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Coordination Compounds of 3*d*-Metals Salicylates with Thiosemicarbazide

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Abstract—Complexes of copper(II), nickel(II), cobalt(III), zinc(II), and iron(III) salicylates with thiosemicarbazide were synthesized. The resulting compounds were characterized by the elemental analysis data, infrared spectroscopy, diffuse reflectance spectroscopy, and thermogravimetry.

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Salicylic acid H_2Sal is a dibasic acid (pK_1 2.7, pK_2 7.5) [1] capable of forming the $HSal^-$ and Sal^{2-} ions. The salicylate ion can coordinate through the carboxylate and phenolic oxygen atoms. This anion can be: (a) monodentate, coordinating to the metal through the carboxy group; (b) bidentate, coordinating through the carboxy group; (c) bridging, bonding different metal ions through the carboxy and phenolic oxygen atoms simultaneously; (d) bidentate, chelating through the carboxy and phenolic oxygen atoms. The coordination mode of the salicylate anion depends essentially on the presence of the additional ligands. So, the coordination mode of the anion changes even when varying the number of the bound water molecules in salicylate $Cu(HSal)_2$. In the tetrahydrate the salicylate ion is monodentate, in the monohydrate it is bidentate through one carboxy group. In the dihydrate both the monodentate and bidentate-bridging coordination of salicylate ion is observed [2]. It is interesting to determine the character of changing coordination of the salicylate ion when adding the ligands, which are capable of forming stable complexes with the metals.

One of these ligands is thiosemicarbazide $NH_2NHC(=S)NH_2$. Owing to the presence of the donor sulfur and nitrogen atoms, which are in a favorable position to form a five-membered ring, thiosemicarbazide forms sufficiently stable coordination compounds with 3*d*-metal ions, including a variety of inorganic and organic anions [3–11].

The aim of this work was studying the reaction of iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) salicylates with thiosemicarbazide.

The complexes were obtained by the action of an aqueous solution of thiosemicarbazide on the dry 3*d*-metal salicylate (metal:thiosemicarbazide = 1:4).

The elemental analysis data (Table 1) indicate that the reaction of thiosemicarbazide with copper(II), nickel(II), and zinc(II) salicylates occurs at the metal:thiosemicarbazide ratio equal to 1:2, and for cobalt(III) and iron(III) salicylates, 1:3.

Compared with the spectrum of free thiosemicarbazide, in the IR spectra of the complexes **I**–**V** the frequency of a thioamide I band increases, which is accompanied by a significant decrease in its intensity, so that in the zinc complex it is manifested as a shoulder on a more intensive band $\nu_s(COO^-)$. An attention is drawn to the difference in the values of the shift of the thioamide I band in the case of the unequal stoichiometry of the complexes. In the complexes $[M(HL)L_2](HSal)$ the thioamide I band frequency increases more than in $[M(HL)_2](HSal)_2$. On complexing, the thioamide II band is also subjected to a high-frequency shift. In the spectra of all the complexes the intensity of thioamide III and the frequency of thioamide IV bands decrease. According to [12], this change corresponds to the bidentate coordination of thiosemicarbazide, which involves the sulfur and nitrogen atoms.

Table 1. The elemental analysis data and colors of complexes **I**–**V**

Comp. no.	Color	Found, %			Formula	Calculated, %		
		M	N	S		M	N	S
I	Brown	11.9	16.3	12.6	$C_{16}H_{20}CuN_6O_6S_2$ [Cu(HL)$_2$(HSal)$_2$]	12.3	16.2	12.3
II	Green	11.2	16.1	12.6	$C_{16}H_{20}N_6NiO_6S_2$ [Ni(HL)$_2$(HSal)$_2$]	11.5	16.3	12.4
III	Brown	12.2	27.2	20.3	$C_{10}H_{18}CoN_9O_3S_3$ [Co(HL)L$_2$(HSal)]	12.6	27.0	20.6
IV	White	12.7	15.7	11.9	$C_{16}H_{20}N_6O_6S_2Zn$ [Zn(HL)$_2$(HSal)$_2$]	12.5	16.1	12.3
V	Brown	12.1	27.1	20.3	$C_{10}H_{18}FeN_9O_3S_3$ [Fe(HL)L$_2$(HSal)]	12.1	27.2	20.7

Table 2. The IR spectroscopy data (cm^{-1}) of complexes **I**–**V**, salicylates, and ligand HL

Compound	Thioamide **I**	Thioamide **II**	Thioamide **III**	Thioamide **IV**	ν(OH)(H_2O)	ν(NH)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	ν(C=C) (aromatic ring)	ν(C–O)	δ(CH) (out-of-plane)
HL	1530	1315	1000	800		3370, 3260, 3170					
Cu(HSal)$_2$·4H_2O					3444, 3341		1606	1473	1456	1249	754, 745
I	1545	1382, 1354	944	770[a]		3409, 3305, 3262, 3177	1601	1486	1458	1259	770[a]
Ni(HSal)$_2$·4H_2O					3392		1572	1400	1456	1237	777
II	1546	1382, 1354	948	765[a]		3307, 3113	1604	1485	1461	1253	765[a]
Co(HSal)$_2$·4H_2O					3392	–	1570	1401	1454	1235	776
III	1585	1339	–	759[a]	–	3295, 3140	1620	1485	1456	1248	759[a]
Zn(HSal)$_2$·2H_2O					3389	–	1571	1404	1452	1232	778
IV	1550 (shoulder)	1355	1000	745[a]	–	3420, 3321, 3181	1604	1492	–	1245	745[a]
Fe(HSal)$_3$·4H_2O					3393	–	1602	1485	1456	1241	758
V	1590	1391[a]	922	759[a]	–	3175	1590	1484	1460	1243	759[a]

[a] Thiosemicarbazide and salicylate anion contribute into the absorption bands.

The IR spectra of the complexes [Co(HL)L$_2$](HSal) and [Fe(HL)L$_2$](HSal) contain very intensive absorption bands at 2061 and 2046 cm^{-1}, respectively. The reactions of some copper(II) aliphatic carboxyates Cu(C_nH_{2n+1}COO)$_2$ with thiosemicarbazide have been previously studied. When $n \geq 4$, the reaction product lacks the carboxyate anion, and thiosemicarbazide acts as a deprotonated form to give CuL$_2$ [4]. The spectrum of this compound also contains the absorption bands at ~2100 cm^{-1}. The range of 2200–1900 cm^{-1} is characteristic of the stretching vibrations of the cumulated double bonds [13], in particular, of the thiocyanate ions. In this case the NCS-group, similar to the SCN moiety, can appear only when the metal is bound to the nitrogen atom adjacent to the carbon atom. Consequently, the deprotonated thiosemicarbazide forms a four-membered ring, where the metal is covalently bound to the nitrogen and coordinated with the sulfur. Thus, for the cobalt(III) and Fe(III) complexes we should assume the presence of two forms of thiosemicarbazide in the complex molecule: molecular and deprotonated.

The IR spectrum of free salicylic acid contains the absorption bands at 1657 (C=O), 1445 (C=C, aromatic ring), 1296 [δ(OH)], 1249 (C–O), and 760 cm^{-1} [δ(CH), out-of-plane bending] [2, 13, 14].

In the IR spectra of salicylates obtained the absorption band ν(C=O) is absent due to equivalence of the carboxy oxygen atoms at eliminating the proton from the carboxy group. This is accompanied by the disappearance of the absorption band of the carbonyl moiety and the appearance of two new bands in the ranges of 1550–1610 and 1300–1400 cm^{-1} [$\nu_{as,s}(COO^-)$] [15]. The difference between the ν_{as} and ν_s values is often used to determine the bond nature of the carboxy moiety with the complexing agent. We believe that the difference $\Delta\Delta\nu(COO^-)$, i.e., the difference between the values $\Delta\nu(COO^-)$ of the reaction product and the initial carboxyate, is more acceptable. For all the compounds obtained the value $\Delta\Delta\nu(COO^-)$ is negative (from –18 to –55 cm^{-1}), probably due to some bond elongation in the salicylate anion owing to its displacement into the outer sphere of the complexes.

The absorption band at 1200 cm^{-1} corresponds to the stretching vibrations ν(C–O) of the aryl-bonded OH-group. In the spectra of thiosemicarbazide complexes the frequencies of these bands increase. In the spectra of the starting salicylates the absorption bands at 1460 cm^{-1} belonging to the “pulsation” vibrations ν(C=C) of the benzene ring are very intensive and narrow. In the spectra of thiosemicarbazide complexes these bands are low-intensive and broad. In the spectra of the coordination compounds the absorption band of the out-of-plane bending vibrations δ(CH) are overlapped with the thioamide IV band which results in a slight increase in their intensity compared with the initial salicylates.

The closeness of the frequencies of the absorption bands of the salicylate anion in the IR spectra of all the synthesized coordination compounds is obviously due to the fact that in $[M(HL)_2](HSal)_2$ and $[M(HL)L_2]\cdot(HSal)$ the salicylate anion is in the same monodeprotonated form. Hence it must be assumed that in the case of the three-charged complexing agent two of the three coordinated thiosemicarbazide molecules are deprotonated.

The diffuse reflectance spectra (Table 3) confirm the octahedral structure of the cobalt(III) complex and the planar structure of the nickel(II) and copper(II) complexes [16]. For the iron(III) complex the bands in the diffuse reflectance spectra do not have a clearly defined maxima.

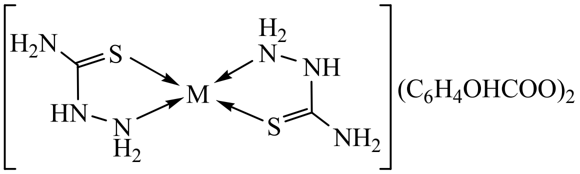
The assumptions made for compounds $[Cu(HL)_2]\cdot(HSal)_2$ and $[Ni(HL)_2](HSal)_2$ were confirmed by XRD [17].

In the thermograms of all the complexes (Table 4) the first effects are endothermic. In addition, only in the nickel(II) complex this effect is not accompanied by a mass loss, which obviously corresponds to the melting. Furthermore, the temperature of the first effect of the nickel(II) compounds is significantly higher than the corresponding temperature for the other complexes. This allows us an assumption that the nickel(II) complex is more thermally stable than the other studied coordination compounds. It can melt without decomposition, whereas in other cases the heating to a temperature of the first effect is accompanied by the destruction of the complexes.

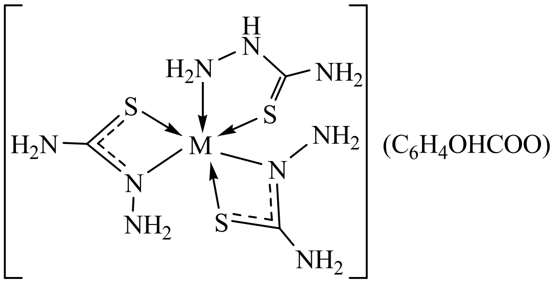
Table 3. The diffusion reflectance spectroscopy data of complexes **I**–**III**

Compound	λ, nm	Assignment
I	460	
II	385	ν_3
	410	ν_2
	560	ν_1
III	460	$^1A_{1g} \rightarrow {}^1T_1$

These experiments make it possible to assign the following structure to the synthesized coordination compounds.



M = Cu (**I**), Ni (**II**), Zn (**IV**).



M = Co (**III**), Fe (**V**).

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer Spectrum BX II FT-IR System instrument from KBr pellets. The diffuse reflectance spectra were registered on a Lambda-9 spectrophotometer (Perkin-Elmer) relative to MgO (β_{MgO} 100%). The TG analysis was performed on a Paulik–Paulik–Erdey derivatograph system in air with the heating rate of 10°C min^{-1}.

Iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) chlorides, salicylic acid, and thiosemicarbazide were of analytical grade.

Table 4. The TG analysis data of complexes **I**–**V**

Comp. no.	Endo-effects		Exo-effects		Total mass loss, %
	t, °C	Δ*m*, %	*t*, °C	Δ*m*, %	
I	78–132(110)	4.5	165–245(193)	39.2	67.5
			245–305(290)	6.2	
			305–380(340)	2.2	
II	140–195(172)	–	195–240(225)	46.9	48.3
III	80–142(118)	7.3	142–178(170)	20.4	53.4
			178–215(200)	15.5	
			215–260(240)	5.7	
IV	90–135(110)	2.7	170–245(205)	25.9	72.9
			245–315(290)	3.2	
			315–350(340)	7.0	
			350–448(430)	13.0	
			448–500(482)	13.5	
V	55–150(112)	5.1	150–250(228)	11.6	41.1
			250–300(282)	7.3	
			300–350(335)	6.6	
			350–400(380)	3.7	

The 3*d*-metal salicylates were obtained via the exchange reactions between sodium salicylate, obtained by the salicylic acid neutralization, and a 3*d*-metal chloride in water.

The metal content in the isolated compounds was determined by the chelatometry [18], the nitrogen content, according to the Dumas method [19], the sulfur content, by the Schoeniger method [19].

Synthesis of complexes (I–V). To a solution of 0.91 g (0.01 mol) of thiosemicarbazide in 100 ml of water was added by portions 0.0025 mol of dry salicylate of the corresponding metal while stirring. The mixture was stirred until a homogeneous precipitate formed, which was filtered off on a glass frit filter, washed with water, and dried in a desiccator over calcium chloride to the constant weight.

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