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Coordination Compounds of 3*d*-Metal 5-Sulfosalicylates with Thiosemicarbazide

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Abstract—Copper(II), nickel(II), and cobalt(III) 5-sulfosalicylate complexes with thiosemicarbazide were synthesized and characterized by elemental analyses, IR spectra, diffuse reflectance spectra, and thermogravimetric data.

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5-Sulfosalicylic acid and its anions are characterized by structural diversity and interesting topology. In recent time, 5-sulfosalicylate ions and their metal complexes attract increasing attention due to their antimicrobial, antifungal, and anti-inflammatory activity. 5-Sulfosalicylic acid molecule possesses three functional groups, SO_3H, COOH, and OH. Five forms of 5-sulfosalicylic acid were distinguished [1]: (1) neutral, (2) singly deprotonated at the sulfo group, (3) singly deprotonated at the carboxy group, (4) doubly deprotonated at the sulfo and carboxy groups, and (5) triply (completely) deprotonated. Reactions of partially or completely deprotonated forms of 5-sulfosalicylic acid (H_2SSal^-, $HSSal^{2-}$, and $SSal^{3-}$) with metal ions may lead to different coordination modes [1].

We previously [2] synthesized and studied coordination of compounds of 3*d*-metal salicylates with thiosemicarbazide. It was interesting to find out how introduction of a sulfo group into salicylate ion affects the composition, structure, and properties of the resulting 3*d*-metal complexes with thiosemicarbazide.

Thus the goal of the present work was to synthesize coordination compounds of cobalt(III), nickel(II), copper(II), and zinc(II) 5-sulfosalicylates with thiosemicarbazide and examine their properties. The targeted complexes were synthesized by reaction of thiosemicarbazide with an aqueous solution of preliminarily prepared 3*d*-metal 5-sulfosalicylate at metal-to-thiosemicarbazide ratios of 1 : 1 and 1 : 2.

According to the elemental analysis data (Table 1), copper(II) and nickel(II) 5-sulfosalicylates reacted with thiosemicarbazide to form 1 : 2 complexes, whereas cobalt(III) 5-sulfosalicylate gave rise to 1 : 3 complex. It should be noted that we obtained two isomeric Ni(II) complexes. Prolonged reaction of nickel(II) 5-sulfosalicylate with an equimolar amount of thiosemicarbazide afforded green complex **II**, whereas pink complex **III** was rapidly formed in the reaction of nickel(II) 5-sulfosalicylate with 2 equiv of thiosemicarbazide. We failed to isolated coordination compound in the reaction of zinc(II) 5-sulfosalicylate with thiosemicarbazide.

Unlike initial thiosemicarbazide, the thioamide **I** absorption band in the IR spectra of all isolated complexes was observed at higher frequency with some reduction in intensity (Table 2). High-frequency shift was also observed for the thioamide **II** band. The thioamide **III** band weakened so strongly that we detected it only in the spectrum of complex **I**, while it was indistinguishable in the spectra of the other complexes. The frequency of the thioamide **IV** band decreased. In keeping with published data [3] the observed variation of thioamide absorption pattern corresponds to bidentate coordination of thiosemicarbazide through the sulfur and nitrogen atoms.

Absorption bands corresponding to vibrations of 5-sulfosalicylate anion were assigned with account taken of the data in [1, 4–6]. The carbonyl stretching vibration frequency ν(C=O) in the spectra of all complexes was lower by no more than 18 cm^{-1} relative

Table 1. Elemental analyses of coordination compounds **I**–**IV** formed by 3*d*-metal 5-sulfosalicylates and thiosemicarbazide

Comp. no.	Color	Found, %			Formula	Calculated, %		
		M	N	S		M	N	S
I	Dark violet	9.3	12.3	18.7	$C_{16}H_{20}CuN_6O_{12}S_4$	9.4	12.4	18.8
II	Green	8.9	12.1	18.8	$C_{16}H_{20}N_6NiO_{12}S_4$	8.7	12.4	19.0
III	Pink	8.9	12.3	18.9	$C_{16}H_{20}N_6NiO_{12}S_4$	8.7	12.4	19.0
IV	Brown	6.3	12.5	19.3	$C_{24}H_{30}CoN_9O_{18}S_6$	6.0	12.8	19.5

Table 2. Absorption bands (cm^{-1}) in the IR spectra of thiosemicarbazide (HL), 5-sulfosalicylic acid (H_3SSal), and coordination compounds **I**–**IV**

Assignment	HL	H_3SSal	**I**	**II**	**III**	**IV**
ν(NH)	3370, 3260, 3170		3371, 3306, 3248, 3178	3352, 3309, 3175	3356, 3306, 3175	
ν(C=O)		1678	1670	1666	1666	1660
Thioamide **I**	1530		1562	1574	1574	1585
ν($C=C_{arom}$)		1477, 1439	1477, 1435	1477, 1423	1477, 1435	1477, 1435
Thioamide **II**	1315		1393, 1369	1370	1373	1377
$ν_{as}(SO_2)$		1234, 1203, 1165, 1134 sh	1215, 1184, 1155, 1126	1223, 1188, 1146, 1122	1219, 1146, 1122	1211, 1180, 1157, 1126
$ν_s(SO_2)$		1084, 1065, 1026	1084, 1030	1080, 1018	1080, 1018	1084, 1030
Thioamide **III**	1000		975 w	–	–	–
Thioamide **IV**	800		706	706	706	720
ν(S–O)		663	667	663	667	667

to ν(C=O) of free 5-sulfosalicylic acid. Proton abstracttion from the carboxy group should lead to disappearance of carbonyl absorption band and appearance of two new bands at considerably lower frequencies due to antisymmetric and symmetric vibrations of carboxylate group (COO^-) where two oxygen atoms are equivalent [7]. The observed pattern suggests that the COOH group remained un-ionized. In all cases, insignificant variations in the absorption pattern of aromatic C=C bonds were detected. Absorption bands of sulfo groups revealed appreciable changes. The $ν_{as}(SO_2)$ frequency decreased by 8–23 cm^{-1} in going from free 5-sulfosalicylic acid to the coordination compounds. The IR spectra of all complexes contained two $ν_s(SO_2)$ bands against three bands for free 5-sulfosalicylic acid. This may be due to higher symmetry of the sulfo group as a result of its deprotonation. Thus the IR spectra indicated that the 5-sulfosalicylate ion in the synthesized complexes is singly deprotonated at the sulfo group.

It should be noted that isomeric nickel complexes $[Ni(HL)_2](H_2SSal)_2$ (**II** and **III**) displayed almost identical IR spectra. A few differences included lower frequency of one ν(C=C) band in the spectrum of green complex **II** and the lack of one $ν_{as}(SO_2)$ band in the spectrum of pink complex **III**. Identical compositions and similar IR spectra led us to presume that nickel(II) 5-sulfosalicylate complexes with thiosemicarbazide are conformational isomers. It is known [8] that just nickel(II) complexes could give rise to conformational isomerism square planar–tetrahedral and that square planar complexes are generally colored red to yellow, while tetrahedral, green to blue. The diffuse reflectance spectra (Table 3) confirmed the square planar structure of the pink complex and tetrahedral structure of the green complex. In keeping with the diffuse reflectance spectra, the cobalt(III) complex has a distorted octahedral configuration of the coordination entity [9].

Table 3. Diffuse reflectance spectra of coordination compounds **I–IV**

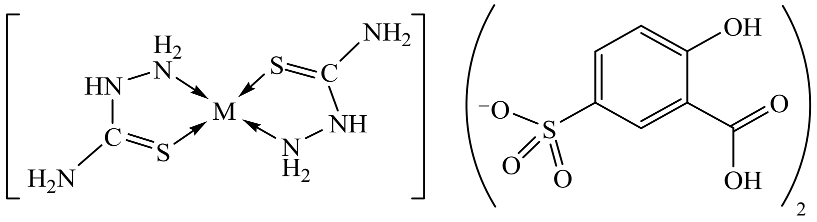
Comp. no.	ν, cm^{-1}	Assignment
I	14860 br	
II	16730	$^3T_1 \rightarrow {}^3T_1(P)$
	4400	$^3T_1 \rightarrow {}^3A_2$
III	32810	ν_1
IV	17510	$^1A_{1g} \rightarrow {}^1A_2$

Table 4. Thermogravimetric analysis of coordination compounds **I–IV**

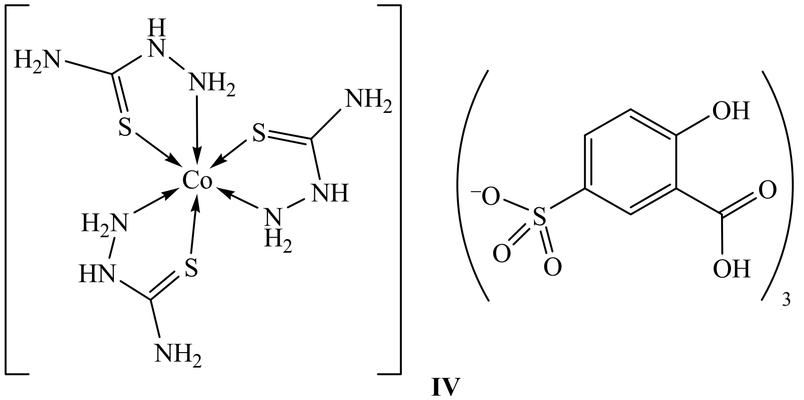
Comp. no.	Endo-effect		Exo-effect		Overall weight loss, %
	T, °C	Δ*m*, %	*T*, °C	Δ*m*, %	
I			220–300 (250)	39.3	80.0
			300–500 (330)	17.2	
			500–600 (590)	13.3	
			600–700 (650)	4.8	
II	300–370 (330)	46.6	400–480 (460)	8.0	83.8
			550–650 (570)	16.1	
III	230–280 (250)	–	380–490 (420)	9.5	85.0
	280–380 (310)	46.0	540–640 (550)	13.0	
IV			230–280 (250)	27.8	77.5
			480–610 (530)	21.9	

The structure of complex **I** was confirmed by X-ray analysis. The centrosymmetric $[Cu(HL)_2]^{2+}$ square in complex **I** is supplemented with Cu–O bonds (2.810 Å) with the sulfonate fragment to form a tetragonal bipyramid. The Cu–O bonds together with hydrogen bonds give rise to a supermolecule. Cations are arranged in layers alternating with anion layers [10].

The results of thermogravimetric analysis of complexes **I–IV** (Table 4) showed the absence of endo-thermic effects for Cu(II) and Co(III) complexes **I** and **IV**, unlike analogous complexes with unsubstituted salicylate. Obviously, this is related to a catalytic effect of Cu(II) and Co(III) on the combustion process. Isomeric nickel(II) complexes **II** and **III** displayed just endothermic effects first. The first endo-effect for pink complex **III** was observed at 250°C almost without weight loss. The other effects on the thermogravimetric curves of nickel(II) complexes **II** and **III** were essentially similar in both temperatures and amounts of lost weights. These findings suggest that the first endo-effect without weight lost



M = Cu (**I**), Ni (**II, III**).



IV

corresponds to the isomerization of the square planar complex into tetrahedral.

Thus we assigned the following structures to coordination compounds **I**–**IV**.

Comparison of our results with the data for analogous complexes derived from unsubstituted Salicylates shows the following. 5-Sulfosalicylate anion provides the possibility for conformational isomerism of Ni(II) coordination polyhedron. Cobalt(III) gives $Co(HL)L_2(HSal)$ complexes with unsubstituted Salicylate and $Co(HL)_3(H_2SSal)_3$ complexes with 5-sulfosalycilate, i.e., in the former case the complexation process involves partial deprotonation of thiosemicarbazide. If there is a sulfo group, proton is abstracted just from it, whereas the carboxy group remains unionized, in contrast to unsubstituted salicylate. Thiosemicarbazide complexes with 3*d*-metal 5-sulfosalicylates are characterized by considerably higher thermal stability, presumably due to much stronger bonds of the central ion with anions, on the one hand, and more potent hydrogen bond system, on the other.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer from samples prepared as KBr pellets. The diffuse reflectance spectra were measured on a Perkin–Elmer Lambda-9 instrument against MgO (β_{MgO} = 100%). Thermogravimetric analysis was performed on a Paulik–Paulik–Erdey derivatograph in air; samples were heated at a rate of 10 deg/min.

Cobalt(II), nickel(II), copper(II), and zinc(II) chlorides, 5-sulfosalicylic acid, and thiosemicarbazide of analytical grade were used. The metal content of the isolated complexes was determined by complexometric tetration [11], nitrogen was determined by the Dumas method [12], and sulfur was determined by the Shöniger oxidation [12].

Complexes I and III (*general procedure***).** Copper (II) or nickel(II) chloride, 0.01 mol, was dissolved in 5 ml of water, a solution of 0.4 g (0.01 mol) of NaOH in 5 ml of water was added, the precipitate of metal hydroxide was filtered off, washed with water, and added in portions to a solution of 2.18 g (0.01 mol) of 5-sulfosalicylic acid in 5 ml of water, and 1.82 g (0.02 mol) of dry finely powdered thiosemicarbazide was added in small portions to the resulting solution. The mixture was stirred for 15 min on a magnetic stirrer, and the precipitate was filtered off, washed with water, and dried at 50°C until constant weight.

Complexes II and IV (*general procedure***).** Nickel(II) or cobalt(III) chloride, 0.02 mol, was dissolved in 5 ml of water, a solution of 0.8 g (0.02 mol) of NaOH in 5 ml of water was added, the precipitate of metal hydroxide was filtered off, washed with water, and added in portions to a solution of 4.36 g (0.02 mol) of 5-sulfosalicylic acid in 5 ml of water, and 0.02 (**II**) or 0.04 mol (**IV**) of dry finely powdered thiosemicarbazide was added in small portions to the resulting solution. The mixture was left to stand for 3 days in a porcelain dish, and the precipitate was filtered off, washed with water, and dried at 50°C until constant weight.

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