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COORDINATION COMPOUNDS

Synthesis and Crystal Structure of a Copper(II) 5-Sulfosalicylate Complex with Thiosemicarbazide

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Abstract—The compound $[Cu(TSC)_2](H_2SSal)_2$ (**I**) has been synthesized (TSC is thiosemicarbazide, H_3SSal is 5-sulfosalicylic acid) and studied by IR spectroscopy and X-ray crystallography. The crystals of **I** are triclinic: $a = 6.728(2)$ Å, $b = 7.772(1)$ Å, $c = 11.600(6)$ Å, $\alpha = 88.60°$, $\beta = 86.68(3)°$, $\gamma = 79.22(4)°$, $V = 594.8(4)$ Å^3, $Z = 2$, space group $P\bar{1}$. The structural units of the crystal are the centrosymmetric $[Cu(TSC)_2]^{2+}$ cation, in which the Cu atom is in a square-planar coordination formed by the bidentate chelating (N,S) TSC ligands, and $(H_2SSal)^-$ anions (Cu(1)–N(3), 2.013(3) Å; Cu(1)–S(1), 2.275(1) Å; intrachelate angle, 86.8°). The coordination polyhedron of the Cu(1) atom is completed to a prolate tetragonal bipyramid (4 + 2) by Cu–O bonds (2.810(3) Å) of the sulfate moieties of both anions, which form together with hydrogen bonds the $[Cu(TSC)_2(H_2SSal)_2]$ supermolecule. The complex cations are packed in layers and alternate with anion-containing layers. Hydrogen bonding and π–π stacking interactions are responsible for formation of supramolecular layer ensembles.

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Our results of studying Ni(II) and Cu(II) bis(thiosemicarbazide) complexes with different anions [1, 2] and available literature data on the structures of analogous compounds [3–9] have revealed a considerable variety of the structures of these compounds in spite of a rather stereotypic structure of the complex cation.

The $[M(TSC)_2]^{2+}$ cation (M = Ni(II), Cu(II)) in these compounds has a square of near-square shape owing to the bidentate chelating (N,S) coordination of the TSC ligand. Sometimes, the metal coordination sphere is completed to tetragonal-pyramidal or tetragonal-bipyramidal by axial atoms at elongated distances. The metal atom is in the plane of the coordination square. The TSC ligand is planar, but its plane can be somewhat out of the coordination plane. In this case, there is a small bend along the N···S line (an envelope conformation). The linear and angular parameters of the coordination polyhedron are almost identical for the same metal but are somewhat different for Ni(II) and Cu(II).

It is worth noting that a considerable role in crystal structure is played by the anion mainly involved in formation of the supramolecular crystal architecture.

The anion of multifunctional 5-sulfosalicylic acid (H_3SSal) used in this work favors the formation of numerous hydrogen bonds, which can be combined in cyclic fragments capable of strengthening of the structure due to π–π stacking interaction.

Depending on the degree of deprotonation of H_3SSal, there are H_2SSal^-, $HSSal^{2-}$, and $SSal^{3-}$ anions. Incomplete deprotonation is possible for different combination of atoms in $[H_{3n}SSal]^{n-1}$.

In this paper, we report the results of X-ray crystallographic analysis of $[Cu(TSC)_2](H_2SSal)_2$ (**I**), containing the monodeprotonated anion.

EXPERIMENTAL

Synthesis of I ($C_8H_{10}Cu_{0.5}N_3O_6S_2$). In separate beakers, solutions of 1.71 g $CuCl_2 \cdot 2H_2O$ (0.01 mol) and 0.4 g NaOH (0.01 mol) in 5 mL water were prepared and then poured together. The resulting precipitate was filtered off on a paper filter, washed with water, and added portionwise to a solution of 2.18 g 5-sulfosalicylic acid (0.01 mol) in 5 mL water. To the resulting solution of copper(II) 5-sulfosalicylate, 1.82 g (0.02 mol) of dry finely ground thiosemicarbazide was added, which was accompanied by formation of a brown precipitate. It was stirred for 15 min with a magnetic stirrer, filtered off through a Schott filter, washed with water, and dried at 50°C to a constant weight.

Crystals suitable for X-ray crystallography were obtained by recrystallization of the powder product from water.

The IR absorption spectra were recorded as KBr pellets on a Shimadzu FTIR-8400S spectrophotometer.

Table 1. Crystallographic parameters and experimental details for compound **I**

Empirical formula	$C_8H_{10}Cu_{0.50}N_3O_6S_2$
FW	340.08
Color, habit	Violet, prisms
Crystal size, mm	0.20 × 0.18 × 0.15
T, K	293
Crystal symmetry	Triclinic
Space group	$P\bar{1}$
Unit cell parameters	
a, Å	6.728(2)
b, Å	7.772(1)
c, Å	11.600(6)
α, deg	88.60(3)
β, deg	86.68(3)
γ, deg	79.22(3)
V, Å^3	594.8(4)
Z	2
ρ_{calc}, g/cm^3	1.899
μ, cm^{-1}	5.294
$F(000)$	347
Scan range	3.82–65.93
Index range	$7 \le h \le 1$, $-8 \le k \le 8$, $-13 \le l \le 13$
Total number of measured reflections	2190
Number of unique reflections	2000 [R(int) = 0.0181]
Number of reflections with $I > 2\sigma(I)$	1897
Correction for absorption	Not introduced
Not introduced	218
GOOF on F^2	1.047
R [$I > 2\sigma(I)$]	$R1 = 0.0504$, $wR2 = 0.1400$
R (for all reflections)	$R1 = 0.0532$, $wR2 = 0.1429$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e/Å^3	0.938 and −1.156

X-ray diffraction. Experimental reflection intensities were collected on an Enraf-Nonius Cad-4 diffractometer (CuK_α radiation, graphite monochromator) using $\theta/2\theta$ scan mode. The structure was solved by the heavy-atom method. The hydrogen atoms were located from difference Fourier syntheses and refined with an individual isotropic temperature parameter. Calculations were performed with the SHELXL-93 program package [10].

Table 2. Atomic coordinates and U_{eq}/U_{iso} (Å$^2 \times 10^3$) for compound **I**

Atom	x	y	z	U_{eq}/U_{iso}
Cu(1)	0	0	0	33(1)
S(1)	1307(1)	2177(1)	780(1)	35(1)
S(2)	3551(1)	7304(1)	2137(1)	29(1)
O(1)	1021(4)	13308(3)	5821(2)	38(1)
O(2)	1115(5)	13447(4)	3895(2)	43(1)
O(3)	2217(4)	10197(4)	6825(2)	38(1)
O(4)	1530(4)	7562(4)	1707(2)	39(1)
O(5)	4438(5)	5468(4)	2307(2)	56(1)
O(6)	4872(4)	8249(4)	1439(2)	43(1)
N(1)	−1073(6)	4993(4)	1622(3)	41(1)
N(2)	−2696(5)	2830(4)	1146(3)	35(1)
N(3)	−2693(5)	1143(4)	732(3)	32(1)
C(1)	−967(6)	3413(4)	1208(3)	31(1)
C(2)	2587(5)	9625(4)	5739(3)	28(1)
C(3)	3318(5)	7842(5)	5594(3)	34(1)
C(4)	3655(5)	7156(5)	4505(3)	32(1)
C(5)	3281(5)	8216(4)	3532(3)	26(1)
C(6)	2582(5)	9998(4)	3655(3)	28(1)
C(7)	2229(4)	10722(4)	4755(3)	26(1)
C(8)	1409(5)	12596(4)	4873(3)	30(1)
H(1N1)	48(68)	5440(56)	1557(35)	35(11)
H(2N1)	−2269(90)	5542(72)	1727(47)	57(15)
H(1N3)	−3128(74)	587(65)	1296(45)	51(13)
H(1N2)	−3769(80)	3359(67)	1248(42)	42(13)
H(2N3)	−3432(78)	1298(63)	134(46)	52(13)
H(1)	473(80)	14384(77)	3968(46)	56(15)
H(2)	1740(73)	11070(66)	6784(41)	41(14)
H(3)	3604(69)	7144(60)	6214(41)	45(11)
H(4)	3992(61)	5973(57)	4446(34)	35(10)
H(6)	2432(66)	10709(58)	3007(40)	42(11)

X-ray diffraction experimental details, crystallographic data, and refinement results are summarized in Table 1, atomic coordinates and temperature factors are presented in Table 2, and bond angles are listed in Table 3. These values were deposited with the Cambridge structural database (CCDC no. 798530).

RESULTS AND DISCUSSION

Crystals of **I** are composed of doubly charged centrosymmetric $[Cu(TSC)_2]^{2+}$ cations and $(H_2SSal)^-$ anions monodeprotonated at the sulfate moiety of 5-sulfosalicylic acid.

As in other 3*d*-metal bis(thiosemicarbazide) complexes, the copper atom in **I** is coordinated in the bidentate chelating (N,S) mode by two TSC ligands, which leads to closing of nearly flat (±0.05 Å) five-membered chelate rings. The Cu(1)–N(3) and Cu(1)–S(1) bond lengths are 2.013(3) and 2.275(1) Å, respectively, and the intrachelate N(3)Cu(1)S(1) angle id 86.8(1)°. These values are also typical for other compounds containing analogous cation [3–9]. The coordination square of the Cu atom is completed to a prolate tetragonal bipyramid (4 + 2) by the Cu(1)–L(4) bonds (2.810(3) Å). Hydrogen bonds (table 4) combine the cation and anion into a neutral $[Cu(TSC)_2(H_2SSal)_2]$ supermolecule, which in the main building unit of the crystal (Fig. 1).

Supermolecules are closely packed in layers formed, on the one hand, due a pair of symmetrically located hydrogen bonds 6 combining the $[Cu(TSC)_2]^{2+}$ cations into chain ensembles and, on the other hand, due to π–π stacking interactions between the anionic parts of the supermolecules. In both cases, cationic and anionic supramolecular ensembles coupled to each other are formed in the *a* direction in the (010) plane (Fig. 2).

The $(H_2SSal)^-$ anion in **I** contains the sulfate and salicylate moieties bonded through the C(5) atom. Hydrogen bond 2 closes a six-membered ring so that the salicylate moiety transforms into two fused rings. Both rings are involved in formation of π–π stacking ensembles (Fig. 3). The distance between stacking planes is 3.51 Å. In addition, $(H_2SSal)^-$ anions are combined by a centrosymmetric pair of hydrogen bonds 1 into planar dimers, which, like bricks, form walls-layers running through the entire crystal.

Parallel to the anionic layers in structure **I**, there are layers of cationic cores of supermolecules linked with each other not only through hydrogen bond 6 but also through hydrogen bonds 4 and 5, involving the N atoms of the thiosemicarbazide ligand and the O(4), O(5), and O(6) atoms if the sulfate moieties of neighboring supermolecules. Thus, the crystal contains supramolecular layers ensembles oriented parallel to the (001) crystallographic plane (Fig. 3). The figure also shows the structure of adjacent anionic layers surrounding the layer of cations. The arrows show bands of planar dimeric anions running perpendicular to the plane of the supramolecular ensemble (i.e., to the plane of the figure). As a whole, joint efforts of hydrogen bonds and electrostatic and π–π stacking interac-

Table 3. Bond lengths (*d*) and bond angles (ω) for compound **I**

Bond	*d*, Å
Cu(1)–N(3)	2.013(3)
Cu(1)–S(1)	2.275(1)
Cu(1)–O(4)	2.810(3)
S(1)–C(1)	1.702(4)
S(2)–O(5)	1.453(3)
S(2)–O(4)	1.452(3)
S(2)–O(6)	1.455(3)
S(2)–C(5)	1.769(3)
O(1)–C(8)	1.236(4)
O(2)–C(8)	1.305(4)
O(3)–C(2)	1.341(4)
N(1)–C(1)	1.317(5)
N(2)–C(1)	1.331(5)
N(2)–N(3)	1.406(4)
C(2)–C(3)	1.392(5)
C(2)–C(7)	1.412(5)
C(3)–C(4)	1.372(5)
C(4)–C(5)	1.388(5)
C(5)–C(6)	1.385(5)
C(6)–C(7)	1.397(4)
C(7)–C(8)	1.464(5)
Angle	ω, deg
N(3)Cu(1)S(1)	86.82(8)
S(1)Cu(1)O(4)	92.69(6)
N(3)Cu(1)O(4)	102.3(1)
C(1)S(1)Cu(1)	95.79(12)
O(5)S(2)O(4)	113.0(2)
O(5)S(2)O(6)	112.8(2)
O(4)S(2)O(6)	111.9(2)
O(5)S(2)C(5)	105.1(2)
O(4)S(2)C(5)	106.4(2)
O(6)S(2)C(5)	106.9(2)
C(1)N(2)N(3)	120.6(3)
N(2)N(3)Cu(1)	113.3(2)
N(1)C(1)N(2)	117.5(3)
N(1)C(1)S(1)	120.7(3)
N(2)C(1)S(1)	121.8(3)
O(3)C(2)C(3)	117.2(3)
O(3)C(2)C(7)	123.5(3)
C(3)C(2)C(7)	119.3(3)
C(4)C(3)C(2)	120.2(3)
C(3)C(4)C(5)	121.0(3)
C(4)C(5)C(6)	119.7(3)
C(4)C(5)S(2)	120.8(3)
C(6)C(5)S(2)	119.3(2)
C(5)C(6)C(7)	120.1(3)
C(6)C(7)C(2)	119.5(3)
C(6)C(7)C(8)	119.5(3)
C(2)C(7)C(8)	120.9(3)
O(1)C(8)O(2)	122.9(3)
O(1)C(8)C(7)	122.6(3)
O(2)C(8)C(7)	114.5(3)

Table 4. Hydrogen bond geometry in structure **I**

No.	A–H···B bond	*d*, Å			AHB angle, deg	B atom position
		A···B	A–H	H···B		
1	O(2)–H(1)···O(1)	2.676(4)	0.78(6)	1.90(6)	178(6)	$-x, -y+3, -z+1$
2	O(3)–H(2)···O(1)	2.663(4)	0.70(5)	2.04(5)	150(5)	x, y, z
3	N(1)–H(1N1)···O(4)	2.898(5)	0.89(5)	2.10(4)	150 (4)	x, y, z
4	N(1)–H(2N1)···O(5)	3.035(6)	0.84(6)	2.29(6)	148(5)	$x-1, y, z$
5	N(2)–H(1N2)···O(5)	2.845(5)	0.77(5)	2.20(5)	142(5)	$x-1, y, z$
6	N(3)–H(1N3)···O(6)	3.090(4)	0.84(5)	2.45(5)	133(4)	$x-1, y-1, z$
7	N(3)–H(2N3)···O(6)	2.971(4)	0.87(6)	2.11(5)	172(5)	$-x, 1-y, -z$
8	C(6)–H(6)···S(1)	3.774(3)	0.92(5)	2.88(5)	163(4)	$x, y-1, z$

tions between the supermolecules create supramolecular crystal architecture.

Analysis of IR spectroscopy data (Table 5) shows that, in the IR spectrum of complex **I**, the thioamide I band frequency increases with some decrease in intensity as compared with the spectrum of free thiosemicarbazide. The thioamide II band is also shifted toward higher frequencies. The intensity of the thioamide III band considerably decreases. The thioamide IV band frequency decreases. According to [11], such changes of thioamide bands correspond to the bidentate coordination of thiosemicarbazide through the sulfur and nitrogen atoms.

The absorption bands related to vibrations of the 5-sulfosalicylate anion were assigned using data in [3, 12–14]. As compared with the IR spectrum of free H_3SSal, the ν(C=O) band remains almost unaltered. It is worth noting that elimination of the proton from the carboxyl group should result in the equivalence of the carboxyl oxygen atoms and the appearance of two new bands corresponding to the antisymmetric and symmetric COO^- vibrations at lower frequencies [15].

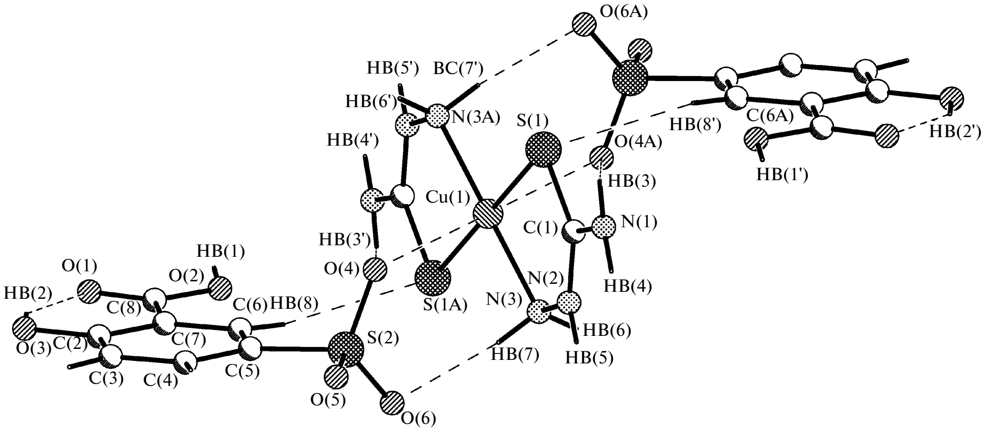

Fig. 1. Structure of a supermolecule in **I**. In Figs. 1–3, hydrogen bonds are designated as HB with numerals as in Table 4 and are shown by dashed lines.

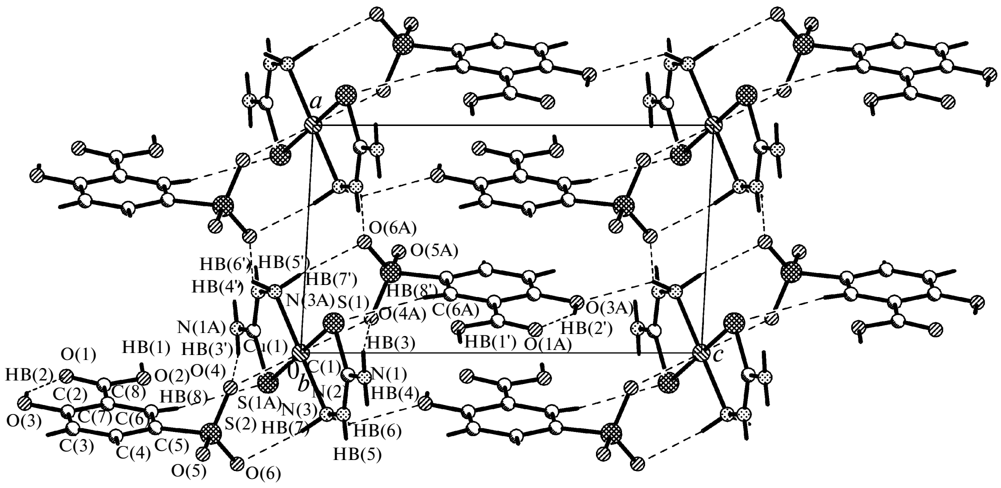

Fig. 2. Packing of supermolecules in the (010) plane.

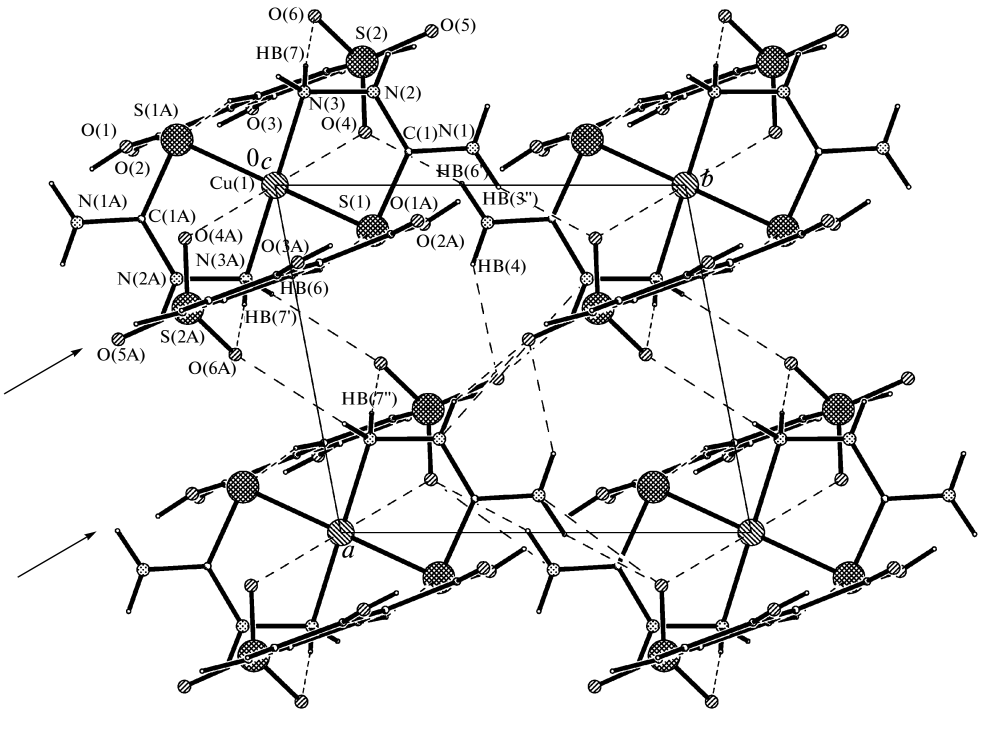

Fig. 3. Structure of the cationic layer.

It is evident that the behavior of the carbonyl absorption band in our case is consistent with the lack of deprotonation of the COOH group. The ν(C=C) bands of the aromatic ring also change only slightly. Noticeable changes are observed for the absorption bands of the SO_3H band. The $\nu_{as}(SO_2)$ frequencies decrease by 8–19 cm^{-1} in going from free 5-sulfosalicylic acid to complex **I**. For $\nu_s(SO_2)$, two bands are observed in the spectrum of complex **I** (against three bands for free 5-sulfosalicylic acid). The decrease in the number of absorption bands arising from symmetric vibrations of the sulfo group is most likely due to the fact that it becomes more symmetric, which is caused by deprotonation of the SO_3H group. Thus, the

Table 5. Wave numbers (frequencies, cm^{-1}) of absorption bands in the IR spectra of thiosemicarbazide, 5-sulfosalicylic acid, and the copper(II) 5-sulfosalicylate complex with thiosemicarbazide

Assignment	TSC	H_3SSal	$[Cu(TSC)_2](H_2SSal)_2$
ν(NH)	3370, 3260, 3170		3371, 3306, 3248, 3178
ν(C=O)		1678	1670
Thioamide I	1530		1562
ν(C=C) (aromatic ring)		1477, 1439	1477, 1435
Thioamide II	1315		1393, 1369
$\nu_{as}(SO_2)$		1234, 1203, 1165, 1134 sh.	1215, 1184, 1155, 1126
$\nu_s(SO_2)$		1084, 1065, 1026	1084, 1030
Thioamide III	1000		975 w.
Thioamide IV	800		706
ν(S–O)		663	667

IR spectrum of **I** is consistent with the form in which the 5-sulfosalicylate anion exists in complex **I**, namely, as the singly charged anion deportonated at the sulfo group.

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