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Coordination Compounds of Co(II), Ni(II), and Cu(II) Valerates and Benzoates with Semicarbazide

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Abstract — Complexes of Co(II), Ni(II), and Cu(II) valerates and benzoates with semicarbazide were prepared. The compounds were characterized by chemical analysis, X-ray phase analysis, IR spectroscopy, diffuse reflection spectroscopy, and thermal gravimetric analysis.

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Coordination compounds with semicarbazide (L) are of both theoretical and practical interest. The practical interest is associated with the wide use of semicarbazide in both inorganic and organic analysis. In inorganic analysis, it is used as reagent for quantitative determination of a series of metals, and in organic analysis, for identification of aldehydes and ketones. Semicarbazide is also of interest for preparative chemistry, as synthetic precursor of semicarbazones and heterocyclic compounds [1]. Apparently, the use of semicarbazide as a complex with a 3*d* metal ion may open new prospects for template synthesis.

The theoretical interest in semicarbazide complexes is caused by the fact that this ligand contains carbonyl and amino groups, i.e., it is potentially bidentate. Like the majority of amides, semicarbazide is capable of tautomeric transformations, which increases the number of possible coordination compounds. The actual dentacity and tautomerism of the ligand largely depend on the anion of the salt taken for preparing the complex. At the same time, available data on coordination compounds of 3*d* metals with semicarbazide concern only compounds with the simplest anions (chloride [2–6], bromide, perchlorate [7, 8], nitrate, sulfate [3, 4, 7–9]) and also with the complex anion, $[CuL_2]_n \cdot [Co(NO_2)_6]_m X_p$ ($X = NO_3^-, ClO_4^-$) [10].

From the viewpoint of possible competition between similar donor groups in different ligands, it is interesting to study the complexation of semicarbazide in the presence of anions that also contain a CO group, in particular, carboxylate anions. As sources of carboxylate anions we chose acyclic (valeric) and cyclic (benzoic) carboxylic acids. Here we report on the synthesis, structure, and properties of coordination compounds of Co(II), Ni(II), and Cu(II) valerates and benzoates with semicarbazide.

Chemical analysis shows (Table 1) that the composition of the semicarbazide complexes obtained essentially depends on the structure of the carboxylate anion. With all the metals examined, the complexation of semicarbazide with benzoates occurs more readily than with valerates, as follows from the following facts. The number of semicarbazide–benzoate complexes formed in the systems is larger than the number of semicarbazide–valerate complexes. With Cu(II), both benzoate and valerate form 1 : 2 complexes with semicarbazide, but with benzoate this complex is formed at any reactant ratio, whereas with valerate it is formed only with excess semicarbazide (1 : 4). Cobalt(II) benzoate adds more semicarbazide molecules than does cobalt(II) valerate. The complexes with 1 : 3 and 1 : 4 ratios of Co(II) benzoate to semicarbazide exhibit isomerism: In both cases, depending on the synthesis conditions, pink or blue products can be obtained. In the case of Ni(II) valerate, the composition of the complex is constant irrespective of the reactant ratio, and with Ni(II) benzoate variation of the reactant ratio leads not to changes in the metal : ligand ratio in the complexes but to the formation of ethanol solvates of different compositions. At 1 : 2 ratio of Ni(II) benzoate to semicarbazide, a 1 : 2 complex containing no alcohol is formed. At the 1 : 4 ratio, the complex containing one alcohol molecule is formed immediately, and the complex containing two alcohol molecules crystallizes from the filtrate after prolonged standing. Similar phenomenon was observed previously with complexes of Ni(II) urates with thiosemicarbazide; depending on the reactant

Table 1. Elemental analyses and color of complexes of Co(II), Ni(II), and Cu(II) valerates and benzoates with semicarbazide

Complex no.	Color	Found, %		Formula	Calculated, %	
		M	N		M	N
I	Dirty pink	14.8	20.1	$CoL_2(Val)_2$	14.4	20.4
II	Lilac	12.5	25.9	$CoL_3(Val)_2$	12.1	26.1
III	Pink	10.8	24.4	$CoL_3(Benz)_2$	11.2	24.0
IV	Gray-blue	11.3	24.1	$CoL_3(Benz)_2$	11.2	24.0
V	Pink	9.8	27.8	$CoL_4(Benz)_2$	9.8	28.0
VI	Gray-blue	9.4	28.4	$CoL_4(Benz)_2$	9.8	28.0
VII	Blue	10.5	30.1	$NiL_4(Val)_2$	10.5	29.9
VIII	Green	13.4	18.4	$NiL_2(Benz)_2$	13.1	18.6
IX	Blue	10.8	15.1	$NiL_2(Benz)_2(C_2H_5OH)_2$	10.9	15.5
X	″	11.6	17.2	$NiL_2(Benz)_2(C_2H_5OH)$	11.9	16.9
XI	Dark green	15.2	20.2	$CuL_2(Val)_2$	15.4	20.2
XII	Gray-blue	14.0	18.1	$CuL_2(Benz)_2$	14.0	18.4

ratio, the complexes contained different amounts of bound water [11]. All the compounds prepared are very poorly soluble in water and organic solvents. Complexes of Ni(II) benzoate with semicarbazide are somewhat more soluble in DMF than the other complexes; however, their solubility does not exceed 10^{-3} M.

Comparison of our results with published data [3, 4, 7, 8] shows that the use of 3*d*-metal carboxylates for preparing semicarbazide complexes allows synthesis of compounds containing larger number of coordinated semicarbazide molecules, despite the higher coordination capacity of carboxylate anions compared to simple anions, such as halides, perchlorate, nitrate, or sulfate. The formation of higher semicarbazide complexes can be accounted for as follows. In the initial salt, the carboxylate anion is bidentate and produces steric hindrance to the bidentate coordination of semicarbazide. Therefore, to attain the coordination number characteristic of a given metal cation (4 or 6), semicarbazide coordinates in the monodentate fashion.

As already mentioned, with Ni(II) benzoate we obtained compounds with the same metal : semicarbazide ratio but different content of alcohol molecules of solvation. To check whether these products are individual compounds, we performed X-ray phase analysis. Below are the calculated interplanar spacings (*d*, Å) and peak intensities (I/I_0). $NiL_2(Benz)_2$ (**VIII**): 17.6 (100), 15.2 (48), 9.0 (22), 8.65 (22), 6.79 (57), 6.40 (14), 5.95 (58), 5.72 (70), 4.86 (31), 4.66 (48), 4.26 (57), 4.00 (35), 3.63 (10), 3.47 (78), 3.13 (31), 3.05 (17), 2.88 (18), 2.84 (17), 2.69 (40), 2.64 (20), 2.51 (9), 2.43 (22), 2.40 (10), 2.31 (10), 2.22 (14), 2.17 (14), 2.135 (13), 2.052 (11), 1.931 (22), 1.84 (9), 1.763 (9), 1.741 (10), 1.705 (8), 1.524 (8). $NiL_2 \cdot (Benz)_2(C_2H_5OH)_2$ (**IX**): 15.2 (100), 9.0 (14), 7.88 (24), 6.49 (10), 5.22 (20), 5.02 (9), 4.71 (10), 3.76 (22), 3.39(17), 3.03 (20), 2.50 (12). $NiL_2(Benz)_2 \cdot (C_2H_5OH)$ (**X**): 17.0 (100), 5.9 (37), 3.15 (57), 2.23 (47).

These data show that all the three compounds have individual sets of interplanar spacings. Incorporation of alcohol decreases the degree of crystallinity, as indicated by the smaller number of peaks in the X-ray diffraction pattern.

The assignment of bands in the IR spectra of semicarbazide hydrochloride and semicarbazide complexes of 3*d*-metal carboxylates, based on data of [4, 6, 12], is given in Table 2. The frequencies of the modes involving stretching vibrations of the CO group decrease upon complexation: ν(C=O), by 19–52 cm^{-1}; ν(CO) + $\delta(NH_2)$, by 20–27 cm^{-1}; and δ(O=C–N) decreases especially noticeably, by 71–112 cm^{-1}. The band originating mainly from ν(CN) shifts toward higher frequencies. For the pink complex $CoL_3(Benz)_2$ (III), ν(CN) shifts to a greater extent than for the blue complex of the same composition and for both complexes $CoL_4(Benz)_2$. As a result of the complexation, the difference between the frequencies of the symmetric and antisymmetric modes of the amino group appreciably increases (from 54 to 85–150 cm^{-1}).

Mashima [12] compared the IR spectra of semicarbazide, semicarbazide hydrochloride, and N-deuterated semicarbazide and showed that the band at 996 cm^{-1} in the IR spectrum of free nondeuterated semicarbazide can be assigned to the $\delta(NH_2)$ vibration of the hydrazine moiety. Our results show that this

Table 2. IR spectra of semicarbazide, valerates and benzoates of Co(II), Ni(II), and Cu(II), and complexes formed from them

Compound	Semicarbazide absorption bands (cm^{-1})	Carboxylate absorption bands (cm^{-1})			
		$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
L · HCl	3425 [ν(NH)], 3314 [$\nu_{as}(NH_2)$], 3260 [$\nu_s(NH_2)$], 2911, 2670, 1946 [ν_s, $\nu_{as}(NH_3^+)$], 1687 [ν(C=O)], 1585 [ν(CO) + $\delta(NH_2)$], 1524 [ν(CN)], 1478 [ν(CN) + δ(NH) + δ(NN)], 1385 [ν(CN) + $\delta(NH_2)$], 1213, 1182, 1090 [$\delta(NH_2)$], 935 [δ(O=C–N)], 770 [$\pi(O=C–N_2)$], 721 [$\omega(NH_2)$ or $\rho(NH_2)$], 562, 512 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]				
$Co(Val)_2 \cdot 2H_2O$	–	1568	1413	155	
I	3432 [ν(NH)], 3220 [$\nu_s(NH_2)$], 1588 [ν(CN)], 1404[a] [ν(CN) + δ(NH) + δ(NN)], 1317 [ν(CN) + $\delta(NH_2)$], 1200, 1109, 931 [$\delta(NH_2)$], 860 [δ(O=C–N)], 758 [$\pi(O=C–N_2)$], 720 [$\omega(NH_2)$ or $\rho(NH_2)$], 544 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1617	1404[a]	213	58
II	3407 [ν(NH)], 3210 [$\nu_s(NH_2)$], 1668 [ν(C=O)], 1550 1411 [ν(CN)], [ν(CN) + δ(NH) + δ(NN)], 1340 [ν(CN) + $\delta(NH_2)$], 1230, 1109, 1001, 941 [$\delta(NH_2)$], 823 [δ(O=C–N)], 762 [π(O=C–N2)], 710 [$\omega(NH_2)$ or $\rho(NH_2)$], 549 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1601	1411	190	35
$Co(Benz)_2 \cdot 2H_2O$	–	1594	1497	97	
III	3413 [ν(NH)], 3320 [$\nu_{as}(NH_2)$], 3190 [$\nu_s(NH_2)$], 1651 [ν(C=O)], 1565 [ν(CO) + $\delta(NH_2)$], 1551 [ν(CN)], 1403 [ν(CN) + δ(NH) + δ(NN)], 1300 [ν(CN) + $\delta(NH_2)$], 1160, 1070, 1024, 975 [$\delta(NH_2)$], 841 [δ(O=C–N)], 717 [$\omega(NH_2)$ or $\rho(NH_2)$], 534 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1602	1501	101	4
IV	3404 [ν(NH)], 3295 [$\nu_{as}(NH_2)$], 3208 [$\nu_s(NH_2)$], 1684, 1665 [ν(C=O)], 1565 [ν(CO) + $\delta(NH_2)$], 1545 [ν(CN)], 1440 [ν(CN) + δ(NH) + δ(NN)], 1325 [ν(CN) + $\delta(NH_2)$], 1205, 1068, 1024, 1000 [$\delta(NH_2)$], 842 [δ(O=C–N)], 770 [$\pi(O=C–N_2)$], 709 [$\omega(NH_2)$ or $\rho(NH_2)$], 555 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1604	1505, 1404	99, 200	2, 103
V	3438 [ν(NH)], 3285 [$\nu_{as}(NH_2)$], 3200 [$\nu_s(NH_2)$], 1637 [ν(C=O)], 1546 [ν(CN)], 1440 [ν(CN) + δ(NH) + δ(NN)], 1380[a] [ν(CN) + $\delta(NH_2)$], 1207, 1115, 1024, 1000 [$\delta(NH_2)$], 835 [δ(O=C–N)], 760 [$\pi(O=C–N_2)$], 726 [$\omega(NH_2)$ or $\rho(NH_2)$], 548 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1602	1380	222	125
VI	3398 [ν(NH)], 3330 [$\nu_{as}(NH_2)$], 3200 [$\nu_s(NH_2)$], 1655 [ν(C=O)], 1558 [ν(CO) + $\delta(NH_2)$], 1545 [ν(CN)], 1440 [ν(CN) + δ(NH) + δ(NN)], 1398 [ν(CN) + $\delta(NH_2)$], 1175, 1070, 1024, 1000 [$\delta(NH_2)$], 841 [δ(O=C–N)], 707 [$\omega(NH_2)$ or $\rho(NH_2)$], 518 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1602	1500	102	5
$Ni(Val)_2 \cdot 2H_2O$	–	1568	1417	151	

Table 2. (Contd.)

Compound	Semicarbazide absorption bands (cm^{-1})	Carboxylate absorption bands (cm^{-1})			
		$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
VII	3404 [ν(NH)], 3254 [$\nu_s(NH_2)$], 1635 [ν(C=O)], 1558[a] [ν(CN)], 1399 [ν(CN) + $\delta(NH_2)$], 1227, 1118, 929 [$\delta(NH_2)$], 772 [$\pi(O{=}C{-}N_2)$], 721 [$\omega(NH_2)$ or $\rho(NH_2)$], 552 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1558[a]	1399	159	8
$Ni(Benz)_2 \cdot 2H_2O$	–	1596	1498	98	
VIII	3469, 3441 [ν(NH)], 3312 [$\nu_{as}(NH_2)$], 3162 [$\nu_s(NH_2)$], 1648 [ν(C=O)], 1560 [ν(CO) + $\delta(NH_2)$], 1545 [ν(CN)], 1381[a] [ν(CN) + $\delta(NH_2)$], 1214, 1118, 1024, 981 [$\delta(NH_2)$], 837 [δ(O=C–N)], 765 [$\pi(O{=}C{-}N_2)$], 725 [$\omega(NH_2)$ or $\rho(NH_2)$], 545 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) +	1601	1381[a]	220	122
IX	3370–3150 [ν(OH)], 3316 [$\nu_{as}(NH_2)$], 3262, 3173 [$\nu_s(NH_2)$], 1642 [ν(C=O)], 1550 [ν(CN)], 1387[a] [ν(CN) + $\delta(NH_2)$], 1215, 1117, 1025, 980 [$\delta(NH_2)$], 839 [δ(O=C–N)], 770 [$\pi(O{=}C{-}N_2)$], 718 [$\omega(NH_2)$ or $\rho(NH_2)$], 552 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1596	1387[a]	209	111
X	3300–3160 [ν(OH)], 3305 [$\nu_{as}(NH_2)$], 3186 [$\nu_s(NH_2)$], 1646 [ν(C=O)], 1550 [ν(CN)], 1393[a] [ν(CN) + $\delta(NH_2)$], 1217, 1114, 1070, 990 [$\delta(NH_2)$], 837 [δ(O=C–N)], 773 [$\pi(O{=}C{-}N_2)$], 720 [$\omega(NH_2)$ or $\rho(NH_2)$], 555 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1598	1393[a]	205	107
$Cu(Val)_2 \cdot 2H_2O$	–	1587	1417	170	
XI	3418 [ν(NH)], 3338 [$\nu_{as}(NH_2)$], 3200 [$\nu_s(NH_2)$], 1670 [ν(C=O)], 1567 [ν(CN)], 1417 [ν(CN) + δ(NH) + δ(NN)], 1330 [ν(CN) + $\delta(NH_2)$], 1204, 1109, 941 [$\delta(NH_2)$], 864 [δ(O=C–N)], 760 [$\pi(O{=}C{-}N_2)$], 727 [$\omega(NH_2)$ or $\rho(NH_2)$], 564 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1606	1417	189	19
$Cu(Benz)_2 \cdot 2H_2O$	–	1591	1434	157	
XII	3407 [ν(NH)], 3300 [$\nu_{as}(NH_2)$], 3208 [$\nu_s(NH_2)$], 1660 [ν(C=O)], 1560 [ν(CO) + $\delta(NH_2)$], 1539 [ν(CN)], 1403[a] [ν(CN) + δ(NH) + δ(NN)], 1340 [ν(CN) + $\delta(NH_2)$], 1240, 1116, 1072, 990 [$\delta(NH_2)$], 844 [δ(O=C–N)], 760 [$\pi(O{=}C{-}N_2)$], 718 [$\omega(NH_2)$ or $\rho(NH_2)$], 554 [ν(CN) + δ(HNN) + δ(NNC) + δ(OCN) + δ(NCN)]	1616	1403[a]	213	56

[a] Overlapping bands of semicarbazide and carboxylate anions.

band is absent in the IR spectrum of the initial semicarbazide hydrochloride, whereas in the spectra of the complexes this band appears; its frequency is somewhat increased relative to free semicarbazide in the spectra of the 1 : 4 complexes and blue complex $CoL_3(Benz)_2$ (**IV**), and somewhat decreased in the spectra of the other complexes. The presence of this band suggests that semicarbazide is incorporated in the complexes without HCl; its low-frequency shift suggests the coordination via the NH_2 group, and the high-frequency shift, the absence of such coordination. The absence of HCl in the compounds prepared is also confirmed by the disappearance of the NH_3^+ stretching band in the spectra of the complexes, compared to the free ligand.

Thus, the spectra of the 1 : 4 complexes and of the blue complex $CoL_3(Benz)_2$ (**IV**) differ from the spectra of the other complexes by the lower ν(CN) and opposite shift of the $\delta(NH_2)$ frequency of the hydrazine moiety. Furthermore, in the spectra of the 1 : 4 complexes, the $\nu_s(NH_2)$ frequency decreases to a lesser extent than in the spectra of other compounds of the same metals; in the spectrum of the blue complex $CoL_3(Benz)_2$ (**IV**), $\nu_s(NH_2)$ also decreases to a considerably lesser extent than in the spectrum of the pink isomer (complex **III**). The ν(CN) + δ(NH) + δ(NN) frequency in the spectra of **IV** and 1 : 4 complexes also decreases to a lesser extent. Hence, it can be concluded that semicarbazide is bidentate and coordinates with metals via O atom and N atom of the hydrazide NH_2 group to form a five-membered chelate ring in complexes **I**–**III** and **VIII**–**XII**, but is monodentate and coordinates only via O atom in complexes **IV**–**VII**. Thus, in the 1 : 4 complexes and blue complex $CoL_3 \cdot (Benz)_2$ the semicarbazide is monodentate.

Carboxylate ions, as a rule, coordinate with metal ions in the bidentate fashion. The deprotonation of the carboxy group makes its oxygen atoms equivalent. In the IR spectra of carboxylate anions, the carbonyl absorption bands disappear, and two new bands appear at 1550–1610 and 1300–1400 cm^{-1} (antisymmetric and symmetric vibrations of the COO^- group) [13]. When the C–O bonds become nonequivalent upon formation of mixed-ligand coordination compounds, the difference between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ absorption frequencies should increase. With respect to the difference $\Delta\Delta\nu(COO^-)$ between the $\Delta\nu(COO^-)$ values for the initial carboxylates and their semicarbazide complexes [$\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-)$] (Table 2), the complexes obtained can be subdivided into two groups. For the first group, $\Delta\nu(COO^-)$ increases very strongly [$\Delta\Delta\nu(COO^-)$ exceeds 100 cm^{-1}]. For the second group, $\Delta\Delta\nu(COO^-)$ is considerably smaller and does not exceed 56 cm^{-1}. It is known [14] that $\Delta\nu(COO^-)$ is the largest at monodentate coordination of the carboxylate anion. Hence, in the complexes with large $\Delta\Delta\nu(COO^-)$, the oxygen atoms of the carboxy group are nonequivalent owing to the formation of mixed-ligand complexes, i.e., the carboxylate anions are incorporated in the inner coordination sphere of these complexes and coordinate in the monodentate fashion. In the complexes with smaller $\Delta\Delta\nu(COO^-)$, the symmetry of the carboxylate anions in the complexes differs insignificantly from that in the initial carboxylates. Apparently, in these complexes the valerate and benzoate anions are displaced to the outer coordination sphere. In the blue complex $CoL_3(Benz)_2$ (**IV**), the $\nu_s(COO^-)$ band is split in two components differing in the frequencies by 101 cm^{-1}. Presumably, the complex contains two different kinds of benzoate anions, one coordinated in the monodentate fashion and the other located in the outer sphere. Thus, the carboxylate anions in complexes **I**, **V**, and **VIII**–**X** are located in the inner sphere and coordinate in the monodentate fashion; in **IV**, one benzoate anion is located in the inner sphere and is monodentate, and the other benzoate anion is in the outer sphere; and in the other compounds obtained, carboxylate anions are displaced to the outer sphere upon complexation with semicarbazide.

The incorporation of alcohol in complexes **IX** and **X** is confirmed by the presence of very broad and strong ν(OH) absorption bands at 3400–3100 cm^{-1} typical of hydrogen-bonded structures. The IR spectrum of **VIII** contains narrow bands of ν(NH) stretching vibrations. In the spectrum of the complex with two alcohol molecules, ν(OH) is broader (220 cm^{-1}) than in the spectrum of the complex with one alcohol molecule (140 cm^{-1}). Similar broadening of the ν(OH) band with an increase in the amount of bound water was reported previously for complexes of 3*d*-metal hexacyanoferrates(II) with thiosemicarbazide [15].

Data of diffuse reflection spectroscopy are given in Table 3. The band positions suggest the tetrahedral structure of blue Co(II) complexes (**IV**, **VI**) and of the Ni(II) valerate complex (**VII**), the pseudotetrahedral structure of the Cu(II) complexes (**XI**, **XII**), and the octahedral structure of all the other complexes [16].

Thermal analysis shows (Table 4) that the thermal stability of the synthesized semicarbazide complexes of 3*d*-metal valerates and benzoates decreases in the order $Co^{2+} > Ni^{2+} > Cu^{2+}$.

The common feature of the thermolysis of almost all the synthesized complexes is major (exceeding 40% in some cases) weight loss accompanying one of the first effects in the thermograms. Such a behavior may be characteristic of other semicarbazide complexes also. Apparently, just due to this fact the complex $ZnL_3(NO_3)_2$ was suggested as a potential gas source for filling safety airbags for cars [9].

For all the valerate complexes, the first two effects in the thermograms are endothermic; the same is true for the Ni(II) benzoate complexes, including those solvated with alcohol. For the Co(II) benzoate complexes, all the effects in the thermograms are exothermic, and for the Cu(II) benzoate complex the thermal decomposition starts with an endoeffect followed by an exoeffect. Cobalt(II) complexes with the same anions of the 1 : 3 composition are less stable than the 1 : 2 and 1 : 4 complexes. Benzoate complexes are more stable thermally than valerate complexes. Pink complexes of Co(II) benzoate are more stable than the blue complexes. Comparison of the nonsolvated Ni(II) benzoate complex and its analogs containing one or two alcohol molecules shows that the solvated com-

Table 3. Diffuse reflection spectra of semicarbazide complexes of 3*d*-metal valerates and benzoates

Comp. no.	λ, nm	Assignment	Comp. no.	λ, nm	Assignment
I	464	${}^4T_{1g}(F) \to {}^4T_{1g}(P)$	**VIII**	347	${}^3A_{2g} \to {}^3T_{1g}(P)$
	1244	${}^4T_{1g}(F) \to {}^4T_{2g}$		581	${}^3A_{2g} \to {}^3T_{1g}$
II	553	${}^4T_{1g}(F) \to {}^4T_{1g}(P)$		957	${}^3A_{2g} \to {}^3T_{2g}$
	1258	${}^4T_{1g}(F) \to {}^4T_{2g}$	**IX**	401	${}^3A_{2g} \to {}^3T_{1g}(P)$
III	483	${}^4T_{1g}(F) \to {}^4T_{1g}(P)$		593	${}^3A_{2g} \to {}^3T_{1g}$
IV, VI	609	${}^4A_2 \to {}^4T_1(P)$		984	${}^3A_{2g} \to {}^3T_{2g}$
	2229	${}^4A_2 \to {}^4T_1(F)$	**X**	615	${}^3A_{2g} \to {}^3T_{1g}$
V	483	${}^4T_{1g}(F) \to {}^4T_{1g}(P)$		1043	${}^3A_{2g} \to {}^3T_{1g}$
	1081	${}^4T_{1g}(F) \to {}^4T_{2g}$	**XI**	720	
VII	350	${}^3T_1 \to {}^1T_2$		1701	
	587	${}^3T_1 \to {}^3T_1(P)$		2015	
	759	${}^3T_1 \to {}^1E$	**XII**	675	
	2229	${}^3T_1 \to {}^3A_2$		1981	

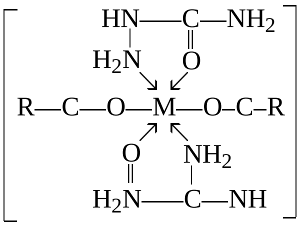
Table 4. Results of differential thermal analysis of semicarbazide complexes of 3*d*-metal valerates and benzoates

Comp. no.	Decomposition step	Temperature, °C[a]			Weight loss, %	Residue at 500°C, %
		T_o	T_e	t_{max}		
I	First (*endo*)	80	170	140	16.1	33.3
	Second (*endo*)	190	240	220	37.5	
II	First (*endo*)	50	150	120	21.5	56.5
	Second (*endo*)	190	300	250	12.1	
III	First (*exo*)	140	230	200	59.5	34.8
IV	First (*exo*)	110	190	165	14.7	23.6
	Second (*exo*)	240	370	325	32.7	
V	First (*exo*)	250	285	260	22.9	20.0
	Second (*exo*)	285	350	300	43.4	
VI	First (*exo*)	140	210	190	23.8	56.4
	Second (*exo*)	250	300	270	17.0	
VII	First (*endo*)	60	100	80	9.6	20.3
	Second (*exo*)	210	280	250	21.3	
VIII	First (*exo*)	110	175	140	7.3	36.0
	Second (*endo*)	230	300	265	43.0	
IX	First (*endo*)	75	190	130	11.4	46.7
	Second (*endo*)	230	300	250	22.1	
X	First (*endo*)	75	200	125	23.5	61.7
	Second (*endo*)	200	300	250	14.9	
XI	First (*endo*)	50	120	75	6.9	35.2
	Second (*endo*)	160	210	200	36.5	
XII	First (*endo*)	65	120	95	7.8	44.2
	Second (*exo*)	120	165	130	13.5	

[a] Temperatures corresponding to (T_o) onset, (T_e) end, and (t_{max}) maximum of the effects.

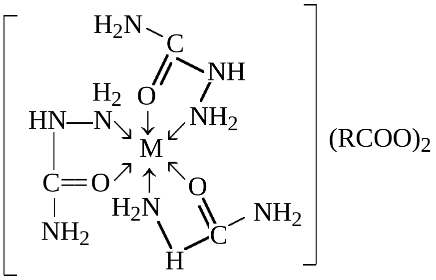
plexes start to decompose at somewhat lower temperatures, whereas the second effects are observed at similar temperatures for all the three compounds. Separate steps corresponding to the elimination of the alcohol cannot be distinguished. Apparently, despite the fact that the alcohol is not coordinated directly with the metal, it forms fairly strong hydrogen bonds with the coordinated semicarbazide and is eliminated virtually simultaneously with the decomposition of the complexes.

The results obtained allow us to ascribe the following structures to the compounds prepared:



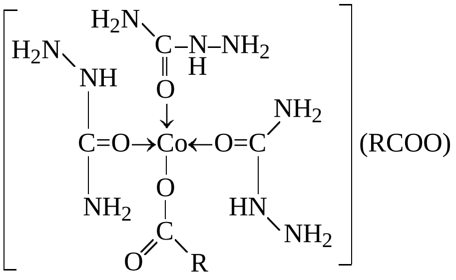
I, VIII–X

M = Co, R = C_4H_9 (**I**); M = Ni, R = C_6H_5 (**VIII–X**).



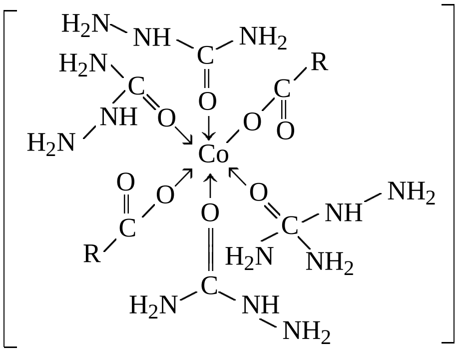
II, III

M = Co, R = C_4H_9 (**II**), C_6H_5 (**III**).



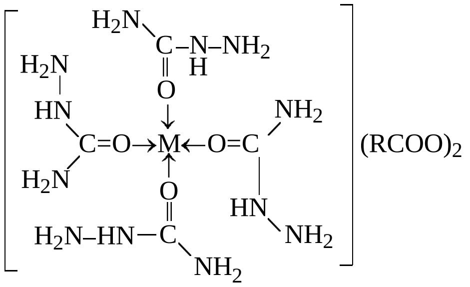
IV

R= C_6H_5.



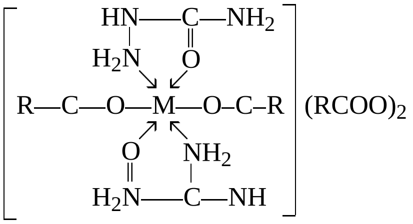
V

R= C_6H_5.



VI, VII

M = Co, R = C_6H_5 (**VI**); M = Ni, R = C_4H_9 (**VII**).



XI, XII

M = Cu, R = C_4H_9 (**XI**), C_6H_5 (**XII**).

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum BX-II FT-IR device; samples were prepared as KBr pellets. The diffuse reflection spectra were recorded on a Perkin–Elmer Lambda-9 spectrophotometer, with MgO (β_{MgO} 100%) as reference. Thermal analysis was performed with a Paulik–Paulik–Erdey derivatograph in air at a heating rate of 10 deg min^{-1}.

Cobalt(II), nickel(II), and copper(II) chlorides, valeric and benzoic acids, and semicarbazide hydrochloride used in the syntheses were of analytically pure grade.

The metal content in the complexes was determined by complexometric titration [17], and the nitrogen content, by the Dumas method [18]. X-ray diffraction patterns were taken with a URS-50IM diffractometer using a copper anticathode and a nickel filter.

Neutralization of semicarbazide hydrochloride [3]. A weighed portion of semicarbazide hydrochloride L · HCl was dissolved in a minimal amount of distilled water. The solution was neutralized by adding dry KOH in one-granule portions. After adding each granule, the pH was checked with a universal indicator. Once the pH exceeded 7, the addition of KOH was terminated. The resulting solution was evaporated to dryness on a water bath. Hot absolute ethanol was added in portions to the dry residue. Therewith, semicarbazide dissolved and KCl remained in the precipitate. The KCl precipitate was filtered off.

Complexes I and II. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 2.97 g of dry cobalt(II) valerate C°$(C_4H_9COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate; the whole portion of the salt dissolved, and the solution became violet. The solvent was allowed to evaporate. A brown product precipitated from the solution; it was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight. The product obtained was dirty pink (complex **I**). The filtrate solidified to form a glassy substance. It was dried in an oven at 70°C to constant weight (complex **II**).

Complexes III and IV. A 2.23-g portion of $L \cdot HCl$ was neutralized, and 3.37 g of dry cobalt(II) benzoate C°$(C_6H_5COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate; the whole portion of the salt dissolved, and the solution became crimson-colored. The solvent was allowed to evaporate. After a certain period, a gray precipitate formed; it was separated and dried in a desiccator over $CaCl_2$ to constant weight. After drying, the precipitate became pink (complex **III**). Drying of the precipitate in an oven at 50°C led to the formation of a complex of identical composition but gray-blue color (complex **IV**).

Complexes V and VI. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 3.37 g of dry cobalt(II) benzoate C°$(C_6H_5COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate; the whole portion of the salt dissolved to give a crimson-colored solution. The solution gradually became turbid and was left for the solvent evaporation. After a certain period, a pink crystalline precipitate formed; it was separated from the mother liquor and dried in a desiccator over $CaCl_2$ to constant weight (complex **V**). Drying of the precipitate in an oven at 50°C led to the formation of a complex of identical composition but a gray-blue color (complex **VI**). A pink precipitate identical to complex **III** formed from the filtrate.

Complex VII. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 2.97 g of dry nickel(II) valerate $Ni(C_4H_9 \cdot COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate. On adding the first portion of the salt, a gray precipitate formed, and the solution became light sky-blue. On adding further portions of the salt, the solution became light blue, and a blue precipitate formed. The mixture was stirred on a magnetic stirrer for a long time, and the precipitate was fitered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

Complex VIII. A 2.23-g portion of $L \cdot HCl$ was neutralized, and 3.37 g of dry nickel(II) benzoate $Ni(C_6H_5COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate. The solution became green, and a green precipitate formed after a certain period. The mixture was stirred for a long time. The precipitate was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

Complexes IX and X. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 3.37 g of dry nickel(II) benzoate $Ni(C_6H_5COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate. The solution became green, and a gray-blue precipitate formed after a certain period. The precipitate was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight (complex **IX**). Another product gradually precipitated from the filtrate; this product was separated, washed with ethanol, and dried in a desiccator over $CaCl_2$ (complex **X**).

Complex XI. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 3.02 g of dry copper(II) valerate $Cu \cdot (C_4H_9COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate. The solution became green, and a dark green precipitate formed. The gas evolution was observed. The mixture was stirred on a magnetic stirrer for several hours and allowed to stand for a day. The precipitate was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

Complex XII. A 4.46-g portion of $L \cdot HCl$ was neutralized, and 2.97 g of dry copper(II) benzoate $Cu(C_6H_5COO)_2 \cdot 2H_2O$ was added to the alcoholic filtrate. The solution became blue, and a gray-blue precipitate gradually formed. The mixture was stirred on a magnetic stirrer for a long time. The solution became brown, and the precipitate became bluish gray. It was filtered off on a glass frit, washed with a small amount of ethanol, and dried in a desiccator over $CaCl_2$ to constant weight.

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