

COORDINATION COMPOUNDS

Template Synthesis and Structure of Ni(II), Cu(II), Co(II), and Co(III) Hexaazamacrocyclic Compounds Based on *S*-Alkylisothiosemicarbazide

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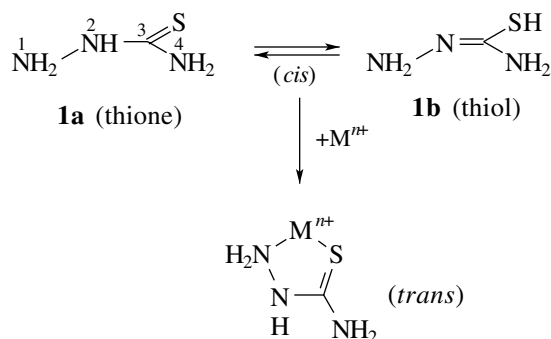
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Abstract—New Cu(II), Co(II), Co(III), and Ni(II) hexaazamacrocyclic complexes based on *S*-alkylisothiosemicarbazide and β -dicarbonyl compounds were synthesized and characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, mass spectrometry, magnetochemistry, EPR, and thermogravimetry. An X-ray diffraction study of [3,9-bis(propylthio)-13-nitro-1,2,4,8,10,11-hexaazacyclotetradeca-2,4,6,9,10,13-hexaenato(2-)- N^1, N^4, N^8, N^{11}]copper(II) confirmed the square-planar structure of the compounds in question.

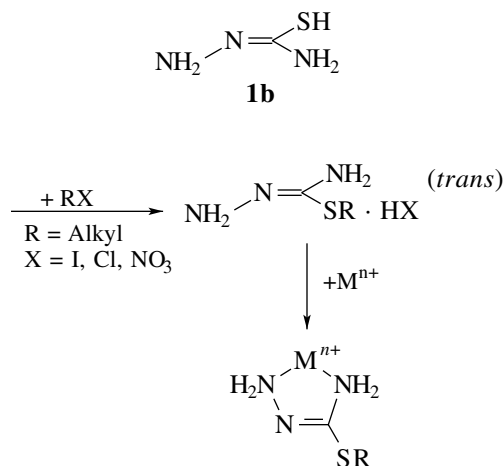
Thiosemicarbazide (TSC) functions as a bidentate ligand coordinated to the central metal ion through the hydrazine nitrogen atom (N^1) and the sulfur atom [1–3]. Some silver complexes in which TSC is coordinated only through sulfur are exceptions [4, 5]. The low reactivity of the thioamide NH_2 group is also displayed in condensation with monocarbonyl compounds giving thiosemicarbazones, which involves exclusively the hydrazine nitrogen (N^1). The thioamide nitrogen (N^4) does not participate in this type of reaction. The thiosemicarbazide molecule undergoes tautomeric and conformational transformations. The TSC configuration in the crystal is characterized by *cis* arrangement of the terminal nitrogen atoms with respect to the $\text{N}^2=\text{C}^3$ bond [6]. Upon complexation, the ligand adopts the *trans* configuration [1–3]. The interconversion of two TSC tautomers (**1a**, **1b**) and *cis*–*trans* conformational transitions are shown in Scheme 1.



Scheme 1.

Alkylation of TSC at the sulfur atom has no influence on the dentation of the ligand but changes cru-

cially both the configuration of the free molecule [7] (transition from *cis* to *trans*) and the coordination mode (Scheme 2).

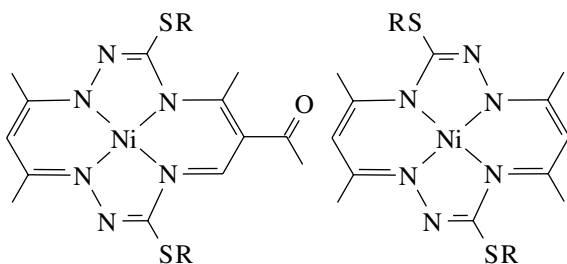


Scheme 2.

X-ray diffraction analysis of some 3d-metal complexes with *S*-alkylisothiosemicarbazide (S(R)TSC, where R is alkyl) and with their Schiff's bases demonstrated that only the N^1 and N^4 nitrogen atoms are involved in the coordination to the central metal atom [8–10].

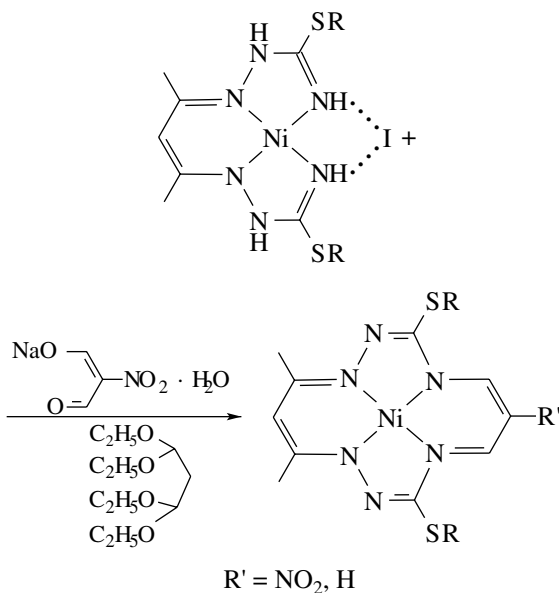
Thus, the template condensation of 2,4-pentanedione and *S*-alkylisothiosemicarbazide hydroiodide on an Ni(II) matrix gave diamagnetic chelates $[\text{Ni}(\text{H}_2\text{L})\text{I}] \cdot n\text{H}_2\text{O}$, where H_3L is pentane-2,4-dione bis(*S*-alkylisothiosemicarbazone) [11]. They were used as precursors for the preparation of macrocyclic systems. Pentane-2,4-dione served as the cross-linking agent in the

presence of ethyl orthoformate, which acted as the dehydrating and formylating reagent. This gave two types of macrocyclic complexes with *cis* and *trans* arrangement of the thiosemicarbazide arms relative to the central nickel(II) atom [12–14] (Scheme 3).



Scheme 3.

The chelate $[\text{Ni}(\text{H}_2\text{L})]\text{I}$ also proved to be a convenient precursor for the design of hexaazamacrocyclic systems with the sodium salt of nitromalonic aldehyde or 1,1,3,3-tetraethoxypropane being used as ring-closure agents.



Scheme 4.

In this work, we extend the range of matrices and dicarbonyl compounds capable of participating in template condensations to give macrocyclic systems.

RESULTS AND DISCUSSION

Several new hexaazamacrocyclic nickel(II), copper(II), cobalt(II), and cobalt(III) compounds based on *S*-alkylisothiosemicarbazide were synthesized.

The template reaction of a methanolic solution of *S*-methylisothiosemicarbazide hydroiodide with pentane-2,4-dione in a 2 : 1 ratio under an inert atmosphere (N_2) in the presence of cobalt(II) acetate gives the che-

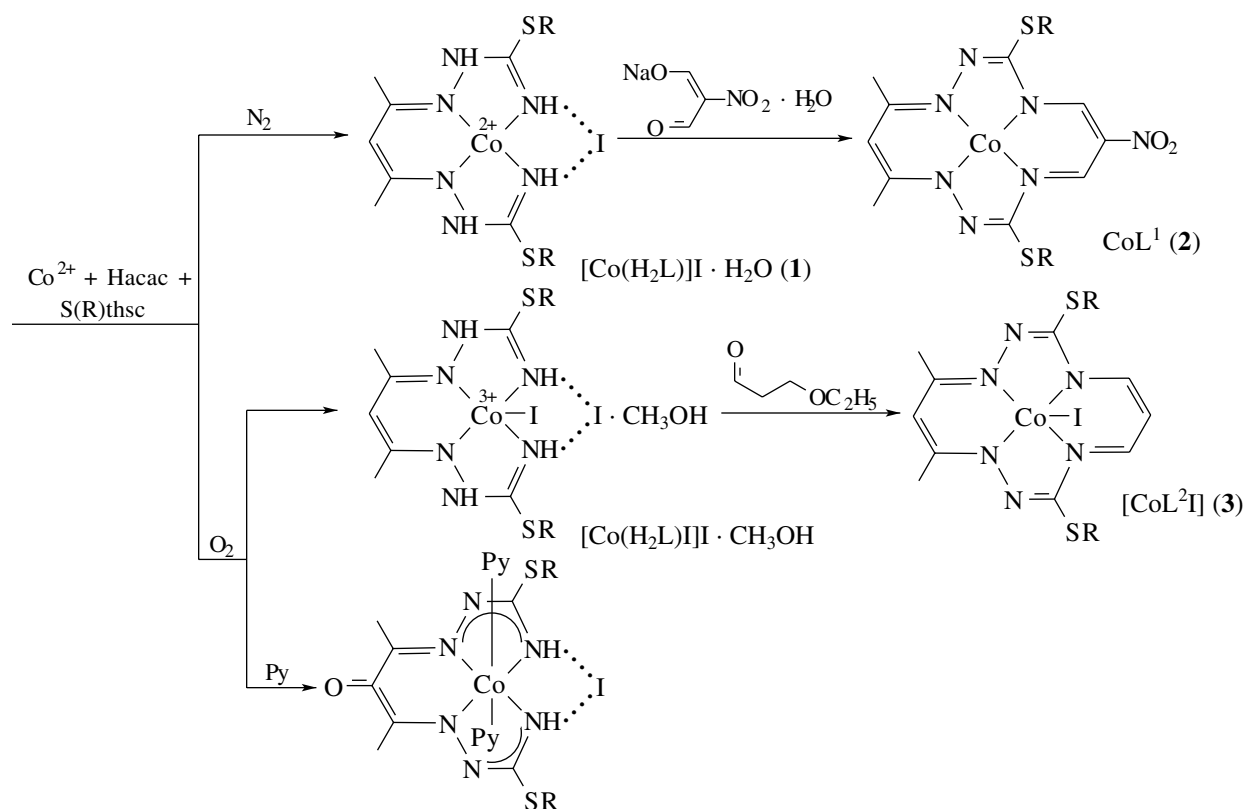
late $[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{H}_2\text{O}$ (**1**). This is a finely crystalline black-brown powder, which undergoes thermolysis below the melting point. According to thermogravimetry, the water molecule contained in the complex is removed at 75°C , which indicates that this is crystal water. The effective magnetic moment of the complex is $2.12 \mu_{\text{B}}$, which corresponds to the low-spin state of $\text{Co}(\text{II})$ [17]. The molecular electrical conductivity in anhydrous methanol corresponds to values typical of binary electrolytes. The most intense peak in the mass spectrum of this compound is $[\text{M}-\text{HI}]^+$. In view of the foregoing and resorting to the dentation of $[\text{H}_3\text{L}]$ and its coordination mode in the diamagnetic $\text{Ni}(\text{II})$ complex, which had been studied by X-ray diffraction [11], a square-planar geometry was proposed for the $\text{Co}(\text{II})$ complex under study.

The ionic structure of $[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{H}_2\text{O}$ with a square-planar geometry of the cation is also supported by the fact that this compound served as the precursor for the template synthesis of the macrocyclic system CoL^1 (**2**). Compound **2** was synthesized by prolonged heating (5–6 h) of freshly prepared **1** with a fivefold excess of the sodium salt of nitromalonic aldehyde in methanol under an inert atmosphere (N_2). The product thus formed was a brown finely crystalline paramagnetic powder stable up to relatively high temperatures; it undergoes destructive thermolysis at 193°C .

The IR spectra of compound **2** exhibit no $\nu(\text{NH})$ stretching vibration bands, pointing to the condensation of acetylacetone bis(*S*-methylisothiosemicarbazone) with sodium nitromalonic dialdehyde (the $\nu(\text{C}=\text{O})$ modes corresponding to the latter were not found in the IR spectrum either). The $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations are exhibited in the region of $1500\text{--}1550 \text{ cm}^{-1}$. The central cobalt ion formally has the oxidation number +2. This is confirmed by the magnetic properties of the complex; according to EPR and magnetic measurements, $\mu_{\text{eff}} = 2.29 \mu_{\text{B}}$, $g = 2.42$ ($S = 1/2$) at room temperature (upon the contact of the complex with atmospheric oxygen, the central metal ion is partly oxidized). On heating *in vacuo*, the complex passes to the vapor phase without decomposition; this enabled recording of the electron impact mass spectrum.

The molecular ion peak $[\text{M}]^+$ is the most intense in the mass spectrum of **2**; fragmentation is insignificant and includes abstraction of side groups, as well as more profound fragmentation.

The five-coordinate macrocyclic cobalt(III) complex $[\text{Co}(\text{L}^2)]\text{I}$ (**3**) was also synthesized. The open-chain square-pyramidal precursor $[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{CH}_3\text{OH}$ (whose structure had been determined previously [18] by X-ray diffraction) was used as the template and 3-ethoxyacrolein was employed as the cross-linking agent (Scheme 5).

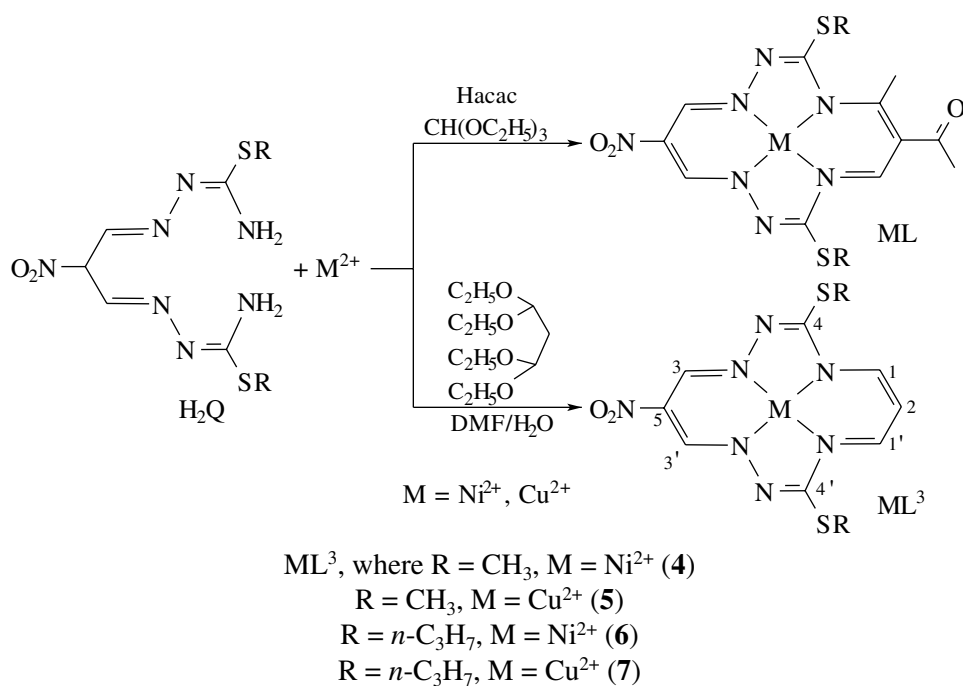


Scheme 5.

The data of IR and mass spectroscopy attest to the condensation of 3-ethoxyacrolein with the thioamide nitrogen atoms of the isothiosemicarbazide fragments to give a macrocyclic system. In addition to the most intense $[\text{M}-\text{I}]^+$ peak corresponding to a cobalt complex with an equatorial macrocyclic ligand, the mass spectra of **3** exhibit a molecular ion peak $[\text{M}]^+$, indicating that I^- is coordinated to the central atom. The above results, the data of elemental analysis, and the fact that **3** is diamagnetic suggest that the environment of the central atom is similar to that in the known structure of the chelate precursor; i.e., the Co(III) ion coordinates four donor $\text{N}(4)$ atoms of the macrocyclic ligand in the equatorial plane and the I^- anion in the apical position of a square pyramid. It should be noted that the *cis*-arrangement of the thiosemicarbazide arms, typical of the chelate precursors, is also retained in products **2** and **3**. We failed to prepare macrocyclic compounds from octahedral Co(III) chelates [19] (Scheme 5) in which equatorial positions are occupied by a tridentate chelating ligand—bis(*S*-alkylisothiosemicarbazone)-3-oxopentane-2,4-dione—and the apical positions are occupied by two pyridine molecules.

Nickel(II) and copper(II) coordination compounds with 14-membered hexaazamacrocyclic ligands (ML) have been synthesized previously [20] from nitromalononic dialdehyde bis(*S*-methylthiosemicarbazone) (H_2Q), pentane-2,4-dione, and ethyl orthoformate. The same procedure was employed in the template synthesis of nickel(II) and copper(II) macrocyclic complexes, using 1,1,3,3-tetraethoxypropane, which is hydrolyzed to give malonic dialdehyde, as the ring-closure agent. This afforded the complexes ML^3 (**4–7**) (see Scheme 6). The products synthesized are light brown, fine crystalline powders soluble in chloroform and acetone, poorly soluble in alcohols, and insoluble in hexane or water.

The absence of absorption bands in the region of $\nu(\text{NH})$ stretching modes in the IR spectra of the compounds considered attests to template condensation of the terminal amino groups in the initial nitromalononic dialdehyde bis(*S*-methylthiosemicarbazone) with the β -dicarbonyl compound. The stretching vibrations of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ double bonds are observed at about $1590\text{--}1520\text{ cm}^{-1}$.



Scheme 6.

The formation of the corresponding cyclic systems is also confirmed by the presence of 100% molecular ion peaks $[\text{M}]^{+}$ in the electron impact mass spectra of compounds **4–7** (Fig. 1). The fragmentation of $[\text{M}]^{+}$ is insignificant and involves mainly the side groups to give $[\text{M-SH}]^{+}$, $[\text{M-R}]^{+}$, and $[\text{M-RH}]^{+}$. This is followed by cleavage of the macrocyclic core yielding $[\text{M}]^{+}$, $[\text{MNCH}]^{+}$, and $[\text{MN}_3\text{C}_3\text{O}_2\text{H}_3]^{+}$ ions ($\text{M} = \text{Ni}, \text{Cu}$). It is noteworthy that a lengthening of the chain at the sulfur atom decreases the stability of the molecular ion against electron impact; this gives rise to peaks formed upon fragmentation of $n\text{-C}_3\text{H}_7$ in the mass spectra of **5** and **7**.

In view of the fact that nickel compounds **4** and **6** are diamagnetic, we proposed a square-planar structure for them.

The ^1H NMR spectrum of a solution of compound **6** in CDCl_3 exhibits six groups of lines, which were

assigned to the $\text{CH}(3,3')$, $\text{CH}(1,1')$, and $\text{CH}(2)$ protons and the protons of the thiosemicarbazide fragments. The number of peaks indicates the presence of a two-fold symmetry axis in the molecule (the ^1H NMR spectrum of the thiomethyl derivative **4** in CDCl_3 was not recorded due to its poor solubility). The downfield shift of the signal of the $\text{CH}(3,3')$ aldimine protons (a singlet at $\delta = 8.19$ ppm) from those for the $\text{CH}(1,1')$ protons (a doublet at $\delta = 7.04$ ppm, $J_{\text{H,H}} = 6.3$ Hz) is due to the close vicinity of the electron-withdrawing NO_2 group. The methine proton ($-\text{CH}=\text{N}-$) is displayed as a triplet with $\delta = 5.20$ ppm and $J_{\text{H,H}} = 6.3$ Hz. The thiopropyl moiety is responsible for three sets of signals: a triplet with $\delta = 3.03$ ppm and $J_{\text{H,H}} = 7.2$ Hz for the SCH_2 protons, a quartet with $\delta = 1.71$ and $J_{\text{H,H}} = 7.2$ Hz for the $-\text{CH}_2$ protons, and a triplet with $\delta = 1.01$ ppm and $J_{\text{H,H}} = 7.3$ Hz for the CH_3 protons.

The ^{13}C NMR data for a solution of compound **6** in CDCl_3 and for solid **4** and those for the initial nitroma-

Table 1. ^{13}C NMR spectra of compounds **4**, **6**, and H_2Q

Compound	C(4)	C(3, 3')	C(1, 1')	C(5)	C(2)	SR
H_2Q	164.2; 153.3	146.6; 145.4	—	118.4	—	14.6; 13.0 (CH_3)
4 ¹	164.6	149.7	147.8	125.9	103.9; 102.9	20.8; 16.8; 16.0; 14.6 (CH_3)
6 ²	162.6	147.5	147.1	124.8	101.6	34.8; 22.4, 13.4 (C_3H_7)

Note: ¹ In the solid state at 400 MHz; ² in CDCl_3 at 270 MHz; for proton assignment, see Scheme 6.

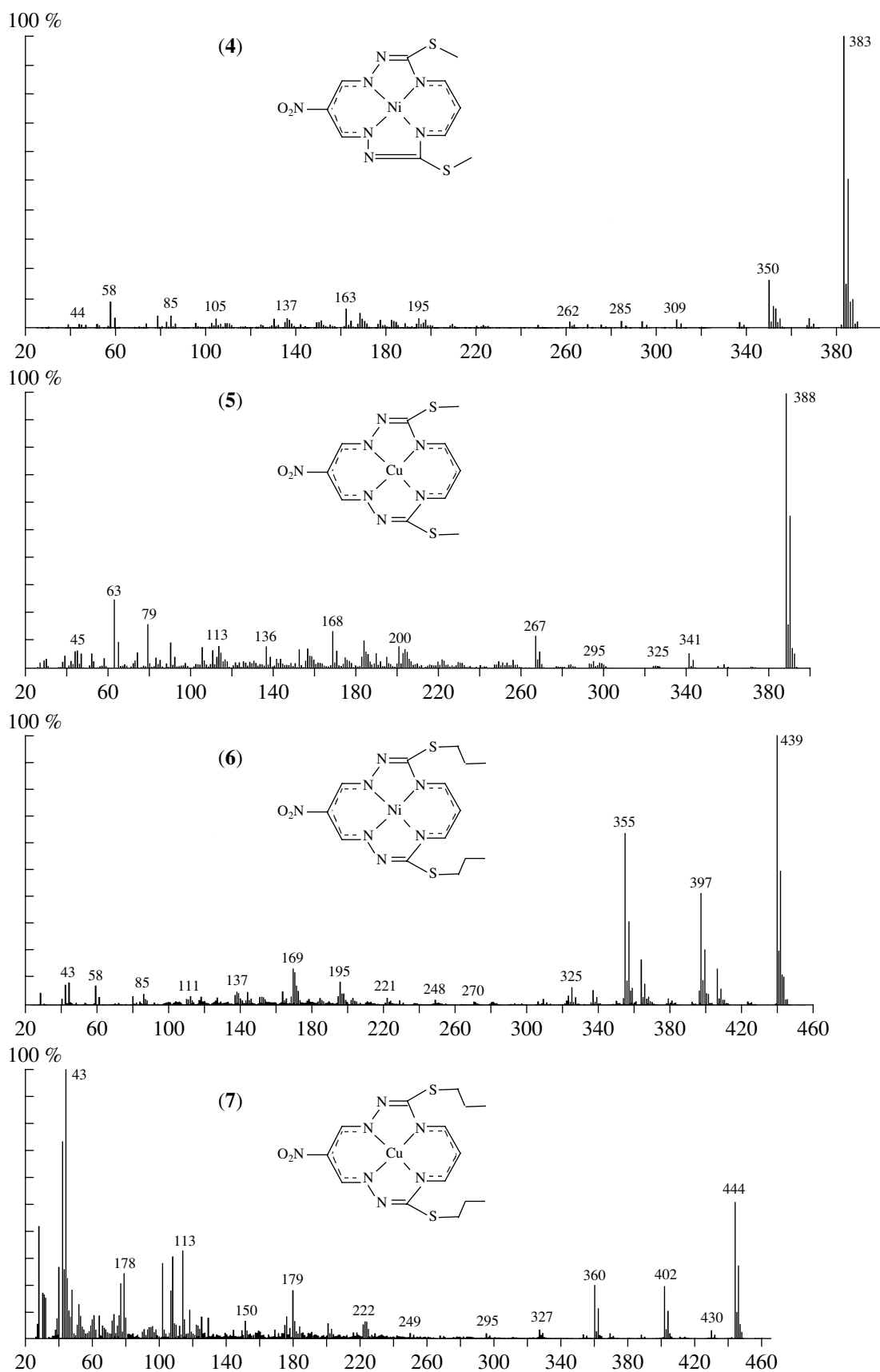


Fig. 1. Electron impact mass spectra for compounds 4–7.

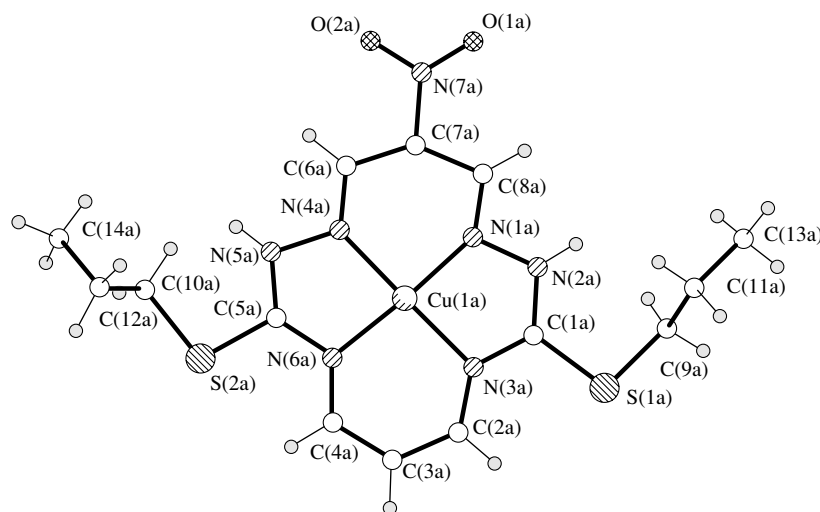


Fig. 2. Structure of the molecule of CuL^3 .

ionic dialdehyde bis(*S*-methylisothiosemicarbazone) are presented in Table 1.

The presence of four signals due to methyl groups and two signals for CH(2) in the NMR spectrum of the solid complex **6** indicates the presence of two independent molecules in the unit cell.

Complexes **5** and **7** of the given series are paramagnetic; the effective magnetic moments at 291 K are 1.76 and 1.78 μ_B , respectively, which implies one unpaired electron at the central atom. The relatively low effective magnetic moment for this complex might be due to intermolecular interactions.

The data of ESR spectra recorded in chloroform at room temperature ($g = 2.060(9)$ and $2.060(6)$) and the isotropic hyperfine coupling constant, $A = 94(7)$ and $95(1)$ for **5** and **7**, respectively, point to the absence of exchange interactions of paramagnetic centers in solution.

To determine the structure of the compounds synthesized, the Cu(II) thiopropyl derivative (**7**) was studied by X-ray diffraction.

Two chemically equivalent complexes **7** differing in the conformation of the *n*-propyl radicals at the sulfur atom were found in the crystal (molecule A is shown in Fig. 2). The weak additional coordination of the copper ions to neighboring molecules ($\text{Cu(1B)} \cdots \text{Cu(1A)}$) (x, y, z) = 3.48 Å, $\text{Cu(1B)} \cdots \text{Cu(1A)}$ ($x, y, 1 + z$) = 3.45 Å) form a chain structure in the crystal (Fig. 3). The short intermolecular contacts $\text{Cu(1B)} \cdots \text{N(4A)}$ (x, y, z) = 3.55 Å, $\text{O(1B)} \cdots \text{C(9A)}$ ($0.5 - x, 0.5 + y, 1z$) = 3.99 Å, and $\text{O(1B)} \cdots \text{C(11A)}$ ($0.5 - x, -0.5 + y, 2 - z$) = 3.41 Å should also be noted. Only van der Waals interactions occur between the chains. "Dimerization" of planar fragments has been reported for copper(II) complexes with tridentate ligands based on *S*-alkylisothiosemicarbazide condensed with salicylaldehyde H_2L^* through sulfur and chlorine atoms in $\text{Cu(HL}^*\text{)Cl}$ [21]

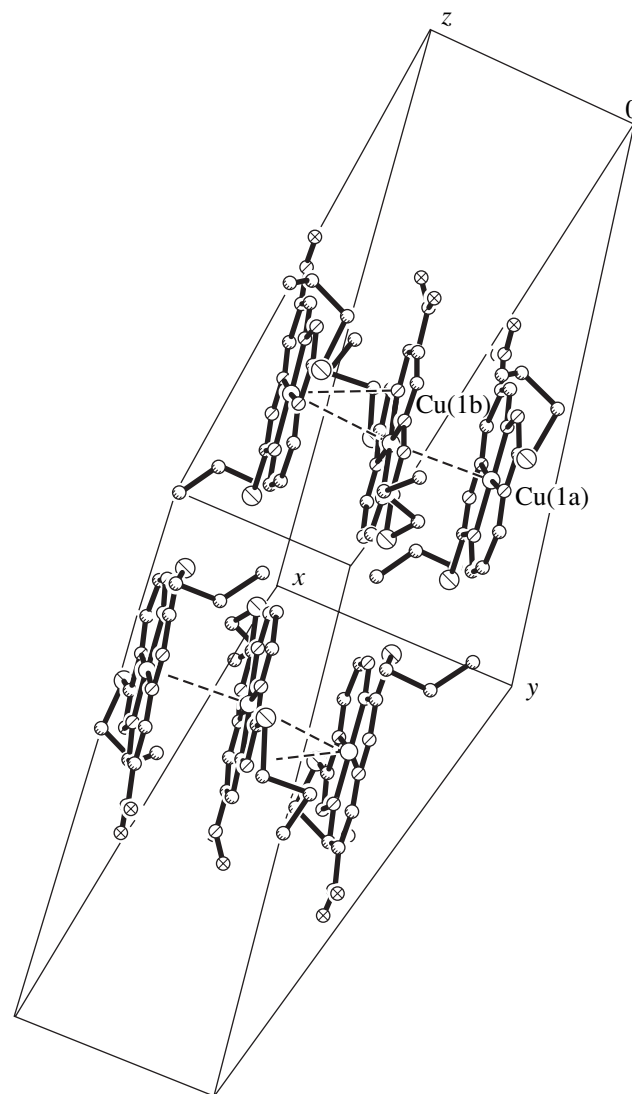


Fig. 3. Fragment of the crystal structure of CuL^3 .

or through the phenolic O atom in $\text{Cu}(\text{HL}^*)\text{PyNO}_3$ [22]. The formation of dimers with the distances $\text{Cu}\cdots\text{Cu}^* = 3.505 \text{ \AA}$ and $\text{Cu}-\text{N} = 2.931 \text{ \AA}$ through the terminal (amide) nitrogen atom of the thiosemicarbazide residue was discovered in [23]. According to [24], the bridging ClO_4^- anions link the $\text{Cu}(\text{HL}^*)^{2+}$ cations into chains and the metal coordination polyhedron is completed to a distorted square pyramid by the oxygen atoms of the anion; the $\text{Cu}\cdots\text{O}$ distances are 2.691 and 2.518 \AA . The crystal structure of $[\text{CuQ}]$, where Q is a nonsymmetrical tetradentate Schiff base [25], is composed of centrosymmetrical associates formed through the amide nitrogen atom of the thiosemicarbazide fragment; the $\text{Cu}\cdots\text{Cu}^*$ distance is 3.342 \AA , and the $\text{Cu}-\text{N}^*$ distance is 3.115 \AA . This type of coupling of planar Cu moieties including four coordinated atoms has been suggested previously for polymeric complexes $\text{Cu}(\text{L}^*)$ [26].

Taking into account the weak $\text{Cu}\cdots\text{Cu}$ bonds, the coordination polyhedron of the central Cu atom approaches a tetragonal bipyramid. The deviations of the coordinated nitrogen atoms of the macrocycles from the plane passing through them are not tetrahedral; they are $\pm 0.0073 \text{ \AA}$ in complex A and $\pm 0.0037 \text{ \AA}$ in complex B. The copper atom is coordinated to the square-planar array of four nitrogen atoms (two amide and two hydrazide ones) of the macrocyclic ligand with an average $\text{Cu}-\text{N}(\text{amide})$ distance of 1.92 \AA and more dissimilar $\text{Cu}-\text{N}(\text{hydrazine})$ bond lengths: $\text{Cu}(1)-\text{N}(1) = 1.83(3) \text{ \AA}$ and $\text{Cu}(1)-\text{N}(4) = 1.92(2) \text{ \AA}$ in complex A and the corresponding distances equal to 1.79(3) and 1.91(3) \AA , respectively, in complex B (the average is 1.864 \AA) (Table 2).

The structure of CuL^3 (7) is characterized by the *cis* arrangement of the isothiosemicarbazide fragments. This arrangement was found for all Ni(II) coordination compounds with 14-membered macrocycles in which the fragments linking two *S*-alkylisothiosemicarbazide units to give the macrocycle are different [12, 16]; *trans* arrangement of these fragments was found only in the "symmetrical" Ni(II) complex with a macrocycle [13, 14]. The ligand coordination through four nitrogen atoms gives four chelate rings, namely, two five-membered isothiosemicarbazide rings and two six-membered rings. The dihedral angles between the planes through the chelate rings do not exceed 0.6° for both complex A and complex B; thus, complexes A and B are roughly planar. The displacement of the sulfur atoms from the planes of the five-membered metal-containing rings does not exceed 0.006 and 0.010 \AA for A and B, respectively. The carbon atoms of the propyl radicals at sulfur substantially deviate from these planes; the deviations reach 1.95 \AA .

Analysis of the interatomic distances in the isothiosemicarbazide fragments (Table 2) does not point to stabilization of the amine form, which implies that $\text{N}^2-\text{C}^1 < \text{C}^1-\text{N}^3$, because these bond lengths coincide to within the experimental error.

The N^2-C^1 and N^5-C^5 interatomic distances in the chemically equivalent complexes A and B are virtually equal. Comparison of these data with those for other macrocyclic ligands, in particular, for the complex of Ni(II) with hexaazamacrocyclic [16] shows that the difference between N^2-C^1 and N^5-C^5 bond lengths in the thiosemicarbazide fragment reaches 0.10 \AA . It can be suggested that equalization of these bonds in 7 is due to the π -delocalization of the electron density over the whole ligand system.

EXPERIMENTAL

IR spectra of compounds 1–7 were recorded as mineral or fluorinated oil mulls on a Specord M-80 spectrophotometer in the 4000–400 cm^{-1} range.

Magnetic susceptibility at room temperature was measured by the Gouy method. Calibration was performed against $\text{Hg}[\text{Co}(\text{NCS})_4]$. Diamagnetic corrections were made in accordance with [27]. The EPR spectra were recorded on an M-40 instrument.

The thermogram of compound 1 was recorded at a rate of 5 K/min using a Paulik–Paulik–Erdey Q-1500D derivatograph in the temperature range 30–300°C.

The ^1H and ^{13}C NMR spectra were recorded in CDCl_3 using Bruker AC 270 and AM 400 instruments operating at 270 and 400 MHz, respectively.

The solid-state CP/MAS ^{13}C NMR spectra were recorded on a Bruker MSL 300 instrument.

Mass spectra were measured on a Finnigan MAT 958 double-focusing mass spectrometer using electron ionization (70 eV) and standard resolution conditions, $m/\Delta m = 2300$.

$[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{H}_2\text{O}$ (1). *S*-Methylisothiosemicarbazide hydroiodide (4.66 g, 20.0 mmol) in methanol (15 ml) and acetylacetone (1.2 ml, 12.0 mmol) was added to $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2.5 g, 10.0 mmol) in methanol (25 ml). The solution was refluxed under an inert atmosphere on a water bath until a brown crystalline compound formed. After cooling, the product was filtered off and washed with methanol. The yield was 30%.

The elemental analysis data for this compound and other synthesized compounds are summarized in Table 3.

$[\text{CoL}^1]$ (2). The sodium salt of nitromalonic aldehyde hydrate (1.57 g, 10.0 mmol) dissolved in methanol (20 ml) was added to freshly prepared $[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{H}_2\text{O}$ (1) (0.96 g, 2.0 mmol). The reaction mixture was refluxed on a water bath under an inert atmosphere (N_2) for 2 to 3 h until a precipitate formed. This was filtered off, washed with methanol, and dried in air. The yield was 18%.

$[\text{CoL}^2\text{I}]$ (3). 3-Ethoxyacrolein (1.8 ml) was added to $[\text{Co}(\text{H}_2\text{L})]\text{I} \cdot \text{CH}_3\text{OH}$ (0.62 g, 1.0 mmol) [18] in methanol (80 ml). The reaction mixture was heated on

Table 2. Interatomic distances (Å) and bond angles (deg) in the structure of CuL³

Bond	Complex A	Complex B	Angle	Complex A	Complex B
Cu(1)–N(1)	1.83(3)	1.79(3)	C(1)S(1)C(9)	102(2)	106(3)
Cu(1)–N(6)	1.91(2)	1.91(2)	C(5)S(2)C(10)	99(2)	104(3)
Cu(1)–N(4)	1.92(2)	1.91(3)	C(8)N(1)N(2)	106(3)	104(3)
Cu(1)–N(3)	1.94(3)	1.92(2)	C(8)N(1)Cu(1)	140(3)	134(4)
S(1)–C(1)	1.77(3)	1.74(3)	N(2)N(1)Cu(1)	114(3)	122(3)
S(1)–C(9)	1.85(3)	1.80(3)	C(1)N(2)N(1)	111(3)	106(3)
S(2)–C(5)	1.76(3)	1.72(3)	C(2)N(3)C(1)	131(4)	129(3)
S(2)–C(10)	1.79(3)	1.79(3)	C(2)N(3)Cu(1)	122(4)	121(3)
N(1)–C(8)	1.32(3)	1.30(2)	C(1)N(3)Cu(1)	107(2)	110(3)
N(1)–N(2)	1.42(4)	1.38(4)	C(6)N(4)N(5)	113(3)	122(4)
N(2)–C(1)	1.36(3)	1.33(3)	C(6)N(4)Cu(1)	131(3)	128(4)
N(3)–C(2)	1.32(3)	1.31(3)	N(5)N(4)Cu(1)	117(2)	111(3)
N(3)–C(1)	1.39(3)	1.38(3)	C(5)N(5)N(4)	104(3)	116(3)
N(4)–C(6A)	1.32(2)	1.31(3)	C(4)N(6)C(5)	126(3)	123(3)
N(4)–N(5)	1.44(4)	1.38(4)	C(4)N(6)Cu(1)	128(3)	126(3)
N(5)–C(5)	1.32(3)	1.34(3)	C(5)N(6)Cu(1)	106(2)	110(3)
N(6)–C(4)	1.31(3)	1.32(3)	O(1)N(7)O(2)	118(5)	130(6)
N(6)–C(5)	1.40(3)	1.37(3)	O(1)N(7)C(7)	124(4)	105(5)
N(7)–O(1)	1.19(3)	1.20(3)	O(2)N(7)C(7)	114(4)	125(5)
N(7)–O(2)	1.22(3)	1.19(3)	N(2)C(1)N(3)	121(3)	121(3)
N(7)–C(7)	1.50(4)	1.49(4)	N(2)C(1)S(1)	123(4)	124(4)
C(2)–C(3)	1.44(3)	1.44(3)	N(3)C(1)S(1)	116(3)	115(3)
C(3)–C(4)	1.41(3)	1.45(3)	N(3)C(2)C(3)	126(5)	127(4)
C(6)–C(7)	1.48(3)	1.48(3)	C(2)C(3)C(4)	127(5)	127(4)
C(7)–C(8)	1.49(3)	1.47(3)	N(6)C(4)C(3)	121(5)	120(4)
C(9)–C(11)	1.52(3)	1.53(3)	N(5)C(5)N(6)	129(3)	118(3)
C(10)–C(12)	1.53(3)	1.52(3)	N(5)C(5)S(2)	116(3)	121(3)
C(11)–C(13)	1.57(3)	1.55(3)	N(6)C(5)S(2)	116(3)	121(3)
C(12)–C(14)	1.55(3)	1.52(3)	N(4)C(6)C(7)	111(4)	120(6)
C(10)–C(12D)	1.51(3)	–	C(6)C(7)C(8)	141(4)	126(5)
C(12D)–C(14D)	1.54(3)	–	C(6)C(7)N(7)	111(3)	125(4)
Angle	Complex A	Complex B	C(8)C(7)N(7)	108(3)	109(4)
N(1)Cu(1)N(6)	177(2)	179.4(8)	N(1)C(8)C(7)	104(4)	118(4)
N(1)Cu(1)N(4)	93(2)	95(2)	C(11)C(9)S(1)	108(3)	110(3)
N(6)Cu(1)N(4)	84(2)	85(2)	C(12)C(10)S(2)	110(3)	111(3)
N(1)Cu(1)N(3)	87(2)	81(2)	C(9)C(11)C(13)	99(5)	105(8)
N(4)Cu(1)N(3)	179.6(8)	176(2)	C(10)C(12)C(14)	83(8)	121(5)
N(6)Cu(1)N(3)	96(2)	99(2)	C(10D)C(12D)C(14)	129(10)	–

a water bath for 3 to 4 h until a black-brown precipitate formed. This was separated, washed with methanol, and dried in air. Yield 21%.

ML³ (4–7), where M = Ni, Cu. Nitromalonic dialdehyde bis(*S*-alkylisothiosemicarbazone) (2.0 mmol)

and 1,1,3,3-tetraethoxypropane (1 ml) were added to nickel(II) or copper(II) acetate (2.00 mmol) dissolved in dimethylformamide (30 ml). The mixture was heated on a water bath for 40 min, then KOH (1.12 g, 2.00 mmol) in water (10 ml) was added, and the solvent

Table 3. Elemental analysis data and some characteristics of compounds 1–7

No.	Compound Gross formula	Yield (%)	Elemental analysis found/calculated, %				<i>m/z</i>
			M*	C	H	N	
1	C ₉ H ₁₉ CoIN ₆ OS ₂	24	$\frac{12.18}{12.35}$	$\frac{22.68}{22.65}$	$\frac{3.85}{4.01}$	$\frac{17.1}{17.61}$	331
2	C ₁₂ H ₁₅ CoN ₇ O ₂ S ₂	14	$\frac{14.37}{14.29}$	$\frac{34.48}{34.95}$	$\frac{3.87}{3.67}$	$\frac{23.97}{23.78}$	412
3	C ₁₂ H ₁₆ CoIN ₆ S ₂	17	$\frac{12.13}{11.92}$	$\frac{30.49}{29.16}$	$\frac{3.41}{3.26}$	$\frac{16.26}{17.00}$	494
4	C ₁₀ H ₁₁ N ₇ NiO ₂ S ₂	16	$\frac{15.18}{15.29}$	$\frac{32.03}{31.27}$	$\frac{2.83}{2.89}$	$\frac{25.68}{25.53}$	383
5	C ₁₀ H ₁₁ N ₇ CuO ₂ S ₂	18	$\frac{16.26}{16.34}$	$\frac{31.04}{30.88}$	$\frac{3.42}{2.85}$	$\frac{25.20}{25.21}$	388
6	C ₁₄ H ₁₉ N ₇ NiO ₂ S ₂	22	$\frac{13.06}{13.34}$	$\frac{37.86}{38.20}$	$\frac{4.57}{4.35}$	$\frac{22.10}{22.27}$	439
7	C ₁₄ H ₁₉ N ₇ CuO ₂ S ₂	20	$\frac{14.13}{14.28}$	$\frac{38.08}{37.79}$	$\frac{4.39}{4.30}$	$\frac{21.90}{22.03}$	444

Note: M = Co, Ni, Cu.

Table 4. Crystallographic data, experimental details, and refinement parameters for the structure of CuL³

Empirical formula	C ₂₈ H ₃₈ Cu ₂ N ₁₄ O ₄ S ₄
FW	890.04
Temperature, K	293(2)
Wavelength, Å	1.54180
System	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>
Unit cell parameters	
<i>a</i> , Å	24.290(9)
<i>b</i> , Å	22.867(8)
<i>c</i> , Å	6.905(3)
β, deg	91.75(5)
<i>V</i> , Å ³	3834
<i>Z</i>	4
ρ(calcd), g/cm ³	1.542
μ _{Mo} , mm ^{−1}	3.861
<i>F</i> (000)	1832
Crystal size, mm	0.30 × 0.10 × 0.10
2θ _{max} for the collected data	60.07
Index ranges for the collected data	−18 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 10
No. of measured reflections	703
No. of independent reflections	657 [<i>R</i> (int) = 0.0424]
No. of refined parameters	246
Goodness-of-fit on <i>F</i> ²	0.863
Final <i>R</i> factor, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0738, <i>wR</i> 2 = 0.1972
<i>R</i> factor (over the whole array)	<i>R</i> 1 = 0.0971, <i>wR</i> 2 = 0.2689
Δρ(max) and Δρ(min) (e Å ^{−3})	0.382 and −0.328
Extinction coefficient	0.00004(9)

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic parameters ($\text{\AA}^2 \times 10^3$) for CuL^3

Atom	Complex A				Complex B			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu(1)	3683(3)	3556(3)	4353(8)	86(3)	3661(3)	3444(4)	9375(8)	101(3)
S(1)	3408(6)	5443(6)	3666(18)	113(6)	2105(7)	4398(8)	9299(18)	153(7)
S(2)	5027(6)	2296(7)	4327(17)	131(6)	5423(6)	3773(7)	8729(17)	125(6)
N(1)	2965(11)	3784(15)	4544(25)	69(11)	3042(13)	3039(16)	9771(26)	83(13)
N(2)	2882(14)	4397(17)	4321(27)	81(12)	2529(15)	3301(17)	9772(27)	74(12)
N(3)	3858(17)	4372(12)	3927(26)	115(15)	3144(14)	4076(14)	9196(27)	95(14)
N(4)	3508(15)	2748(12)	4792(26)	83(12)	4135(18)	2780(17)	9589(29)	125(16)
N(5)	3960(14)	2341(16)	4761(26)	75(13)	4678(13)	2940(13)	9334(25)	47(10)
N(6)	4420(10)	3275(16)	4150(26)	74(12)	4321(11)	3876(15)	8980(24)	69(11)
N(7)	2040(17)	2626(18)	5453(35)	107(16)	3367(18)	1441(22)	10485(38)	136(18)
O(1)	1619(15)	2880(16)	5661(50)	143(15)	2886(18)	1355(17)	10730(57)	177(17)
O(2)	2086(14)	2133(16)	6113(50)	128(13)	3740(18)	1104(19)	10435(54)	176(17)
C(1)	3364(19)	4679(14)	4008(28)	103(20)	2619(16)	3866(18)	9417(28)	87(16)
C(2)	4366(16)	4554(22)	3655(30)	99(19)	3308(16)	4611(17)	8866(29)	67(16)
C(3)	4849(18)	4189(18)	3604(31)	90(17)	3866(15)	4804(19)	8622(31)	90(16)
C(4)	4868(17)	3575(19)	3842(29)	83(17)	4357(17)	4446(17)	8686(30)	89(18)
C(5)	4395(13)	2672(17)	4438(28)	75(15)	4768(13)	3510(17)	9038(26)	75(15)
C(6)	3032(15)	2489(18)	5080(30)	72(17)	3996(22)	2234(23)	9907(33)	158(26)
C(7)	2578(16)	2920(16)	5081(30)	58(14)	3410(17)	2082(20)	10143(32)	79(15)
C(8)	2474(15)	3560(18)	4847(20)	76(15)	2942(16)	2489(16)	10076(29)	54(14)
C(9)	2680(14)	5633(23)	3119(70)	139(21)	1463(17)	4001(23)	9235(71)	145(23)
C(10)	4795(21)	1586(18)	5010(72)	140(21)	5824(21)	3126(19)	8365(68)	166(25)
C(11)	2388(17)	5667(31)	5033(89)	222(34)	1342(28)	3775(38)	11258(101)	291(46)
C(12)	4999(48)	1442(35)	7070(103)	168(35)	6076(22)	2908(20)	10274(76)	155(24)
C(13)	1787(25)	5801(30)	4242(98)	206(30)	1050(52)	4287(50)	12267(192)	483(86)
C(14)	4852(77)	808(48)	6459(274)	340(75)	6442(25)	3304(27)	11538(93)	188(28)
C(12D)	4887(49)	1149(20)	3419(135)	168(35)	—	—	—	—
C(14D)	4501(68)	660(69)	2667(276)	340(75)	—	—	—	—

was removed under a reduced pressure. The residue was extracted into chloroform, the solvent was evaporated on a rotary evaporator, and the product was chromatographed on a column with silica gel. A 2 : 1 hexane–chloroform mixture was used as the eluent, and the first fraction was collected. The eluent was completely removed, and the resulting complex was studied. The elemental analysis data and the product yields are listed in Table 3.

A brown single crystal with dimensions $0.30 \times 0.10 \times 0.10$ mm was selected for an X-ray diffraction study. Experimental data were collected on a DAR-UMB diffractometer interfaced with an M-600 control computer using $\text{CuK}\alpha$ radiation and the ω scan mode.

The structure was solved by the heavy-atom method with the SHELX86 program package [28]. The propyl substituents at the sulfur atoms in complex A are disordered over two positions (marked by letter D in Tables 2 and 5). The structure was refined by least-squares calculations in the anisotropic approximation for the Cu and S atoms and in the isotropic approximation for the C, N, and O atoms with the SHELXL93 program package [29]. The hydrogen atoms were not revealed from a difference Fourier synthesis. The final *R* factor for 657 reflections with $I > 2\sigma(I)$ was 0.0738. The crystallographic data for structure **7** are given in Table 4, and the coordinates of the basis atoms and the U_{eq} are in Table 5.

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