

Coordination Compounds of 3d-Metal Valerates and Benzoates with Nicotinamide

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Abstract—Complexes of iron(II), cobalt(II), nickel(II), copper(II), and zinc valerates and benzoates with nicotinamide were synthesized. The products were characterized by chemical analysis, IR spectroscopy, diffuse reflection spectroscopy, and thermogravimetry.

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Synthesis and study of coordination compounds of microelements with bioactive organic substances can be one of promising ways of creating potential highly effective pharmaceuticals. It is known [1] that coordinated metals are more bioactive and less toxic than their inorganic salts. Furthermore, a combination of a microelement and a bioactive organic substance in the same complex can lead to synergism in their action. Nicotinamide (vitamin PP) enters into the composition of two coenzymes (cozymase and co-dehydrase). The mechanism of their action consists in redox reactions, whereas the nicotinamide part is

hydrogen carrier [2]. Modeling complicated metallo-enzymes and metallocoenzymes by fairly simple metal complexes is a routine experimental approach. To synthesize and analyze the structures and properties of coordination compounds of iron(II), cobalt(II), nickel(II), coppers(II), and zinc valerates and benzoates with nicotinamide (L), we used valeric and benzoic acids as carboxylic acids, sources of carboxylate anions.

The chemical analysis (Table 1) shows that the metal-to-nicotinamide ratio in the resulting compounds

Table 1. Elemental analyses and colors of products **I–XIII** of the reactions of 3d-metal valerates and benzoates with nicotinamide

Comp. no.	Color	Found, %		Formula	Calculated, %	
		M	N		M	N
I	Brown	8.3	12.8	C ₃₂ H ₂₈ FeN ₆ O ₇ [FeL ₃ (Benz) ₂]	8.4	12.7
II	Pink	11.6	10.8	C ₄₄ H ₆₀ Co ₂ N ₈ O ₁₂ ·H ₂ O[CoL ₂ (Val) ₂] ₂ ·H ₂ O]	11.5	10.9
III	Pink	9.7	13.8	C ₂₈ H ₃₆ CoN ₆ O ₇ [CoL ₃ (Val) ₂]	9.4	13.4
IV	Pink	10.1	9.8	C ₂₆ H ₂₂ CoN ₄ O ₆ ·2H ₂ O[CoL ₂ (Benz) ₂ ·2H ₂ O]	10.2	9.6
V	Pink-lilac	7.3	14.4	C ₃₈ H ₃₄ CoN ₈ O ₈ [CoL ₄ (Benz) ₂]	7.5	14.2
VI	Light green	10.6	10.1	C ₂₂ H ₃₀ N ₄ NiO ₆ ·2H ₂ O[NiL ₂ (Val) ₂ ·2H ₂ O]	10.9	10.4
VII	Light green	9.1	13.2	C ₂₈ H ₃₆ N ₆ NiO ₇ [NiL ₃ (Val) ₂]	9.4	13.4
VIII	Blue	9.9	9.8	C ₂₆ H ₂₂ N ₄ NiO ₆ ·2H ₂ O[NiL ₂ (Benz) ₂ ·2H ₂ O]	10.2	9.6
IX	Green	16.5	7.1	C ₁₆ H ₂₄ CuN ₂ O ₅ [CuL(Val) ₂]	16.5	7.2
X	Dark blue	12.1	11.2	C ₂₂ H ₃₀ CuN ₄ O ₆ [CuL ₂ (Val) ₂]	12.5	11.0
XI	Dark blue	11.2	9.8	C ₂₆ H ₂₂ CuN ₄ O ₆ [CuL ₂ (Benz) ₂]	11.6	10.2
XII	White	12.4	11.1	C ₂₂ H ₃₀ N ₄ O ₆ Zn[ZnL ₂ (Val) ₂]	12.7	11.0
XIII	White	11.7	10.1	C ₂₆ H ₂₂ N ₄ O ₆ Zn[ZnL ₂ (Benz) ₂]	11.8	10.2

depends on the carboxylate anion used. We were unable to obtain a pure iron(II) valerate, probably because of hydrolysis. Therefore, the corresponding complex with nicotinamide was not prepared either, whereas with the other metals under study we could prepare nicotinamide complexes both with valerates and benzoates. Metal benzoates form nicotinamide complexes of the composition 1:3 with iron(II), 1:2 with nickel(II), copper(II), and zinc(II), and only in the case of cobalt(II) it was possible to isolate 1:2 and 1:4 complexes. Metal valerates form more diverse nicotinamide complexes: in addition to the 1:2 composition which was obtained with all the metals (except for iron), the composition 1:1 is realized with copper(II) and 1:3, with nickel(II) and cobalt(II). This suggests that 3d-metal valerates more readily than benzoates react with nicotinamide. The complexes of 3d-metal valerates and benzoates with nicotinamide are soluble in water and DMF and slightly poorer soluble in ethanol.

The structure of compounds (**II**, **VIII–X**) was determined by X-ray diffraction analysis [3–6]. It was found that $[\text{CoL}_2(\text{Val})_2]_2 \cdot \text{H}_2\text{O}$ (**II**) is binuclear with octahedral coordination of the cobalt atom, nicotinamide is monodentate and is bound via the pyridine nitrogen atom, the valerate anions are present both in a monodentate and in a bidentate bridging forms, and the water molecule plays the role of a bridge between two cobalt atoms [3]. In $\text{NiL}_2(\text{Benz})_2 \cdot 2\text{H}_2\text{O}$ (**VIII**), the octahedral coordination environment of the nickel atom includes two atoms of oxygen and two atoms of nitrogen of monodentate benzoate anions and nicotin-

amide molecules, respectively, as well as two oxygen atoms of water [4]. A green complex $\text{CuL}(\text{Val})_2$ (**IX**) consists of binuclear molecules in which two copper atoms are bound through four bidentate bridging valerate anions, nicotinamide is bound to copper through the pyridine nitrogen atom, and the coordination polyhedron of each copper atom in the 1:1 complex represents a tetragonal pyramid [5]. In a pale blue complex $\text{CuL}_2(\text{Val})_2$ (**X**), the copper atom has a tetragonal–bipyramidal coordination due to four oxygen atoms of two valerate anions and two pyridine nitrogen atoms of the nicotinamide ligands, and the valerate anions function as bidentate pseudo-bis-chelate ligands [6].

Conclusions as to the coordination modes of the ligands in the coordination polyhedra of compounds **I**, **III–VII**, and **XI–XIII** were drawn on the basis of spectral data. To assign the principal absorption bands in the IR spectra of nicotinamide and the complexes (Table 2), we used published data [2, 7, 8]. Owing to the presence of hydrogen bonds, uncoordinated nicotinamide molecules are coordinated in the solid state, which affects the frequencies of certain bands in the IR spectra. This effect is most pronounced in the spectra of crystalline amides and less pronounced in the spectra of crystalline metal complexes with amides in the absence of coordination of L through the amide nitrogen atom, as evidenced by spectral and X-ray diffraction data for a great number of complexes [8]. Therefore, for correct interpretation of coordination-induced shifts of nicotinamide absorption bands, we considered it necessary to take the IR spectra of the

Table 2. IR spectra of nicotinamide (L), 3d-metal valerates and benzoates, and their reaction products **I–XIII**

Comp. no.	Absorption bands (cm^{-1}) of nicotinamide and carboxylate anions	Absorption bands (cm^{-1}) of the COO^- group			
		$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\Delta\Delta\nu(\text{COO}^-)$
L (KBr tablets)	3376, 3300, 3170 [$\nu(\text{NH})$], 3090, 3035, 2970, 2960, 2910, 2890, 2820 [$\nu(\text{CH})$], 1687 [$\nu(\text{C}=\text{O})$], 1627 [$\delta(\text{NH}_2)$], 1580 (ν_{ring}), 1380, 1360, 1340 [$\delta(\text{CCH})$], 1290, 1250, 1205 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1160, 1134 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1030, 1005 (ν_{ring}), 890, 835, 760 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 702 [$\delta(\text{CCN})_{\text{ring}}$], 635, 610 [$\delta(\text{CNC})_{\text{ring}}$], 550 [$\delta(\text{CCN})$, $\delta(\text{CCC})$]				
L (Nujol suspension)	3350, 3145 [$\nu(\text{NH})$], 1665 [$\nu(\text{C}=\text{O})$], 1610 [$\delta(\text{NH}_2)$], 1585, 1560 (ν_{ring}), 1365, 1330 [$\delta(\text{CCH})$], 1295, 1195 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1145, 1120 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1020, 965 (ν_{ring}), 880, 820, 765 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 710 [$\delta(\text{CCN})_{\text{ring}}$], 635, 615 [$\delta(\text{CNC})_{\text{ring}}$], 595, 500 [$\delta(\text{CCN})$, $\delta(\text{CCC})$]				

Table 2. (Contd.)

Comp. no.	Absorption bands (cm ⁻¹) of nicotinamide and carboxylate anions	Absorption bands (cm ⁻¹) of the COO ⁻ group			
		$\nu_{as}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\Delta\Delta\nu(\text{COO}^-)$
Fe(Benz) ₂ · 2H ₂ O I	3365, 3193 [$\nu(\text{NH})$], 3070 [$\nu(\text{CH})$], 1683 [$\nu(\text{C=O})$], 1567 (ν_{ring}), 1201 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1177 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1071, 1027 (ν_{ring}), 837, 786 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 718 [$\delta(\text{OCO})$], 707 [$\delta(\text{CCN})_{\text{ring}}$], 675, 626 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 481 $\nu(\text{MO})$, (CH), (CC)	1601 1620 sh, 1602	1407 1405	194 215, 197	21, 3
Co(Val) ₂ · 2H ₂ O II	3428 [$\nu(\text{OH})$], 3376, 3197 [$\nu(\text{NH})$], 2958, 2932, 2872 [$\nu(\text{CH})$], 1678 [$\nu(\text{C=O})$], 1615 sh [$\delta(\text{NH}_2)$], 1590 sh (ν_{ring}), 1380 ^a sh, 1315 [$\delta(\text{CCH})$, $\delta(\text{CH}_3)$], 1290, 1240, 1202 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1101 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1051, 1034 (ν_{ring}), 942 [$\nu(\text{CC})$ (C ₄ H ₉ -)], 831, 790, 757 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 720 sh [$\delta(\text{OCO})$], 700 [$\delta(\text{CCN})_{\text{ring}}$], 664, 648 [$\delta(\text{CNC})_{\text{ring}}$], 595 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 434 $\nu(\text{MO})$, (CH), (CC)	1568 1600 v.s	1413 1411 v.s, 1380 ^a sh	155 189, 220	34, 65
III	3348, 3187 [$\nu(\text{NH})$], 2958, 2932, 2872 [$\nu(\text{CH})$], 1680 [$\nu(\text{C=O})$], 1590 sh (ν_{ring}), 1202 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1100 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1050, 1032 (ν_{ring}), 831, 789, 756 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 735 [$\delta(\text{OCO})$], 702 [$\delta(\text{CCN})_{\text{ring}}$], 647, 626 [$\delta(\text{CNC})_{\text{ring}}$], 427 $\nu(\text{MO})$, (CH), (CC)	1602	1423, 1410	179, 192	24, 37
Co(Benz) ₂ · 2H ₂ O IV	3474 [$\nu(\text{OH})$], 3342, 3186 [$\nu(\text{NH})$], 3064, 2817 [$\nu(\text{CH})$], 1676 [$\nu(\text{C=O})$], 1609 [$\delta(\text{NH}_2)$], 1585 (ν_{ring}), 1200 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1139 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1070, 1053, 1031 (ν_{ring}), 820, 742 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 730 [$\delta(\text{OCO})$], 691 [$\delta(\text{CCN})_{\text{ring}}$], 677, 649, 639 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 506 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 451, 427 $\nu(\text{MO})$, (CH), (CC)	1594 1598	1497 1395	97 203	106
V	3372, 3219 [$\nu(\text{NH})$], 3068 [$\nu(\text{CH})$], 1675 [$\nu(\text{C=O})$], 1636 [$\delta(\text{NH}_2)$], 1580 (ν_{ring}), 1196 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1115 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1068, 1054, 1027 (ν_{ring}), 860, 838, 826, 777 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 719 [$\delta(\text{OCO})$], 699 [$\delta(\text{CCN})_{\text{ring}}$], 649, 641, 625 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 517 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 452, 437 $\nu(\text{MO})$, (CH), (CC)	1594	1422	172	75
Ni(Val) ₂ · H ₂ O VI	3450 [$\nu(\text{OH})$], 3357, 3182 [$\nu(\text{NH})$], 2959, 2932, 2873 [$\nu(\text{CH})$], 1698 [$\nu(\text{C=O})$], 1635 [$\delta(\text{NH}_2)$], 1585 sh (ν_{ring}), 1202 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1100 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1052, 1034 (ν_{ring}), 832, 792, 758 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 730 [$\delta(\text{OCO})$], 703 [$\delta(\text{CCN})_{\text{ring}}$], 674, 648 [$\delta(\text{CNC})_{\text{ring}}$], 440 $\nu(\text{MO})$, (CH), (CC)	1568 1603	1417 1396	151 207	56
VII	3364, 3191 [$\nu(\text{NH})$], 2958, 2932, 2871 [$\nu(\text{CH})$], 1680 [$\nu(\text{C=O})$], 1585 sh (ν_{ring}), 1202 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1108 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1053, 1032 (ν_{ring}), 830, 794, 758 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 740 [$\delta(\text{OCO})$], 699 [$\delta(\text{CCN})_{\text{ring}}$], 655, 626 [$\delta(\text{CNC})_{\text{ring}}$], 520 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 437 $\nu(\text{MO})$, (CH), (CC)	1614	1408, 1390	206, 224	55, 73
Ni(Benz) ₂ · 2H ₂ O VIII	3472 [$\nu(\text{OH})$], 3397, 3193 [$\nu(\text{NH})$], 3068, 2905 [$\nu(\text{CH})$], 1693, 1670 [$\nu(\text{C=O})$], 1590 sh (ν_{ring}), 1202 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1170, 1135 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1070, 1053 (ν_{ring}), 855, 840, 795, 755 [$\nu(\text{CC})$,	1596 1602 v.s	1498 1398 v.s	98 204	106

Table 2. (Contd.)

Comp. no.	Absorption bands (cm ⁻¹) of nicotinamide and carboxylate anions	Absorption bands (cm ⁻¹) of the COO ⁻ group			
		$\nu_{as}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\Delta\Delta\nu(\text{COO}^-)$
Ni(Benz) ₂ · 2H ₂ O VIII	$\delta(\text{CCC})$, 726 [$\delta(\text{OCO})$], 698 [$\delta(\text{CCN})_{\text{ring}}$], 677, 652 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 518 [$\delta(\text{CCN})$, $\delta(\text{CCC})$]				
Cu(Val) ₂ · 2H ₂ O IX	3395, 3326, 3190 [$\nu(\text{NH})$], 3085, 2960, 2940, 2875, 2780 [$\nu(\text{CH})$], 1695 [$\nu(\text{C=O})$], 1605 sh [$\delta(\text{NH}_2)$], 1595 sh (ν_{ring}), 1385, 1330 [$\delta(\text{CCH})$, $\delta(\text{CH}_3)$], 1305, 1250, 1208 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1160, 1115 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1060, 1045 (ν_{ring}), 945 [$\nu(\text{CC})$ (C ₄ H ₉ -)], 870, 840, 800, 760 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 725 [$\delta(\text{OCO})$], 702 [$\delta(\text{CCN})_{\text{ring}}$], 650, 615 [$\delta(\text{CNC})_{\text{ring}}$], 530 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 430 $\nu(\text{MO})$, (CH), (CC)	1587 1600 v.s	1417 1420 v.s	170 180	10
X	3368, 3267, 3197 [$\nu(\text{NH})$], 3050, 2960, 2935, 2872, 2786 [$\nu(\text{CH})$], 1687 [$\nu(\text{C=O})$], 1624 [$\delta(\text{NH}_2)$], 1590 (ν_{ring}), 1350, 1330 [$\delta(\text{CCH})$, $\delta(\text{CH}_3)$], 1305, 1270, 1203 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1130, 1124 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1059, 1030, 970 (ν_{ring}), 936 [$\nu(\text{CC})$ (C ₄ H ₉ -)], 865, 831, 761 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 720 [$\delta(\text{OCO})$], 703 [$\delta(\text{CCN})_{\text{ring}}$], 646, 626 [$\delta(\text{CNC})_{\text{ring}}$], 512 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 444, 412 $\nu(\text{MO})$, (CH), (CC)	1602	1400	202	32
Cu(Benz) ₂ · 2H ₂ O XI	3374, 3216 [$\nu(\text{NH})$], 3071, 2779 [$\nu(\text{CH})$], 1673 [$\nu(\text{C=O})$], 1637 [$\delta(\text{NH}_2)$], 1585 (ν_{ring}), 1195 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1116 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1068, 1027 (ν_{ring}), 856, 838, 777 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 718 [$\delta(\text{OCO})$, 697 ($\delta(\text{CCN})_{\text{ring}}$), 658, 641, 626 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 532 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 443 $\nu(\text{MO})$, (CH), (CC)	1591 1598	1434 1395	157 203	46
Zn(Val) ₂ · 2H ₂ O XII	3370, 3173 [$\nu(\text{NH})$], 2959, 2930, 2863, 2781 [$\nu(\text{CH})$], 1705 [$\nu(\text{C=O})$], 1624 [$\delta(\text{NH}_2)$], 1596 (ν_{ring}), 1204 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1137, 1102 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1056, 1026 (ν_{ring}), 830, 797, 784, 765 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 712 [$\delta(\text{OCO})$], 691 [$\delta(\text{CCN})_{\text{ring}}$], 659, 626, 606 [$\delta(\text{CNC})_{\text{ring}}$], 524 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 430 $\nu(\text{MO})$, (CH), (CC)	575 1609	1395 1398	180 211	31
Zn(Benz) ₂ · 2H ₂ O XIII	3369, 3178 [$\nu(\text{NH})$], 1702 [$\nu(\text{C=O})$], 1630 [$\delta(\text{NH}_2)$], 1570 (ν_{ring}), 1200 [$\delta(\text{CCH})$, $\delta(\text{CCC})$], 1138 [$\delta(\text{NH}_2)$, $\delta(\text{CCH})$], 1070, 1053 (ν_{ring}), 843, 836, 793, 759 [$\nu(\text{CC})$, $\delta(\text{CCC})$], 720 [$\delta(\text{OCO})$], 691 [$\delta(\text{CCN})_{\text{ring}}$], 675, 650, 625 [$\delta(\text{CNC})_{\text{ring}}(\text{L})$], 575 [$\delta(\text{CCN})$, $\delta(\text{CCC})$], 458, 430 $\nu(\text{MO})$, (CH), (CC)	1599 1600	1417 1383	182 217	35

^a Both the nicotinamide and valerate anions contribute to the absorption band.

ligand both as KBr tablets and as suspension in Nujol. The IR spectra of suspensions of the starting 3*d*-metal carboxylates and their nicotinamide complexes in Nujol are poorly informative, as the absorption bands of Nujol and the carboxy group partially overlap.

The absorption frequencies of nicotinamide change similarly in going to all the complexes synthesized. The $\nu(\text{NH})$ frequencies in the IR spectra of the complexes are higher than in the spectrum of free nicotinamide in Nujol and sometimes than in the spectrum

of the solid sample. The $\nu(\text{C}=\text{O})$ frequency (amide I) also increases for complexes in comparison with the spectrum of the ligand suspended in Nujol. The ν_{ring} bands both near 1600 and near 1000 cm^{-1} are shifted to high frequencies in comparison with free nicotinamide. The similarity in the behavior of the absorption bands of nicotinamide in going to compounds **II**, **VIII–X** in which the monodentate coordination through the pyridine nitrogen atom is proved by means of X-ray diffraction, on the one hand, and to compounds **I**, **III–VII**, **XI–XIII**, on the other, suggests that nicotinamide in all the synthesized complexes acts as a monodentate ligand coordinated through the pyridine nitrogen atom.

Carboxylate anions generally coordinate to metal ions in a bidentate mode. Detachment of a proton from the carboxy group in a carboxylic acid makes the oxygen atoms equivalent. Carbonyl absorption bands disappear from the IR spectra and two new bands appear in the region of 1550–1610 cm^{-1} and 1300–1400 cm^{-1} (antisymmetric and symmetric vibrations of the COO^- group) [9]. As the bond equivalence is violated due to formation of mixed-ligand coordination compounds, the difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ should increase. Examination of such differences (Table 2) for the starting carboxylates and their complexes with nicotinamide shows that all the synthesized compounds can be separated into three groups in terms of this difference. In the first group of complexes, $\Delta\nu(\text{COO}^-)$ is 56–106 cm^{-1} , in the second, $\leq 46 \text{ cm}^{-1}$, and in the third, the $\nu_{\text{s}}(\text{COO}^-)$ band is split into a doublet [in the spectrum of the iron(II) complex the $\nu_{\text{as}}(\text{COO}^-)$ band is split]. It is known [10] that the largest difference between $\nu_{\text{s}}(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ corresponds to monodentate coordination of carboxylate anions. Hence, in the complexes with large $\Delta\nu(\text{COO}^-)$ values, the equivalence of carboxyl oxygen atoms is violated to formation of mixed-ligand complexes, i.e. the carboxylate anions enter into the inner sphere of these coordination compounds as monodentate ligands. As to the compounds with modest $\Delta\nu(\text{COO}^-)$ values, we should assume that there the carboxy groups remain bidentate. The band splitting, i.e. the observation of two $\Delta\nu(\text{COO}^-)$ values for the same compound, suggests that it contains differently coordinated carboxylate anions: both monodentate and bidentate.

The above assumptions agree with the X-ray diffraction data: The carboxylate anion in complex **VIII** coordinates as a monodentate ligand [$\Delta\nu(\text{COO}^-)$ 106 cm^{-1}], those in complexes **IX** and **X** are bidentate [$\Delta\nu(\text{COO}^-)$ 10 and 32 cm^{-1} , respectively], and those in complex **II** act as both monodentate and bidentate bridging ligands [$\Delta\nu(\text{COO}^-)$ 65 and 34 cm^{-1} , res-

Table 3. Diffuse reflection spectra of nicotinamide complexes of 3d-metal valerates and benzoates **I–XI**

Comp. no.	λ_{max} , nm	Assignment
I	1369	${}^5T_{2g} \rightarrow {}^5E_g$
II	493	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
	1138	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$
III	491	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
	1138	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$
IV	500	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
	1131	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$
V	497	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
	638	${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$
	1138	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$
VI	626	${}^3A_{2g} \rightarrow {}^3T_{1g}$
	1058	${}^3A_{2g} \rightarrow {}^3T_{2g}$
VII	627	${}^3A_{2g} \rightarrow {}^3T_{1g}$
	1048	${}^3A_{2g} \rightarrow {}^3T_{2g}$
VIII	626	${}^3A_{2g} \rightarrow {}^3T_{1g}$
	1043	${}^3A_{2g} \rightarrow {}^3T_{2g}$
IX	681	
X	595	
XI	630	

pectively]. Thus, we can assume that the carboxylate anions in complexes **IV–VI** are monodentate, in complexes **XI–XIII**, bidentate, and in complexes **I**, **III**, and **VII**, both monodentate and bidentate. Hence, the coordination mode of carboxylate anions depends on the nature of the complex-forming metal and anion, and the stoichiometry of the resulting compound. With copper(II) and zinc(II), all carboxylate anions are bidentate; in cobalt(II) benzoate anions, they are monodentate, and in valerate anions, monodentate coordination is realized simultaneously with bidentate coordination; in 1:2 nickel(II) complexes, both carboxylate anions are monodentate, and in the 1:3 complexes, both types of anion coordination take place. Thus, monodentate coordination is more characteristic for benzoate anions than for valerate anions; in all complexes with a 1:3 metal-to-ligand ratio, mixed anion coordination is observed.

The $\nu(\text{OH})$ bands of water molecules in the IR spectra of the obtained compounds lay in the region characteristic for stretching O–H vibrations in aqua complexes [9].

The diffuse reflection spectra are presented in Table 3. The positions of the bands suggest that iron(II), cobalt(II), and nickel(II) compounds are octahedral and $\text{CuL}_2(\text{Benz})_2$ (**XI**) has a tetragonal–bipyramidal structure [11].

Table 4. Results of thermal analysis of nicotinamide complexes of 3d-metal valerates and benzoates

Comp. no.	Endo effects		Exo effects		Total weight loss, %
	<i>t</i> , °C	Δm , %	<i>t</i> , °C	Δm , %	
III	260–330 (298)	24.0	330–442 (418)	51.7	87.6
	82–140 (90)	–	310–400 (350)	8.1	55.7
	140–260 (230)	39.4			
III	155–178 (163)	–	178–330 (289)	75.4	82.3
IV	70–103 (90)	4.5	250–460 (415)	41.0	82.5
	210–250 (230)	28.6			
V	82–180 (130)	14.6	310–400 (360)	56.8	90.0
	230–252 (240)	7.5			
VI	82–162 (135)	15.4			83.7
	162–202 (180)	2.9			
	255–300 (290)	56.9			
VII	128–180 (155)	–	350–450 (400)	6.0	64.8
	238–300 (270)	57.4			
VIII	93–170 (140)	17.9	300–400 (350)	45.0	82.2
IX	173–210 (180)	–	210–262 (235)	41.2	80.4
			262–410 (350)	19.6	
			430–500 (480)	9.8	
X	160–205 (175)	–	205–280 (240)	70.1	75.0
XI	178–200 (190)	14.5	330–400 (350)	14.8	79.2
	200–280 (245)	33.0			
XII	118–150 (130)	–	300–400 (350)	9.8	63.8
	230–300 (263)	42.9			
XIII	135–160 (144)	1.4	400–480 (440)	2.2	78.2
	160–240 (192)	3.8			
	240–350 (288)	69.9			

The thermogravimetric data for the synthesized compounds are given in Table 4. In all the valerate complexes of 3d metals with nicotinamide, except for $\text{NiL}_2(\text{Val})_2 \cdot 2\text{H}_2\text{O}$ (**VI**), the first effect with a maximum at 90–180°C is endothermic and not accompanied by weight loss.

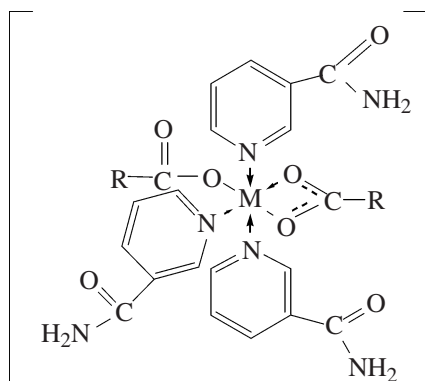
Obviously, it should be assigned to melting. The fact that complex **VI** is an exception may well be caused by the presence of a weakly bound water in it. The benzoate complexes decompose without melting. Their thermal stability decreases in the following order depending on the nature of the complex-forming metal: $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$.

Except for the cobalt compounds, the benzoate complexes are more thermally stable than the valerate ones. The dependence of the thermal stability on the stoichiometry of the compounds is traced also. In all $\text{ML}_n(\text{RCOO})_2$ compounds with the same $\text{M}(\text{RCOO})_2$ salt and two different *n* values, except for the copper complexes, compounds with higher *n* values are more stable. The reverse dependence for the copper(II)

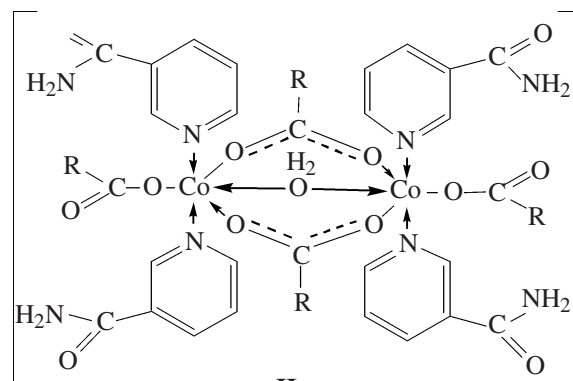
valerate complexes with nicotinamide is attributable to the following. The X-ray diffraction analysis showed that the general configuration of $\text{CuL}_2(\text{Val})_2$ is similar to the configuration of half the $[\text{CuL}(\text{Val})_2]_2$ molecule. As a blue $\text{CuL}_2(\text{Val})_2$ is heated to the temperature of the first endo effect, it turns to a green $[\text{CuL}(\text{Val})_2]_2$. Hence, the temperature of this endo effect corresponds to bond cleavage between the copper atom and the second coordinated nicotinamide molecule; simultaneously chelated valerate anions transform to bridging anions, i.e. one of the oxygen atoms in each valerate anion (weaker bound to copper) passes from its own copper atom to the neighboring atom, which corresponds to formation of bridges. Thus, the endo effect at 160–205°C (with a maximum at 175°C) for $\text{CuL}_2(\text{Val})_2$ can be assigned to the following process.



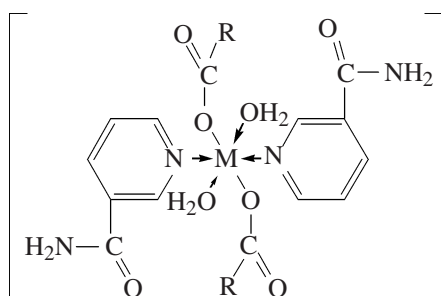
Our research suggests that coordination compounds **I–XIII** have the following structures.

**I, III, VII**

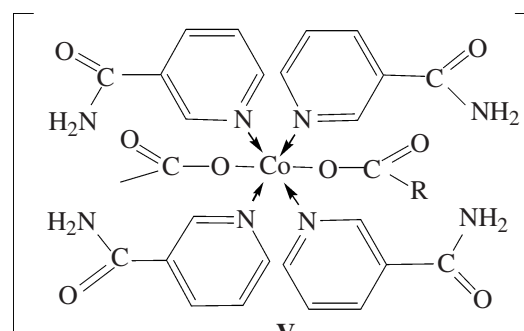
M = Fe, R = C₆H₅ (**I**); M = Co, R = C₄H₉ (**III**); M = Ni, R = C₄H₉ (**VII**).

**II**

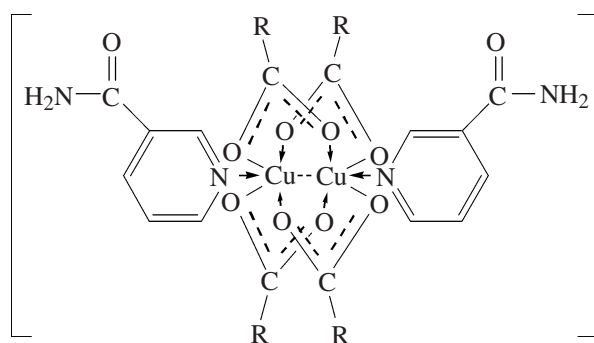
R = C₄H₉ (**II**) [3].

**IV, VI, VIII**

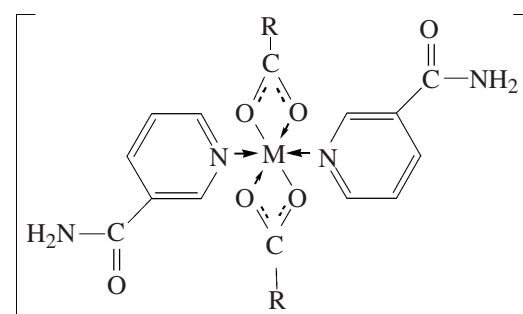
M = Co, R = C₆H₅ (**IV**); M = Ni, R = C₄H₉ (**VI**), R = C₆H₅ (**VIII**) [4].

**V**

R = C₆H₅ (**V**).

**IX**

R = C₄H₉ (**IX**) [5].

**X-XIII**

M = Cu, R = C₄H₉ (**X**) [6], C₆H₅ (**XI**); M = Zn, R = C₄H₉ (**XII**), C₆H₅ (**XIII**).

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer Spectrum BX-II-FT-IR device in KBr. The diffuse reflection spectra were recorded on a Perkin-Elmer Lambda-9 spectrophotometer against MgO (β_{MgO} 100%). Thermal analysis was performed on a Paulik-Paulik-Erdey derivatograph in air, heating rate 10 deg min⁻¹.

Analytical grade iron(II), cobalt(II), nickel(II), copper(II), and zinc chlorides, valeric and benzoic acids, and nicotinamide were used in the work.

Analysis for metals was performed by complexometry [12] and for nitrogen, by Dumas [13].

Complexes I, V, VII, and X. Nicotinamide (0.61 g) was dissolved in 5 ml of ethanol. Dry iron(II), cobalt(II), nickel(II), or copper(II) valerate or benzoate

(0.00125 mol) was added in portions with stirring. The resulting mixture was stirred for 1 h. The precipitate that formed was filtered off, washed with a little ethanol, and dried in a desiccator over CaCl_2 to constant weight.

Complex III. Nicotinamide (0.61 g) was dissolved in 5 ml of ethanol. Dry $\text{Co}(\text{C}_4\text{H}_9\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added in portions with stirring. The resulting mixture was stirred for 15 min, and in this time the carboxylate dissolved completely. The solution was left for spontaneous ethanol evaporation. The precipitate was filtered off, washed with a little ethanol, and dried in a desiccator over CaCl_2 to constant weight.

Complexes II, IV, VI, VIII, IX, and XI–XIII. Nicotinamide (0.61 g) was dissolved in 5 ml of ethanol. Dry cobalt(II), nickel(II), copper(II), or zinc valerate or benzoate (0.0025 mol) was added in portions with stirring. The resulting mixture was stirred for 1 h, the precipitate that formed was filtered off, washed with a little ethanol, and dried in a desiccator over CaCl_2 to constant weight.

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