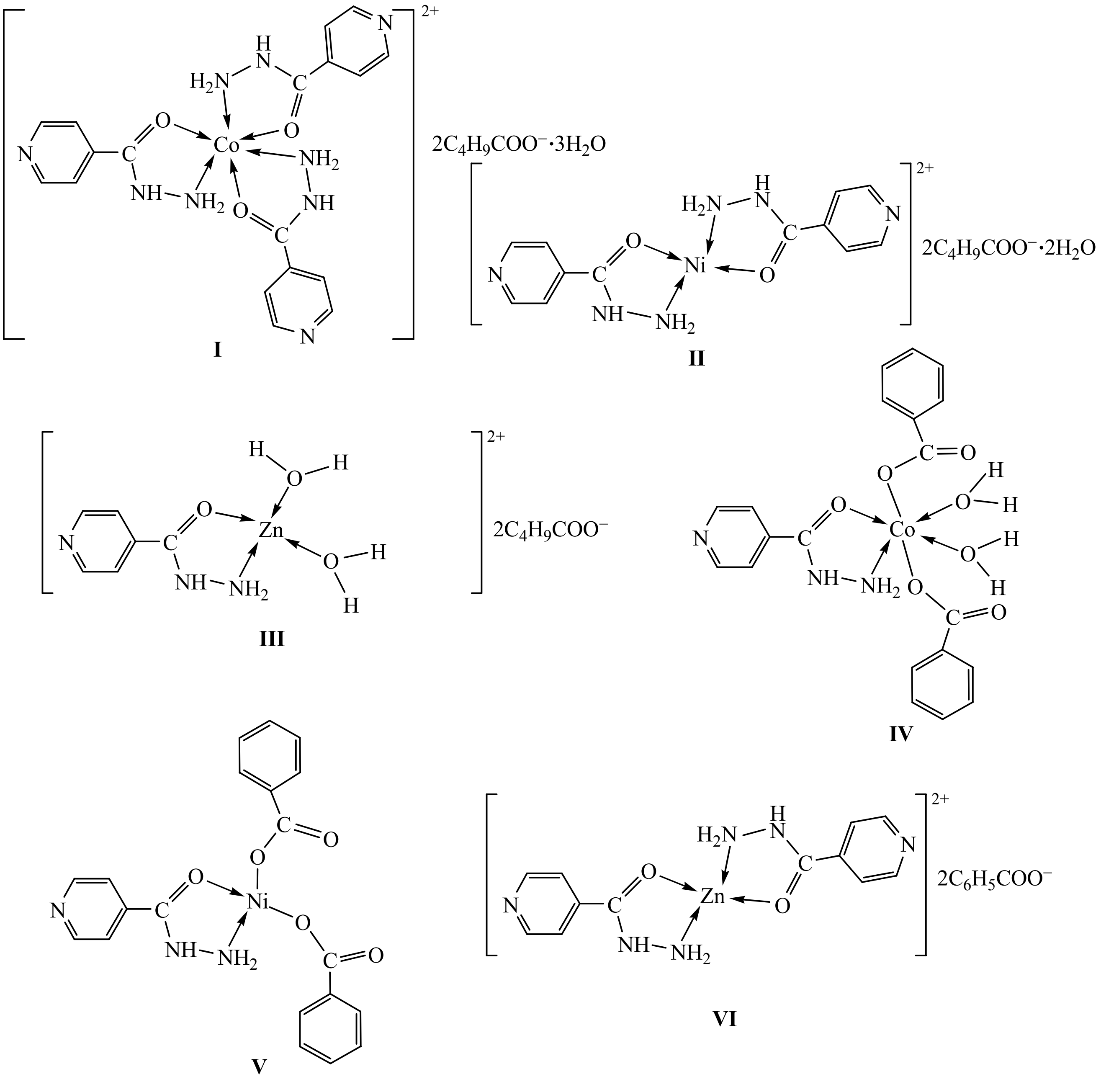
We have earlier investigated the products of the reaction of biometals valerates and benzoates with semicarbazide [5] and nicotinamide [6–11]. In the present work we report on synthesis of the complexes of cobalt(II), nickel(II), and zinc(II) valerates and benzoates with isonicotinic hydrazide, **I–VI** (Scheme 1). The complexes were prepared via addition of the corresponding dry 3*d*-metal valerate or benzoate to an aqueous solution of isonicotinic hydrazide at the metal : ligand ratio of 1 : 2. The starting valerates and benzoates were prepared via addition of the 3*d*-metal chloride to sodium valerate or benzoate.

The elemental analysis data (Table 1) revealed the following complexes composition: 1 : 1 in the cases of

Table 1. Elemental analysis data for the complexes **I–VI**

Comp. no.	Color	Found, %		Formula	Calculated, %	
		M	N		M	N
I	Pink	7.7	17.7	$C_{28}H_{45}CoN_9O_{10}$	8.1	17.4
II	Light-violet	9.9	14.8	$C_{22}H_{36}N_6NiO_8$	10.3	14.7
III	White	15.2	9.1	$C_{16}H_{29}N_3O_7Zn$	14.8	9.5
IV	Pink	12.4	8.7	$C_{20}H_{21}CoN_3O_7$	12.4	8.9
V	Light-violet	13.1	9.5	$C_{20}H_{17}N_3NiO_5$	13.5	9.6
VI	White	11.6	14.2	$C_{26}H_{24}N_6O_6Zn$	11.2	14.5

Scheme 1.



nickel(II) and cobalt(II) benzoates as well as zinc(II) valerate; 1 : 2 in the cases of nickel(II) valerate and zinc(II) benzoate, and 1 : 3 for cobalt(II) valerate. Therefore, valerates coordinated more of the hydrazide molecules than benzoates in the complexes of cobalt(II) and nickel(II), but for zinc(II) complexes the situation was the opposite. Water was recognized as a component of all the valerate complexes and the cobalt(II) benzoate complex. Apparently, valerate anions were weaker bound with the metals, thus allowing for water molecules more efficient competition for the coordination sites.

Analysis of IR spectra of isonicotinic hydrazide and the prepared complexes (Table 2) performed via comparison with the reference data [12–14] revealed a low-frequency shift of the ν(C=O) stretching band in the spectra of the complexes as compared to that of the parent isonicotinic hydrazide; the shift was larger in the cases of the valerate complexes. At the same time,

Table 2. Parameters of the IR spectra (cm^{-1}) of isonicotinic hydrazide (L), the 3*d*-metals valerates and benzoates, and their complexes with isonicotinic hydrazide **I–VI**

Compound	Absorption bands of isonicotinic acid hydrazide and water, cm^{-1}	Absorption bands of the anion			
		$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\Delta\Delta\nu(\text{COO}^-)$
L	3306, 3112, 3052, 3013, 2866 [(ν(NH)], 1668 s [ν(C=O)], 1636 [$\delta(\text{NH}_2)$], 1604 (ν_{rings}), 1557 [ν_{rings} + ν(CC)], 1493 (ν_{rings}), 1413 [ν(CC) + ν(C–N)], 1335, 1222 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1200 sh, 1142 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1062, 996, 888, 846 [$\nu_{\text{puls. rings}}$ + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 747 [ρ(CCH) + δ(CCH)], 676, 661 [δ(CNH) + δ(CCC)], 504 [δ(CCN) + δ(NCO)]				
$\text{Co(Val)}_2\cdot2\text{H}_2\text{O}$		1568	1413	155	
Complex **I**	3248 br [ν(OH)], 1640 [ν(C=O)], 1601$^{\text{a}}$ (ν_{rings}), 1551 [ν_{rings} + ν(CC)], 1480 sh (ν_{rings}), 1425 [ν(CC) + ν(CN)], 1231 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1125 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1061, 1010, 910, 837 [$\nu_{\text{puls. rings}}$ + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 775 [ρ(CCH) + δ(CCH)], 690, 650 [δ(CNH) + δ(CCC)], 480 [δ(CCN) + δ(NCO)]	1601$^{\text{a}}$	1385	216	61
$\text{Ni(Val)}_2\cdot2\text{H}_2\text{O}$		1568	1417	151	
Complex **II**	3421 [ν(OH)], 3124, 2940, 2870 [ν(NH)], 1655 [ν(C=O)], 1609$^{\text{a}}$ (ν_{rings}), 1547 [ν_{rings} + ν(CC)], 1425 [ν(CC) + ν(CN)], 1366, 1219 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1146 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1060, 1018, 906, 852 [$\nu_{\text{puls. rings}}$ + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 760 [ρ(CCH) + δ(CCH)], 702 [δ(CNH) + δ(CCC)], 552 [δ(CCN) + δ(NCO)]	1609$^{\text{a}}$	1416	193	42
$\text{Zn(Val)}_2\cdot2\text{H}_2\text{O}$		1575	1395	180	
Complex **III**	3472 [ν(OH)], 3232, 3128, 2966, 2870 [ν(NH)], 1655 [ν(C=O)], 1605$^{\text{a}}$ (ν_{rings}), 1543 [ν_{rings} + ν(CC)], 1450 (ν_{rings}), 1480 [ν(CC) + ν(CN)], 1360, 1211 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1126 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1060, 1040, 1022, 906, 852 [$\nu_{\text{puls. rings}}$ + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 764 [ρ(CCH) + δ(CCH)], 698 [δ(CNH) + δ(CCC)], 544 [δ(CCN) + δ(NCO)]	1605$^{\text{a}}$	1375	230	50
$\text{Co(Benz)}_2\cdot2\text{H}_2\text{O}$		1594	1497	97	
Complex **IV**	3416 [ν(OH)], 3231, 3064, 2884 [ν(NH)], 1664 [ν(C=O)], 1595$^{\text{a}}$ (ν_{rings}), 1543 [ν_{rings} + ν(CC)], 1460 sh (ν_{rings}), 1435 [ν(CC) + ν(CN)], 1356 w, 1227 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1203, 1126 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1070, 1039, 1020, 903, 857, 846 [$\nu_{\text{puls. rings}}$) + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 748 [ρ(CCH) + δ(CCH)], 718, 690 [δ(CNH) + δ(CCC)], 545 [δ(CCN) + δ(NCO)]	1595$^{\text{a}}$	1407	188	91
$\text{Ni(Benz)}_2\cdot2\text{H}_2\text{O}$		1596	1498	98	
Complex **V**	3115, 3063 [ν(NH)], 1657 [ν(C=O)], 1598$^{\text{a}}$ (ν_{rings}), 1549 [ν_{rings} + ν(CC)], 1504 (ν_{rings}), 1425 [ν(CC) + ν(CN)], 1374$^{\text{a}}$, 1265, 1245, 1223 [ν(CN) + $\delta(\text{NH}_2)$ + δ(CCH)], 1174, 1149 [ν(NN) + $\tau(\text{NH}_2)$ + δ(CCH)], 1068, 1022, 996, 904, 854, 846 [$\nu_{\text{puls. rings}}$ + $\rho(\text{NH}_2)$ + $\tau(\text{NH}_2)$], 760 [ρ(CCH) + δ(CCH)], 721, 706, 698 [δ(CNH) + δ(CCC)], 546, 480 [δ(CCN) + δ(NCO)]	1598$^{\text{a}}$	1374$^{\text{a}}$	224	126
$\text{Zn(Benz)}_2\cdot2\text{H}_2\text{O}$		1599	1417	182	

Table 2. (Contd.)

Compound	Absorption bands of isonicotinic acid hydrazide and water, cm^{-1}	Absorption bands of the anion			
		$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
Complex **VI**	3232, 3150, 3080, 3040 [ν(NH)], 1666 [ν(C=O)], 1597[a] (ν_{rings}), 1547 [ν_{rings} + ν(CC)], 1490 sh (ν_{rings}), 1480 [ν(CC) + ν(CN)], 1340 w, 1220 [ν(CN) + δ(NH_2) + δ(CCH)], 1150 [ν(NN) + τ(NH_2) + δ(CCH)], 1060, 1040, 1022, 930, 860 [$\nu_{puls.\ rings}$ + ρ(NH_2) + τ(NH_2)], 750 [ρ(CCH) + δ(CCH)], 687 [δ(CNH) + δ(CCC)], 540 [δ(CCN) + δ(NCO)]	1597[a]	1408	189	7

[a] Both isonicotinic hydrazide and the carboxylate anion contributed to the absorption band.

the frequency of the ν(C–N) absorption bands increased. On top of that, the complex formation led to a low-frequency shift of the N–H stretching band, and the separate band of the δ(NH_2) vibration disappeared. Those changes evidenced about bidentate coordination of isonicotinic hydrazide via oxygen and nitrogen atoms of the hydrazide group. Heterocyclic nitrogen atom did not participate in the binding with metals, as confirmed by the unchanged location of the pyridine ring bands (around 1600 cm^{-1}). Earlier examples of certain 3*d*-metals valerates and benzoates have revealed that participation of heterocyclic nitrogen atom in the coordination with metals should have increased the latter mentioned bands frequency [6–9, 11]. The breathing bands of the heterocycle at 1000 cm^{-1} were practically not changed as well.

Analysis of the X-ray diffraction and IR spectroscopy data showed the change of the spacing between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ absorption bands for the hybrid–ligand complexes as compared to that of the starting carboxylates can serve as an indication of the carboxylate anions character [8]. The higher values of $\Delta\Delta\nu(COO^-)$ were typical of monodentate carboxylate anions; the smaller values characterized the bidentate or outer-sphere anions. In particular, the $\Delta\Delta\nu(COO^-)$ value of >> 90 cm^{-1} for the complexes of cobalt(II) and nickel(II) benzoates suggested the monodentate coordination of benzoate anion. The corresponding values for all the studied valerates did not exceed 61 cm^{-1}, and for complex of zinc(II) benzoate it was of 7 cm^{-1}, evidencing about the outer-sphere coordination of valerate anions in all the complexes and benzoate anion in the zinc complex.

The presence of water in the complexes **I–IV** was confirmed by the broadened ν(O–H) bands in the IR spectra. Since molecules of water participated in the complex system of hydrogen bonds, the bands could not be used for identification of the inner- or the outer-sphere coordination of the molecules.

Location of the bands in the diffuse reflectance spectra of the prepared compounds (Table 3) corresponded to the octahedral structure for cobalt complexes **I** and **IV** and to tetrahedral structure for nickel complexes **II** and **V** [15].

Thermal analysis of the complexes (Table 4) showed that the decomposition onset temperature was the lowest for compounds **I** and **II**, confirming the outer-sphere coordination of the water molecules. The thermogravigrams of all the investigated compounds first revealed the endothermic effects, and further heating gave rise to endothermic effects in the cases of the water-free complexes and to the exothermic ones in the cases of the water-containing complexes. The final stages of pyrolysis were in all the cases exothermic with the maxima at 450–600°C, corresponding to burning out of the intermediate decomposition pro-

Table 3. Parameters of diffuse reflectance spectra of complexes **I**, **II**, **IV**, and **V**

Comp. no.	λ, nm	Assignment
I	491	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	1666	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
II	552	$^3T_1 \rightarrow {}^3T_1(P)$
	894	$^3T_1 \rightarrow {}^1E$
	2413	$^3T_1 \rightarrow {}^3A_2$
IV	501	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	1139	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
V	546	$^3T_1 \rightarrow {}^3T_1(P)$
	949	$^3T_1 \rightarrow {}^1E$
	2456	$^3T_1 \rightarrow {}^3A_2$

Table 4. Thermal analysis data for complexes **I–VI**[a]

Comp, no.	Endothermic effects		Exothermic effects		Total mass loss, %
	t, °C	Δm, %	t, °C	Δm, %	
I	100–140 (130)	4.0	250–270 (260)	19.9	78.8
			390–600 (480)	48.8	
II	80–150 (110)	7.7	180–320 (300)	28.9	83.8
	320–410 (380)	14.4	410–550 (480)	31.8	
III	140–160 (150)	5.9	230–410 (280)	30.0	86.3
			490–650 (600)	30.0	
IV	120–175 (150)	10.2	240–280 (260)	24.3	83.8
			400–540 (450)	44.8	
V	160–190 (170)	5.8	400–580 (480)	38.9	83.8
	200–280 (250)	37.5			
VI	120–150 (140)	9.8	450–600 (560)	27.0	80.0
	250–310 (290)	16.7			
	400–450 (430)	18.2			

[a] Temperatures of the strongest effects are given in the parentheses.

ducts formed at the previous stages. Comparison of the thermal stability of the complexes showed that compounds **III–V** with the metal : hydrazide ratio 1 : 1 were the most stable.

To conclude, the study confirmed the following structure of the prepared complexes: tris(isoniazido)-cobalt(II) divalerate trihydrate (**I**), bis(isoniazido)-nickel(II) divalerate dihydrate (**II**), isoniazido(diaqua)-zinc(II) divalerate (**III**), isoniazido(diaqua)cobalt(II) dibenzoate (**IV**), isoniazidonickel(II) dibenzoate (**V**), and bis(isoniazido)zinc(II) dibenzoate (**VI**).

EXPERIMENTAL

Cobalt(II), nickel(II), and zinc(II) chlorides, valeric and benzoic acids, and isonicotinic hydrazide were of the “analytical pure” grade.

IR spectra were recorded using a FTIR-8400S (Shimadzu) instrument (KBr pellets). Diffuse reflectance spectra were registered with a Lambda-9 (Perkin-Elmer) spectrophotometer using MgO (100% β_{MgO}) as a reference. Thermogravigrams were obtained using a Paulik–Paulik–Erdey system derivatograph in air, heating at 10 deg min^{-1}. The isolated compounds were used for the metal amount determination (by means of complexonometry [16]), and the nitrogen amount was determined via the Dumas method [17].

Synthesis of complexes I–VI. Crystalline metal valerate or benzoate (5 mmol) was added portionwise upon stirring to a solution of isonicotinic hydrazide (1.37 g, 10 mmol) in 40 mL of water, and the mixture was stirred till complete dissolution. The solution was left for natural evaporation of the solvent. The formed precipitate was filtered off, washed with water several times, and dried in a desiccator over $CaCl_2$ to a constant weight.

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