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Bis(Thiosemicarbazide)Copper(II) 1,5-Naphthalenedisulfonate Complex $[Cu(Tsc)_2](1,5\text{-}Nds)$: Synthesis and Crystal and Molecular Structures

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Abstract—The synthesis, analysis, and IR spectroscopic, thermogravimetric, and X-ray diffraction study of $[Cu(Tsc)_2](Nds)$ (**I**), where Tsc is thiosemicarbazide $NH_2NHC(=S)NH_2$, and 1,5-Nds^{2-} is the doubly deprotonated 1,5-naphthalenedisulfoacid anion $C_{10}H_6(SO_3)_2^{2-}$, have been performed. Crystal structure units in complex **I** are $[Cu(Tsc)_2]^{2+}$ centrosymmetric complex cations and $(Nds)^{2-}$ anions (including those in inversion centers). The copper atom is coordinated to the vertices of a square via the two sulfur and two nitrogen atoms of the two bidentate-chelate (S,N) ligands Tsc. Crystal structure units in complex **I** are linked together by a branched network of weak nonlinear N—H···O hydrogen bonds with participation of donors (all the five independent hydrogen atoms of the two NH_2 groups and NH group of the $[Cu(Tsc)]^{2+}$ complex cation) and acceptors (all the three independent oxygen atoms of the sulfato group of the 1,5-Nds^{2-} anion).

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The coordination behavior of the Cu^{2+} ion with respect to SO_3^- in arenesulfonates can be chemically simulated [1]. Due to weak coordination ability with respect to the firth Series transition-metal ions, most of the known sulfonates separated from an aqueous medium are formed of aquated metal cations and sulfonate anions. When organic ligands, such as amines, are added to the bivalent central transition-metal ions, oxygen of the SO_3^- group becomes able to compete with water molecules and coordinate to the metal. The authors [2] have synthesized from aqueous solution and structurally characterized six arenedisulfonate copper(II) complexes, namely, $[Cu(En)_2](1,5\text{-}Nds) \cdot 2H_2O$, $[Cu(N\text{-}Meen)_2](2,6\text{-}Nds) \cdot 2H_2O$, $Cu(Dpn)_2](Bpds)$, $[Cu(Cyclam)](1,5\text{-}Nds)$, $[Cu(Dpn)_2](1,5\text{-}Nds) \cdot 2H_2O$, and $[Cu(N,N'\text{-}Meen)_2](1,5\text{-}Nds) \cdot 3H_2O$ (where Bpds is biphenyldisulfonate, N-Meen is *N*-methylethylenediamine, Dpn is 2,3-diaminopropane, N,N'-Meen is N,N'-dimethylethylenediamine, and Cyclam is 1,4,8,11-tetraazacyclotetradecane). In the first four complexes, the SO_3^- groups are monodentately coordinated in the axial position of the Cu^{2+} ion, which is equatorially coordinated to the four nitrogen atoms of amino groups. In the last two complexes, water molecules are coordinated in the axial positions of the Cu^{2+} ion instead of the bulky SO_3^- group due to steric hindrances produced by the methyl substituents of amino ligands and the rigidity of the naphthalene ring. We have not found any literature data on the coordination compounds of 1,5-naphthalenedisulfonates with ligands that contain donating atoms other than nitrogen. At the same time, there is an interesting organic ligand, which allows us to trace the mutual effect and competition for the inner-sphere sites in coordination compounds, namely, thiosemicarbazide, an ambidentate ligand able to form five-membered chelate rings or monodentately coordinate by sulfur. A number of copper(II) complexes with thiosemicarbazide and different anions have been synthesized and structurally characterized in our earlier works [3–5].

This paper describes the synthesis, crystal and molecular structures, IR spectra, and thermogravimetric analysis (TGA) results for the copper(II) 1,5-naphthalenedisulfonate complex with thiosemicarbazide $[Cu(Tsc)_2](Nds)$ (**I**).

Table 1. Crystallographic data, parameters of X-ray diffraction experiment, and refinement details for the structure of complex **I**

Bulk formula	$C_{12}H_{16}CuN_6O_6S_4$
Formula weight	823.53
Crystal size, mm	0.08 × 0.08 × 0.01
Symmetry system, space group	Monoclinic, $P2_1/c$
T, K	293(2)
Unit cell parameters	
a, Å	11.894(1)
b, Å	7.498(1)
c, Å	12.596(1)
β, deg	117.50(1)
V, Å^3	996.4(2)
Z	2
ρ_{calc}, g/cm^3	1.773
μ, mm^{-1}	5.881
F(000)	542
θ range, deg	4.71–64.95
Total number of reflections	4342 (R_{int} = 0.071)
Index ranges	$-13 > h > 13$; $-8 > k > 8$; $-14 > l > 14$
Number of independent reflections	1437
Number of reflections with $I > 2\sigma(I)$	927
Number of refined parameters	166
GOOF on F^2	0.896
R_1 [$I > 2\sigma(I)$], wR_2	0.043, 0.109
R_1, wR_2 (for all data)	0.098, 0.134
T_{min}/T_{max}	0.591/0.944
Residual electron density (min/max), e/Å^3	–0.382, 0.553

EXPERIMENTAL

Synthesis of complex I. Thiosemicarbazide (1.82 g, 0.02 mol) was dissolved in water (100 mL) under heating. The solution was cooled to 35°C, thereupon copper(II) 1,5-naphthalenedisulfonate $Cu(C_{10}H_6O_6S_2)(H_2O)_6$ (3.05 g, 0.0067 mol) was added by portions under stirring. The mixture was stirred on a magnetic agitator until complete homogeneity. The settled precipitate was filtered out through a Schott filter, washed with a small amount of water, and dried in a drying cabinet at 60°C to a constant weight. Complex **I** crystals suitable for study were obtained by recrystallizing the powder product from water.

Initial $Cu(C_{10}H_6O_6S_2)(H_2O)_6$ was synthesized by the exchange reaction between copper(II) nitrate and disodium salt of 1,5-naphthalenedisulfoacid in an aqueous solution.

X-ray diffraction analysis of complex I. Experimental material was obtained on a Enraf-Nonius automatic diffractometer (CuK_α radiation, $\lambda = 1.54178$ Å, ω-scanning). The structure of complex **I** was solved by direct methods and refined by the least-squares technique in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [6]. The positions of all hydrogen atoms were located and refined in the isotropic approximation. Unit cell parameters and selected characteristics of X-ray diffraction experiment are given in Table 1, selected bond lengths and bond angles are presented in Table 2, and geometric parameters of hydrogen bonds are listed in Table 3. Full crystallographic data were deposited with the Cambridge Structure Database (no. 1540829; http://www.ccdc.cam.ac.uk/deposit/).

IR spectra were taken on a Shimadzu FTIR-8400S spectrometer, and samples were prepared as KBr pellets.

Thermogravimetric curve was recorded on a Paulik-Erdey-Paulik derivatograph in air at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

The structure of complex **I** (Fig. 1) was characterized by X-ray diffraction. Crystal structure units in complex **I** are centrosymmetric complex cations $[Cu(Tsc)_2]^{2+}$ and anions $(1,5\text{-Nds})^{2-}$ (including those in inversion centers). The copper atom is coordinated to square apices by means of the two sulfur and two nitrogen atoms of two bidentate-chelate (S,N) ligands, i.e., Tsc molecules. Being coordinated to the copper atom, Tsc closes the CuN_2CS five-membered chelate ring, which is nearly planar (±0.001–0.020 Å). The Cu–N and Cu–S distances are 2.001(5) and 2.2663(16) Å, respectively; the NCuS chelate angle is 86.68(15)°.

The Cambridge Structure Database (February, 2017) [7] contains data on the crystal structure of 11 copper(I) and copper(II) compounds, including cationic complexes with thiosemicarbazide molecules as ligands. One of them, $[Cu(Tsc)_2](SO_4)$ (**II**) [8], contains the doubly charged complex cation $[Cu(Tsc)_2]^{2+}$ and a double charged anion (SO_4^{2-} for complex **II**) similarly to complex **I**. The Cambridge Structure Database also contains structural data on five complexes with the general formula $[Cu(Tsc)_2]^{2+}(An^-)_2$, where An^- is HSal (salicylic acid anion) (**III**) [3], Cr(EDTA) (EDTA is the ethylenediaminetetraacetic acid anion) (**IV**) [9], H_2SSal (5-sulfosalicylic acid anion) (**V**) [4], SCN (**VI**) [5], and NO_3 (**VII**) [10]. Similarly to complex **I**, the copper(II) atoms in the centrosymmetric complex cations of complexes **II**–**VI** have a square coordination (as well

Table 2. Bond lengths (*d*) and bond angles (ω) in the structure of complex **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(1)	2.001(5)	C(3)–C(4)	1.435(9)
Cu(1)–S(1)	2.2663(16)	C(4)–C(5)	1.361(10)
S(2)–O(2)	1.426(4)	C(2)–C(6)#2	1.356(10)
S(2)–O(3)	1.457(5)	C(5)–C(6)	1.406(11)
S(2)–O(1)	1.459(4)	N(1)–N(2)	1.409(7)
S(2)–C(2)	1.783(6)	S(1)–C(1	1.702(6)
C(3)–C(2)	1.404(8)	N(2)–C(1)	1.323(7)
C(3)–C(3)#2	1.427(12)	N(3)–C(1)	1.320(8)
Angle	**ω, deg**	**Angle**	**ω, deg**
		C(5)C(4)C(3)	120.7(7)
N(1)Cu(1)S(1)	86.68(15)	C(6)#1C(2)C(3)	120.9(6)
O(2)S(2)O(3)	113.1(3)	C(6)#1C(2)S(2)	117.8(5)
O(2)S(2)O(1)	113.0(3)	C(3)C(2)S(2)	120.9(5)
O(3)S(2)O(1)	109.9(3)	C(4)C(5)C(6)	120.6(7)
O(2)S(2)C(2)	111.5(3)	C(2)#1C(6)C(5)	120.5(7)
O(3)S(2)C(2)	106.0(3)	N(2)N(1)Cu(1)	114.5(4)
O(1)S(2)C(2)	102.6(3)	C(1)S(1)Cu(1)	96.8(2)
C(2)C(3)C(3)#1	119.8(7)	C(1)N(2)N(1)	120.6(5)
C(2)C(3)C(4)	122.7(6)	N(3)C(1)N(2)	118.6(6)
C(3)#1C(3)C(4)	117.5(7)	N(3)C(1)S(1)	120.0(5)
		N(2)C(1)S(1)	121.3(5)

Symmetry codes: #1 – *x* – 1, –*y* + 1, –*z*.

as in complex **VII**) complemented to an elongated tetragonal bipyramid (4 + 2) by axial contacts Cu–O(H_2SSal) (2.810(3) Å), Cu–O(NO_3) (2.773 Å), and Cu–S(SCN) (3.015(1) Å) in complexes **V**, **VI**, and **VII**, respectively. In the structure of [Cu($Tsc)_2$(OSO_3)] (**VIII**) [11], the copper atom is coordinated to tetragonal pyramid vertices with the oxygen atom of the sulfato ligand in the axial position. In [Cu(Tsc)Cl_2] (**IX**) [12] which contains one thiosemicarbazide ligand (instead of two Tsc as in complexes **I–IX**), the copper(II) atom has a square coordination with chlorine atoms in *cis*-positions. In complex **IX**, as well as in complexes **V–VII**, the copper(II) atom coordination is complemented to an elongated tetragonal bipyramid by the two very weak Cu···S(Tsc) axial contacts (3.355(2) and 2.392(2) Å with a corresponding SCuS angle of 159.8°) between two thiosemicarbazide molecules linked to the initial inversion center and axis 2_1. The S(Tsc) atom fulfils a chelating pseudo-bridging (μ_3) function to form a supramolecular polymeric structure. In all copper(II) complexes **I–IX**, Tsc coordinates the metal atom in the bidentate-chelate (N,S) mode to close their $CuSCN_2$ five-membered chelate rings. Table 4 contains the geometric parameters of Cu–N, Cu–S, and NCuS of the five-membered chelate rings in the [Cu($Tsc)_n$] complex cations (n = 1, 2) of six of the above described complexes (there are no atomic coordinates for complexes **II**, **VII**, and **VIII** in the Cambridge Structure Database [7]). As can be seen from Table 4, the ranges of geometric parameters in complexes **I**, **III–VI**, and **IX** are rather narrow: Cu–N; 2.001–2.013 Å, Cu–S, 2.266–2.276 Å; SCuN angles are 85.42°–87.10° with two exceptions: Cu–N is 1.946 Å in complex **IV**, and Cu–S is 2.3034 Å in complex **VI**.

In three copper(I) compounds, ligand Tsc has other than bidentate-chelate (N,S) function. Tsc has a monodentate (S) function in two complexes, such as [Cu($Tsc)_2$(NCS)] [13] (with a triangular coordination of the metal atom, 2S(Tsc) + N(NCS)) and [Cu(Tsc)($PPh_3)_2$Cl] H_2O [14] (with a tetrahedral coordination of the copper atom, S(Tsc) + 2P(PPh_3) + Cl). In the binuclear cation of [{Cu($Tsc)_2$}$_2$(μ-$Tsc)_2$]I_2 [15], each copper(I) atom is coordinated via two monodentate and two doubly bridging sulfur atoms of four thiosemicarbazide ligands.

The crystal structure units of complex **I** are linked together by a branched network of weak nonlinear interionic N–H···O hydrogen bonds with participation of donors, i.e., all the five independent hydrogen atoms of the NH_2 and NH groups of Tsc molecules in the complex cation and acceptors, i.e., all the three independent oxygen atoms of the SO_3 group in the Nds^{2-} anion (H···O, 2.12–2.64 Å; N···O, 2.847–3.291 Å; NHO angles, 128°–168°) (Table 3; Figs. 2a and 2b).

The assignment of absorption bands in the IR spectra of thiosemicarbazide and synthesized complex **I** is

Table 3. Geometric parameters of hydrogen bonds in complex **I**

D–H···A	D–H, Å	H···A, Å	D···A, Å	<DHA, deg
N(1)–H(1)···O(1) #1	0.99(6)	2.17(6)	3.036(7)	145(5)
N(1)–H(1)···O(3) #1	0.99(6)	2.43(6)	3.132(7)	128(5)
N(1)–H(1A)···O(1) #2	0.77(6)	2.12(7)	2.870(7)	164(6)
N(2)–H(2)···O(3) #3	0.73(6)	2.13(6)	2.847(7)	168(6)
N(3)–H(3)···O(1)	0.72(5)	2.38(5)	2.955(7)	138(5)
N(3)–H(3A)···O(2) #3	0.78(5)	2.17(6)	2.910(7)	159(5)
N(3)–H(3A)···O(3) #3	0.78(5)	2.64(5)	3.291(8)	142(5)

Symmetry codes: #1 –*x*, –*y* + 1, –*z*; #2 *x*, –*y* + 0.5, –*z* – 0.5; #3 *x*, –*y* + 1.5, *z* – 0.5.

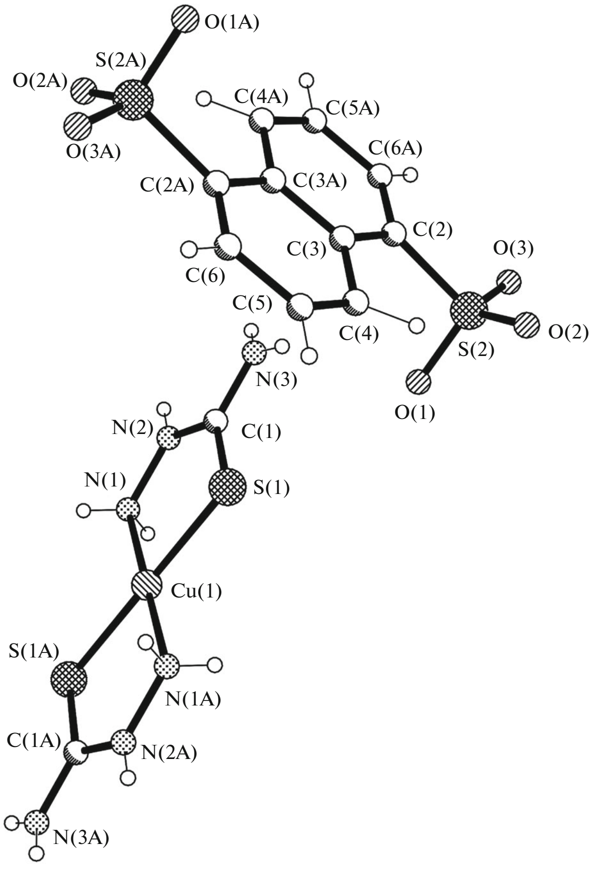

Fig. 1. Structure of complex **I**.

given in Table 5. In comparison with the spectrum of free thiosemicarbazide, the thioamide I band in the spectrum of its complex with copper(II) (1,5-naphthalenedisulfate) increases in frequency and slightly decreases in intensity. The thioamide II band also sustains a high-frequency shift upon complexation and splits into a doublet. A decrease of the thioamide III band in intensity is so appreciable that the spectrum of complex **I** does not contain it at all. The frequency of the thioamide IV band decreases. According to the literature data [16], the described behavior of the thioamide bands corresponds to the bidentate coordination of thiosemicarbazide with participation of sulfur and nitrogen atoms.

The absorption bands of the 1,5-naphthalenedisulfoacid anion were assigned with consideration for the literature data [2, 17–21]. The stretching vibrations of C–H bonds produce the only weak band at ~2950 cm^{-1} in the IR spectrum. The vibrations of naphthalene rings, whose strongest band appears at 1635 cm^{-1}, are much more pronounced in the IR spectra by both the number of bands and their intensity. It is probable that the intensity of this band is so high due to that the bending vibrations of thiosemicarbazide amino groups make a contribution to it in addition to naphthalene ring vibrations. For the SO_3^- group, the band at 1029 cm^{-1} is most intensive throughout the entire IR spectrum and produced by symmetric stretching vibrations. The isolated band at 1238 cm^{-1}, a doublet at ~1200 cm^{-1}, and a triplet at ~1150 cm^{-1} correspond to the anisymmetric vibrations of this group.

Hence, the vibrational spectroscopy data agree with X-ray diffraction results.

According to the TGA data (Table 6), synthesized complex **I** shows very high thermal stability typical of many complexes of naphthalenedisulfoacids. Thus, $[Sc_2(1,5\text{-Nds})(OH)_4]_n$ in a nitrogen flow is stable up to 400°C [18], and $[Y(1,5\text{-Nds})(OH)(H_2O)]_n$ and $Cu_3(OH)_4[(2,6\text{-Nds})]$ are stable up to 375°C [18, 22].

An interesting feature of the TGA curve of studied complex **I** is an increase in weight at a high temperature. A reason for this phenomenon may be the formation of copper nitrides or carbides at lower temperatures as intermediates, whose further conversion into

Table 4. Geometric parameters (bond lengths (Å) and bond angles (deg)) of the five-membered CuNNCS chelate rings of $[Cu(Tsc)_n]^{2+}$ (n = 1, 2) complex cations with bidentate-chelate thiosemicarbazide ligands

Complex no.	Complex	Cu–N	Cu–S	SCuN	Source
I	$[Cu(Tsc)_2](Nds)$*	2.001(5)	2.2663(16)	86.68(15)	This work
III	$[Cu(Tsc)_2](HSal)_2$**	2.003(4)	2.271(1)	87.1(4)	[3]
IV	$[Cu(Tsc)_2][Cr(EDTA)]_2$***	1.946(3)	2.276(1)	86.89(8)	[9]
V	$[Cu(Tsc)_2](H_2SSal)_2$****	2.013(3)	2.275(1)	86.82(8)	[4]
VI	$[Cu(Tsc)_2](SCN)_2$	2.002(3)	2.3034(8)	85.42(8)	[5]
IX	$[Cu(Tsc)Cl_2]$*****	2.002(4)	2.266(1)	86.2(1)	[12]

* Nds^{2-} is the 1,5-naphthalenedisulfonic acid anion.

** $HSal^-$ is the salicylic acid anion.

*** $EDTA^{4-}$ is the ethylenediaminetetraacetic acid anion.

**** H_2SSal^- is the 5-sulfosalicylic acid anion.

***** Cu–Cl 2.257(1) ± 0.015 Å.

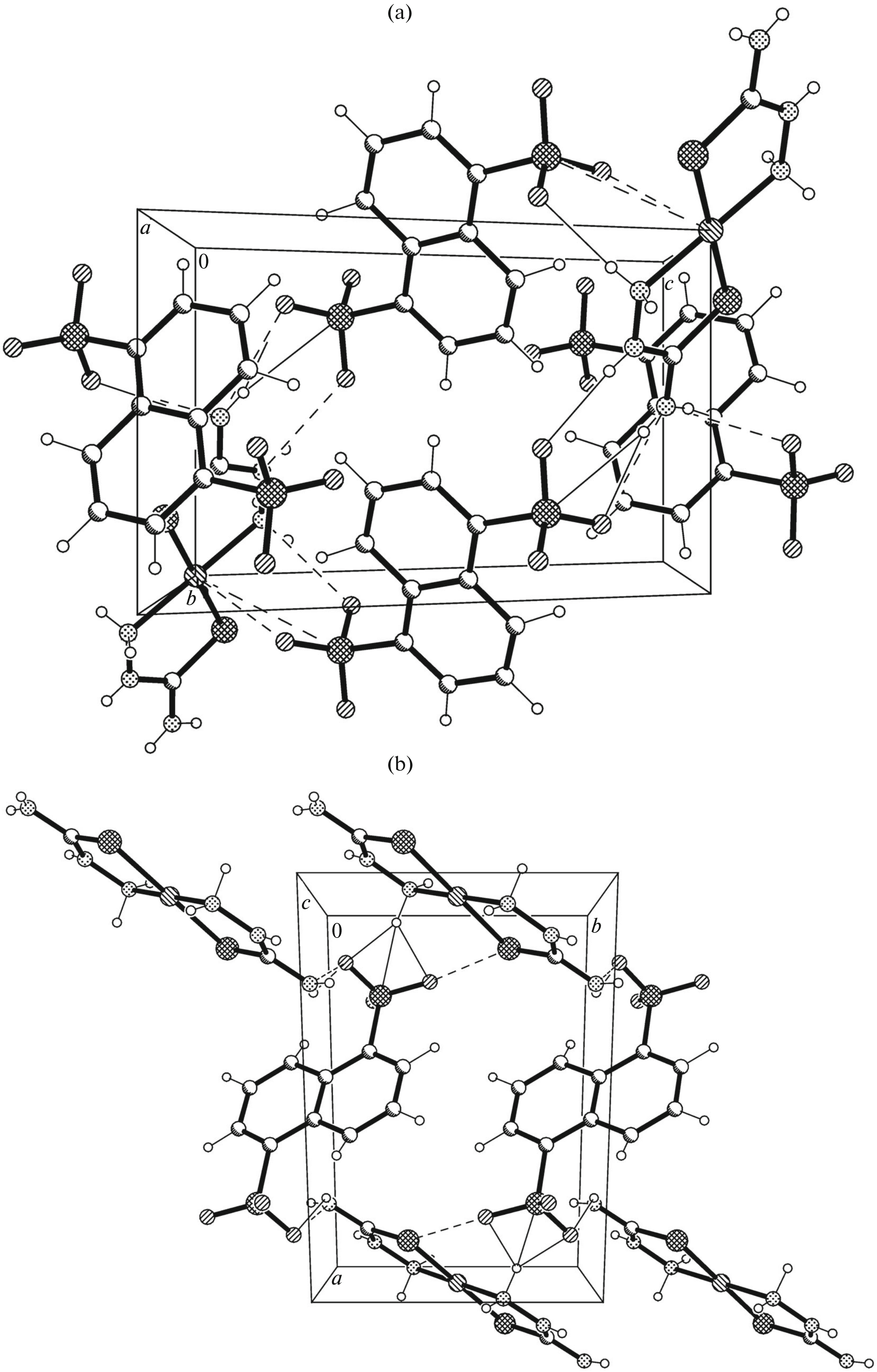

Fig. 2. Packing of crystal structure units in complex **I**: (a) projection onto plane *bc* and (b) projection onto plane *ab*. Dashed lines are hydrogen bonds.

Table 5. Wavenumbers (frequencies, cm^{-1}) of absorption band maxima in the IR spectra of thiosemicarbazide and $[Cu(Tsc)_2](Nds)$ (**I**)

Assignment	Tsc	$[Cu(Tsc)_2](Nds)$
ν(NH)	3370 s, 3260 s, 3170 s	3385 m, 3291 m, 3218 s, 3179 s
ν(C–H) aromatic		2943 w
Naphthalene ring bands		1635 vs, 1497 m, 1448 m, 793 s, 769 s, 663 m, 607 s, 570 m, 529 m
Thioamide I	1530 s	1576 m
$\nu_{as}(SO_3^-)$		1238 m, 1209 s, 1197 s, 1170 s, 1155 s, 1133 s
Thioamide II	1315 m	1380 m, 1334 m
$\nu_s(SO_3^-)$		1029 vs
Thioamide III	1000 s	–
Thioamide IV	800 s	703 s

Table 6. Derivatographic data for complex **I**

Exotherms		Total weight loss, %
T, °C	Δ*m*, %	
300–320(310)	–12.7	81.3
420–600(440)	–52.5	
600–870(850)	+6.8	

oxides must be accompanied by an increase in weight. A similar picture was observed by us earlier for thiosemicarbazide complexes of malonates and glutarates [23], *p*-hydroxy- and *p*-aminobenzoates [24] of 3*d* metals.

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