

Copper(II) Complexes Based on 2-Thenoyltrifluoroacetone Aroyl Hydrazones: Synthesis, Spectroscopy, and X-ray Diffraction Analysis

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Abstract—Copper(II) complexes $\text{CuL} \cdot \text{NH}_3$ are synthesized by the interaction of ethanol solutions of *para*-substituted 2-thenoyltrifluoroacetyl methane aroyl hydrazones ($\text{H}_2\text{L}^1\text{—H}_2\text{L}^4$) and an aqueous-ammonia solution of copper(II) acetate in an equimolar ratio. The copper(II) complexes are studied by elemental analysis, IR spectroscopy, and EPR spectroscopy. Single crystals of $\text{CuL}^3 \cdot \text{NH}_3$ are grown from 1-(2-thenoyl)-3,3,3-trifluoroacetone *para*-methylbenzoyl hydrazone and studied using X-ray diffraction analysis (CIF file CCDC 1045841).

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INTRODUCTION

Hydrazones of fluorinated β -dicarbonyl compounds are presently leading among the organic ligands used for the synthesis of coordination compounds with metals. The introduction of the fluorine atom into the ligand molecules enhances their complexation activity or changes the range of action [1–3]. The results of studying complexes $\text{CuL} \cdot \text{NH}_3$ based on *para*-substituted 2-thenoyltrifluoroacetyl methane aroyl hydrazones (H_2L) are presented in this work.

EXPERIMENTAL

Synthesis of complex $\text{CuL}^1 \cdot \text{NH}_3$ (I). A hot solution of 1-(2-thenoyl)-3,3,3-trifluoroacetone benzoyl hydrazone (H_2L^1) (0.34 g, 0.001 mol) in ethanol (30 mL) was poured into a 100-mL round-bottom flask, and an aqueous-ammonia solution of copper(II) acetate (0.2 g, 0.001 mol) was added with stirring. The reaction mixture in the flask was heated with a reflux condenser for 30 min. In 48 h, a green precipitate was filtered off, washed with water and ethanol, and dried in air. The yield of product **I**, $\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_2\text{SF}_3\text{Cu}$, was 0.27 g (65%). Single crystals of compound **I** were obtained the recrystallization of the complex from ethanol.

Other complexes, $\text{CuL}^2 \cdot \text{NH}_3\text{—CuL}^4 \cdot \text{NH}_3$ (**II—IV**), were synthesized similarly. The elemental analysis results, yields, and melting points of the complexes are presented in Table 1.

The EPR spectra of the polycrystalline samples and solutions in toluene were recorded on an SE/X-2542 radiospectrometer (Radiopan) with a working frequency of 9.4 GHz. The magnetic field was calibrated using an NMR magnetometer.

The X-ray diffraction analysis of complex $\text{CuL}^3 \cdot \text{NH}_3$ (**III**) was carried out on a Bruker P4 automated diffractometer ($\lambda(\text{MoK}\alpha)$ radiation, graphite monochromator, ω scan mode, $2\theta_{\text{ma}} = 50^\circ$). The θ scan mode ranged from 2.5° to 25° , the ranges of indices were $-8 \leq h \leq 9$, $-14 \leq k \leq 15$, $0 \leq l \leq 11$, and the crystal sizes were $0.1 \times 0.2 \times 0.4$ mm. The structure was solved by a direct method with the total number of measured reflections 3190 and refined by full-matrix least squares in the anisotropic approximation of non-hydrogen atoms for 2840 independent reflections ($R_{\text{int}} = 0.0603$) with 266 refinement parameters; GOOF = 1.092 (SHELXL [4], Olex2) [5]. The hydrogen atoms were localized from difference syntheses and refined isotropically. The R factors were $R_1 = 0.052$, $wR_2 = 0.153$ for reflections with $I > 2\sigma(I)$. The residual electron density was $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.99/-0.63 \text{ e}/\text{\AA}^3$.

The coordinates of atoms and other parameters for complex **II** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1045841; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Elemental analysis results, yields, and melting points of the Cu(II) complexes based on 1-(2-thenoyl)-3,3,3-trifluoroacetone benzoyl hydrazones

Compound	Empirical formula	$T_m, ^\circ\text{C}$	Yield, %	Content (found/calculated), %		
				M	C	H
$\text{CuL}^1 \cdot \text{NH}_3$ (I)	$\text{CuC}_{15}\text{H}_{12}\text{N}_3\text{O}_2\text{SF}_3$	235	65	15.02/15.17	42.85/43.01	2.60/2.89
$\text{CuL}^2 \cdot \text{NH}_3$ (II)	$\text{CuC}_{16}\text{H}_{14}\text{N}_3\text{O}_3\text{SF}_3$	*	75	14.00/14.16	42.60/42.81	3.10/3.14
$\text{CuL}^3 \cdot \text{NH}_3$ (III)	$\text{CuC}_{16}\text{H}_{14}\text{N}_3\text{O}_2\text{SF}_3$	261	78	14.50/14.68	44.33/44.39	2.15/3.26
$\text{CuL}^4 \cdot \text{NH}_3$ (IV)	$\text{CuC}_{15}\text{H}_{11}\text{N}_3\text{O}_2\text{SClF}_3$	248	67	13.97/14.02	39.61/39.74	2.36/2.45

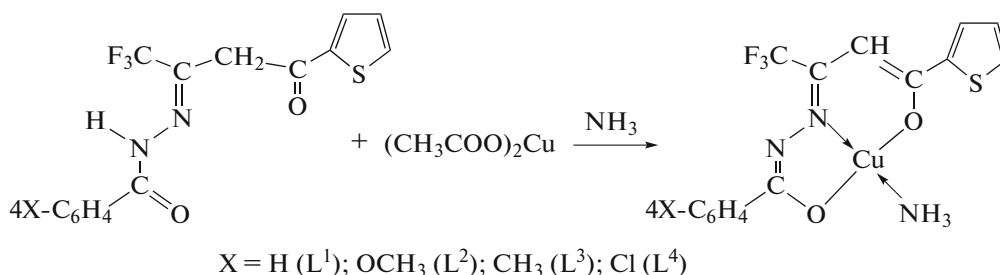
* Melting with decomposition.

RESULTS AND DISCUSSION

We studied the condensation reaction and the tautomeric behavior of the condensation products of the reactions of aromatic acid hydrazides with 1,3-diketone bearing the trifluoromethyl group as a strong electron-accepting substituent and the electron-donating thienyl group [3, 6, 7]. The chosen β -dicarbonyl compound is nonsymmetric. Its reactions with nucleophilic reagents can result in the formation of positional isomers. The reaction of 1-(2-thenoyl)-3,3,3-trifluoroacetone with aromatic acid hydrazides, $\text{NH}_2\text{NHCOC}_6\text{H}_4\text{X}-4$, under mild conditions (ethanol as a reaction medium, room temperature, without catalysts), results, as indicated earlier, in the condensation products at trifluoroacetyl carbonyl,

which has a hydrazone structure in the crystalline state [3, 6, 8–10].

The interaction of equimolar amounts of an aqueous-ammonia solution of copper(II) acetate and an ethanolic solution of 1-(2-thenoyl)-3,3,3-trifluoroacetone aroyl hydrazones afforded copper(II) complexes $\text{CuL}^n \cdot \text{NH}_3$, where L^n is doubly deprotonated residues of ligands $\text{H}_2\text{L}^1-\text{H}_2\text{L}^4$. The compositions and structures of the synthesized inner-complex compounds were established by elemental analysis, IR and EPR spectroscopy, and X-ray diffraction analysis (for complex II). According to the IR and EPR spectral data, the synthesized inner-complex copper(II) compounds in the solid state and in solution have the following structure:



The IR spectra of complexes $\text{CuL}^n \cdot \text{NH}_3$ have no absorption bands in ranges of 1660–1670 and 3400 cm^{-1} characteristic of free compounds $\text{H}_2\text{L}^1-\text{H}_2\text{L}^4$. This indicates the deprotonation of the ligands upon complex formation. The absorption bands at 3344–3382 cm^{-1} are characteristic bands in the spectrum and are due to symmetric and antisymmetric stretching vibrations of the coordinated molecule NH_3 . The IR spectra exhibit a series of bands of medium and strong intensity at 1068–1075, 1494–1507, 1523–1532, and 1570–1600 cm^{-1} corresponding to the stretching, bending, and stretching–bending vibrations of the formally ordinary and double bonds in the five- and six-membered metallocycles, which is consistent, on the whole, with the proposed structure

[1–3, 6, 7]. The IR spectra of complexes II–IV are identical, to many respects, with the IR spectra of the earlier studied copper(II) complexes [1, 3, 6, 7].

The conclusions about the structures of the copper(II) complexes made on the basis of the results of the IR spectra were supplemented by the EPR spectral data. According to these data, the synthesized inner-complex Cu(II) compounds in chloroform and toluene solutions have the EPR spectra characteristic of the mononuclear copper(II) complexes with the square structure. They are similar to the spectra of the previously studied compounds and represent a superposition of the ^{63}Cu and ^{65}Cu EPR spectra ($I_{\text{Cu}} = 3/2$).

The isotropic EPR spectra are described by the symmetric spin-Hamiltonian of type (1) with four

hyperfine structure (HFS) lines from equally remote components with different intensities and linewidths

$$\bar{H} = g\beta H_0 S + \langle a_{\text{Cu}} \rangle I_{\text{Cu}} S + a_{\text{Nj}} I_{\text{Nj}} S, \quad (1)$$

where $S = 1/2$, β is Bohr's magneton for electron, $I_{\text{Cu}} = 3/2$ is the spin of the copper atom nucleus, and I_{Nj} is the spin of the nitrogen atom nucleus. The lines from two isotopes ^{63}Cu and ^{65}Cu are manifested on the narrowest high-field component (Table 2, Fig. 1) [1, 3, 6, 7, 11].

A small linewidth of the HFS lines should be mentioned along with the improvement of the resolution for the lines of an additional hyperfine structure (AHFS) in the EPR spectra of the complexes compared to the earlier studied similar complexes with the coordination sphere $\text{Cu}[\text{N}_2, \text{O}_2]$. The observed changes in the EPR parameters should be explained by different electronic natures of the oxygen and sulfur atoms, since the sulfur atom of the thienyl core, which is present in the organic ligand, has a free d orbital, unlike oxygen. The presence of two conjugated five- and six-membered metallocycles, regardless of the nature of the coordinated atoms, in the copper(II) complexes leads to a planar configuration. Therefore, the changes observed in the parameters of the EPR spectrum (g factor and HFS and AHFS constants; Table 2, Fig. 1) should be explained by different electronic natures of the substituents in position 4 of the phenyl substituent of the benzoyl moiety of the ligand. In compounds **II** and **III**, the *para*-positions of the phenyl core contain the OCH_3 and CH_3 substituents, respectively, which weakly affect the spin-Hamiltonian parameters. It is well known that the replacement of far-range substituents by more electron-donating groups results in an increase in the g factor and a decrease in the HFS constant (Table 2). For example, the appearance of the chlorine atom in position 4 of the phenyl ring in complex **IV** improves the resolution of the g factor and HFS constant in the EPR spectrum compared to the spectrum of compound **III** due to the mesomeric effect. Since, unlike the CH_3 group, the free electron pairs of the chlorine atom enter into the p - π - π conjugation with the phenyl ring and further with the pseudo-aromatic five-membered metallocycle of the coordination polyhedron, they thus enhance the electron-donor properties of the nitrogen and oxygen atoms of the hydrazide moiety of the dianion in ligand L^n . These conclusions are confirmed by the spin-Hamiltonian parameters (Table 2) and the degree of covalence of the copper–ligand bond ($\alpha^2 = 0.82$ – 0.85) calculated from the isotropic EPR parameters using the known equation (Eq. (2)) [11]

$$\alpha^2 = \frac{1}{0.43} \left(\frac{a_{\text{Cu}}}{0.036} + g - 2 \right) + 0.02. \quad (2)$$

The coefficients α and α' at the atomic orbitals of copper ($d_{x^2-y^2}$) and coordinated atoms of the ligands characterize the degree of covalence of the copper–

Table 2. EPR spectral parameters of the copper(II) complexes in a toluene solution at 293 K

Compound	$\langle g \rangle \pm 0.001$	$a_{\text{Cu}}, \text{cm}^{-1}$	$a_{\text{N}} \pm 0.1 \text{ Oe}$	α^2	$(\alpha')^2$
I	2.102	93	11.3	0.85	0.15
II	2.099	92.19	9.4	0.83	0.17
III	2.101	89.9	7.8	0.82	0.18
IV	2.104	87.54	12.4	0.82	0.18

ligand bond. If α^2 and $(\alpha')^2$ are equal to 0.5, the metal–ligand bond is purely covalent. In the case where $\alpha^2 = 1$ and $(\alpha')^2 = 0$, the bond is ionic. The coefficient α can be expressed through its square as the density of the probability of unpaired electron residence on the orbital $|x^2 - y^2\rangle$. Then, the value of $(\alpha')^2$ naturally determines the degree of localization of the unpaired electron on the orbital of the ligand atoms. The values of coefficients α^2 and $(\alpha')^2$ indicate that in compounds **I**–**IV** the degree of covalence of the Cu–N bond changes substantially, depending on the nature of substituents in the benzene ring. The degree of covalence for complex **I** is maximum ($\alpha^2 = 0.85$), whereas for compounds **I**–**IV** it decreases insignificantly (Table 2).

The conclusions about the planar structure of copper(II) complexes **I**–**IV** with the tridentate coordination mode of dianion L^n , which were made on the

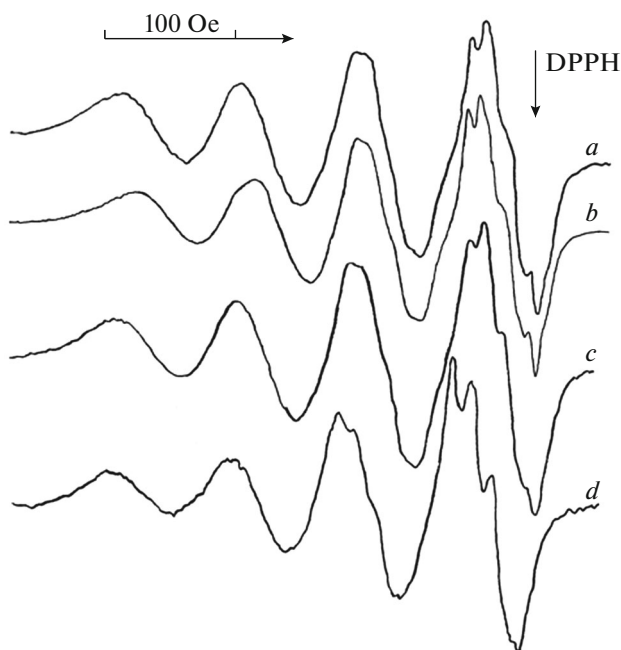


Fig. 1. EPR spectra of complexes (a) **I**, (b) **II**, (c) **III**, and (d) **IV** in a toluene solution at 293 K.

Table 3. Selected bond lengths and bond angles in molecule **III**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cu–O(1)	1.900(3)	O(1)–C(5)	1.294(5)
Cu–N(1)	1.913(4)	O(2)–C(9)	1.307(5)
Cu–O(2)	1.940(3)	N(1)–C(7)	1.319(5)
Cu–N(3)	1.980(4)	N(1)–N(2)	1.403(5)
S–C(1)	1.672(6)	N(2)–C(9)	1.307(5)
S–C(4)	1.702(4)		
Angle	ω , deg	Angle	ω , deg
O(1)CuN(1)	94.85(14)	C(7)N(1)Cu	125.6(3)
O(1)CuO(2)	175.83(12)	N(2)N(1)Cu	115.1(3)
N(1)CuO(2)	81.25(13)	C(9)N(2)N(1)	109.2(3)
O(1)CuO(2)	175.83(12)	C(2)C(1)S	113.3(4)
N(1)CuO(2)	81.25(13)	C(3)C(4)S	112.2(3)
O(1)CuN(3)	88.58(17)	C(5)C(4)S	122.9(3)
N(1)CuN(3)	176.06(18)	O(1)C(5)C(6)	125.6(4)
O(2)CuN(3)	95.37(17)	O(1)C(5)C(4)	114.4(4)
O(2)CuN(3)	95.37(17)	N(1)C(7)C(6)	123.0(4)
C(1)SC(4)	92.6(3)	N(1)C(7)C(8)	118.8(4)
C(5)O(1)Cu	124.7(3)	N(2)C(9)O(2)	123.9(4)
C(9)O(2)Cu	110.5(2)	N(2)C(9)C(10)	117.4(4)
C(7)N(1)N(2)	119.2(3)	O(2)C(9)C(10)	118.7(3)

basis of the results of IR and EPR spectroscopy, were unambiguously confirmed by X-ray diffraction analysis for the grown single crystal of compound **III**. The crystals of $C_{16}H_{14}N_3O_2F_3SCuH_2O$ are triclinic ($FW = 450.92$): $a = 7.7000(15)$, $b = 12.977(3)$, $c = 9.567(6)$ Å, $\alpha = 80.40(3)^\circ$, $\beta = 84.07(3)^\circ$, $\gamma = 74.12(3)^\circ$, $V = 904.9(6)$ Å³, $\rho_{\text{calcd}} = 1.655$ g/cm³, $Z = 2$, space group $P\bar{1}$.

In molecule **III**, the copper atom is localized at the center of the square polyhedron consisting of the tri-

dentate (O,O,N) ligand L^3 (Cu–O(1) 1.900(3), Cu–O(2) 1.940(3), Cu–N(1) 1.913(4) Å) and N(3) atom of the NH₃ molecules (Cu–N(3) 1.980(4) Å, Table 3). A difference of 0.067 Å between the Cu–N(1) and Cu–N(3) bond lengths is explained by the chelate effect for the tridentate ligand L^3 and is consistent with the differences in chemical bonds of similar complexes [2, 3, 6, 12–16]. The deviation of the bond angles from 90° is explained by the sizes of the five- and six-membered metallocycles and the conjugation system (Table 3).

Table 4. Deviations of atoms from the “mean” planes in structure **III**

Atom and its deviation, Å								
Cu	O(1)	O(2)	N(1)	N(3)	N(2)*	C(5)*	C(7)*	C(9)*
0.0045	0.0279	0.0291	–0.0323	–0.0291	–0.0662	–0.0926	–0.0418	–0.0436
Cu	O(1)	N(1)	C(5)	C(6)	C(7)	O(2)*	N(2)*	C(4)*
–0.0215	0.0443	–0.0078	–0.0296	–0.0147	0.0293	–0.0365	–0.0575	–0.1259
Cu	O(2)	N(1)	N(2)	C(9)	N(3)*	C(7)*	C(10)*	
–0.0136	0.0175	0.0129	–0.0035	–0.0134	–0.1127	0.0305	–0.0869	
C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	C(9)*	C(16)*	
–0.0067	–0.0008	0.0060	–0.0035	–0.0041	0.0093	–0.0550	–0.0126	
S	C(1)	C(2)	C(3)	C(4)	C(5)*			
–0.0110	–0.0021	0.0158	–0.0236	0.0209	0.0466			

* Atoms omitted from the calculation of the plane.

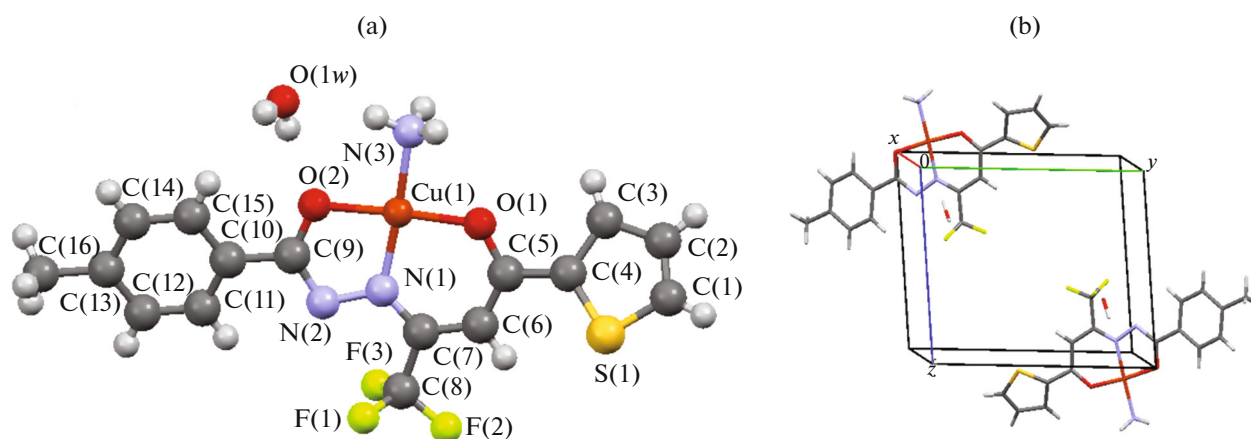


Fig. 2. (a) Crystal structure and (b) molecular packing of the cell of complex **III**.

An analysis of the bond lengths in the $(L^3)^{2-}$ ligand shows that the C(9)–C(10) and N(1)–C(7) bonds are predominantly double (Table 3). In the molecule of the complex, the distance metal–phenoxide oxygen atom (Cu–O(2)) is somewhat longer than the distances metal– α -oxyazine oxygen atom (Cu–O(1)) (Table 3, Fig. 2a), which correlates with the values for other similar complexes with chelating ligands [2, 3]. The CuO(1)O(2)N(1)N(3) polyhedron is nearly planar (within 0.0296 Å). The five- and six-membered metalocycles are almost coplanar. The deviation of the atoms from the root-mean-square planes is 0.0130 and 0.0272 Å, respectively, and the dihedral angle between the planes of the metalochelates is 1.373° (Table 4). The O(1)Cu(N(1)N(2)) torsion angle is 1.9°. The benzene ring and five-membered metalocycle CuO(2)C(9)N(2)N(1) are somewhat turned out relative to each other (dihedral angle 13.943°), which is indicated by the values of torsion angles O(2)C(9)C(10)C(11) 167.7(4)° and O(2)C(9)C(10)C(15) –13.5(6)°. The planes of the six-membered metalocycle and thienyl ring are also turned out relative to each other, which is indicated by the values of torsion angles S(1)C(4)C(5)O(1) and S(1)C(4)C(5)C(6) (156.7(3)° and 23.8(6)°, respectively) [2, 3, 14–16].

The molecular packing in crystal **III** is shown in Fig. 2b. Water of crystallization participates in the intermolecular hydrogen bonds O(1w)–H(2w)⋯O(2) (x, y, z) and O(1w)–H(1w)⋯N(2) ($-x, -y + 1, -z$) (O(1)–H(2) 0.82(1), H(2)⋯O(2) 2.06(2), O(1)⋯O(2) 2.857(5) Å, angle O(1)–H(2)⋯O(2) 166(8)°; O(1)–H(1) 0.82(1), H(1)⋯N(2) 2.44(3), O(1)⋯N(2) 3.211(6) Å, angle O(1)–H(1)⋯N(2) 156(6)°). The molecules in the cell are arranged according to the centered motif along the x axis.

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