

Copper(I) Nitrate Complexes. Synthesis and Crystal Structure of $[\text{Cu}_2(\mu\text{-DATU})_2(\text{DATU})_4](\text{NO}_3)_2$ (DATU = *N,N'*-Diallylthiourea)

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Abstract—Crystal complex $[\text{Cu}_2(\mu\text{-DATU})_2(\text{DATU})_4](\text{NO}_3)_2$ (DATU = *N,N'*-diallylthiourea) is obtained by an electrochemical synthesis on copper electrodes, and its crystal structure is determined [CAD-4 diffractometer, rotating copper anode, space group *C2/c*, $a = 28.824(3)$, $b = 11.831(1)$, $c = 18.238(2)$ Å, $\beta = 101.777(5)^\circ$, $Z = 8$, $R = 0.071$ for 1672 reflections]. The ligand molecules are coordinated to the copper atoms solely through the sulfur atoms. The centrosymmetric Cu_2S_2 core is formed due to one (bridging) of the three independent DATU molecules. The copper(I) atoms have a slightly distorted tetrahedral environment. The $[\text{Cu}_2(\text{DATU})_6]^{2+}$ and NO_3^- ions are joined together by the short contacts of the $\text{N}\cdots\text{H}\cdots\text{ONO}_2$ type [$\text{N}\cdots\text{O}$ 2.81(1)–2.94(1) Å]. A comparative analysis of the ligand affinity to the central atom is carried out for the copper(I) nitrate complexes.

Although copper(I) nitrate was not obtained in the free state, several CuNO_3 complexes, e.g., with organic nitriles are known [1–3]. The Cu(I) state is stabilized by the tetrahedral coordination due to the N atoms of cyano groups, while the nitrate ions occupy the outer coordination sphere of Cu(I). Our previous studies of a series of copper(I) nitrate π -complexes with diallylcyanamide $\{\text{CuNO}_3 \cdot (\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NCN}$ [4], diallylamine $\{\text{CuNO}_3 \cdot (\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}$ (A and B modifications) [5, 6] and $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}_2][\text{Cu}(\text{NO}_3)_2]$ [7], and allylcyanide $\{\text{CuNO}_3 \cdot \text{CH}_2=\text{CH}-\text{CH}_2-\text{CN}$ [8] have shown that CuNO_3 can also be stabilized by the Cu(I)–(C=C) interaction. The distorted tetrahedral coordination sphere of copper(I) is formed by the C=C, N(\equiv C), N(H), and O(NO_2)[–] ligands, which can compete with each other. As a consequence, the C=C bond is not necessarily involved in the π interaction (one of the olefin groups is not coordinated in the complex with diallylcyanamide), whereas the NO_3^- group can act both as an equatorial and a somewhat distant axial ligand. Thus, the simultaneous coordination of the C=C bond and nitrate ion to copper(I) results in the formation of the π -complexes having predominantly molecular structure. As to the thiocarbonyl group, whose sulfur atom exhibits a rather high affinity to Cu(I), its presence results in the formation of the typically ionic compounds containing outer-sphere NO_3^- anions. An example of such behavior of copper(I) is the π -complex $[\text{Cu}(\text{C}_3\text{H}_5\text{NHC}(\text{S})\text{NH}_2)(\text{CH}_3\text{CN})]\text{NO}_3$, in which the trigonal-pyramidal coordination sphere of Cu(I)

includes, along with the C=C bond, two sulfur atoms (in equatorial and axial positions) and the nitrile nitrogen atom of the acetonitrile molecule [9]. The allylthiourea (ATU) molecule functions as a chelating π , σ ligand coordinated to the copper atom through both the C=C bond and sulfur atom. However, being a strong donor, the sulfur atom can displace other ligands from the coordination sphere of Cu(I). This occurs, e.g., in the 1 : 3 complex of copper(I) nitrate with ATU, $[\text{Cu}(\text{C}_3\text{H}_5\text{NHC}(\text{S})\text{NH}_2)_3]\text{NO}_3$ [9], in which the planar-trigonal environment of the Cu(I) atom is comprised of the sulfur atoms alone.

To continue investigations into the competition of ligands in the complexes of CuNO_3 , the compound of copper(I) nitrate with *N,N'*-diallylthiourea, $[\text{Cu}(\text{C}_3\text{H}_5\text{NHC}(\text{S})\text{NHC}_3\text{H}_5)_3]\text{NO}_3$ (**I**), was synthesized and structurally characterized.

EXPERIMENTAL

N,N'-Diallylthiourea (DATU) was obtained by treating a water–alcohol solution of allylthiocyanate with an ethanolic solution of allylamine [10]. Complex **I** was synthesized via the ac ($U = 0.4$ V) electrochemical (using copper electrodes) reduction of a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and DATU in acetonitrile. The air stable crystals of **I** were grown as prisms during the electrolysis of the solution for 24 h and upon cooling to -10°C .

The crystallographic data and data collection parameters for complex **I** are summarized in Table 1.

Table 1. Crystallographic data and summary of X-ray data collection for complex **I**

Parameter	I
<i>M</i>	594.3
Crystal size, mm	0.06 × 0.09 × 0.09
Space group	<i>C2/c</i>
<i>a</i> , Å	28.824(3)
<i>b</i> , Å	11.831(1)
<i>c</i> , Å	18.238(2)
β, deg.	101.777(5)
<i>V</i> , Å ³	6088(1)
<i>Z</i>	8
ρ(calcd), g/cm ³	1.2967(4)
Diffractometer, temperature	CAD-4; 293 K
Radiation	CuK _α (rotating anode)
Scan technique	ω/2θ
2θ range, deg	3 < 2θ < 140
Number of reflections:	
measured	4886
independent	4758
used for structure solution (<i>F</i> ≥ 4σ <i>F</i>)	1672
<i>F</i> (000)	2496
μ _{Cu} , cm ⁻¹	31.41
Number of refined parameters	316
<i>R</i>	0.071
<i>R</i> _w	0.072
Weighting scheme	[σ(<i>F</i> _o) ² + 0.001 <i>F</i> _o ²] ⁻¹
GOOF	1.45

The structure was solved using the array of diffraction data collected on a single-crystal CAD-4 diffractometer at room temperature. The intensities of reflections were corrected for Lorentz and polarization effects, and absorption correction was applied using the DIFABS program. The positions of all non-hydrogen atoms were determined by the direct method and subsequent Fourier syntheses. The structure was refined in the full-matrix anisotropic approximation using the CSD program package [11].

Coordinates of atoms and their thermal parameters for structure **I** are listed in Table 2, and selected bond lengths and angles are given in Table 3.

RESULTS AND DISCUSSION

Typically ionic compound **I** is composed of the dimeric complexed [Cu₂(μ-DATU)₂(DATU)₄]²⁺ cations and NO₃⁻ anions. The DATU molecules are coordinated to copper solely through the sulfur atoms. One

of the three independent DATU molecules, which functions as a bridge owing to the sulfur atom, is involved in the formation of the centrosymmetric Cu₂S₂ core. The Cu–Cu distance in the dimer is 2.836(4) Å. The polyhedra of the copper(I) atoms (slightly distorted tetrahedra) are arranged in pairs by the sharing of the S(3)–S(3)' edge (figure). The Cu–S distances are different; they are somewhat shortened for the terminal DATU molecule [Cu–S(1) 2.298(5) Å and Cu–S(2) 2.288(5) Å] and elongated for μ-DATU [Cu–S(3) 2.367(5) Å and Cu–S(3)' 2.431(4) Å].

The three-dimensional structure is formed owing to the rather short N–H...ONO₂⁻ contacts combining the [Cu₂(DATU)₆]²⁺ cations and NO₃⁻ anions [N...O 2.81(1)–2.94(1) Å].

Inasmuch as the metal atoms are not coordinated by the C=C bond of the DATU molecules, the latter are not

Table 2. Coordinates of atoms and thermal parameters* for structure **I**

Atom	x	y	z	$B_{eq}, \text{\AA}^2$
Cu	0.29465(6)	0.2113(2)	0.4890(1)	5.51(7)
S(1)	0.3587(1)	0.2841(3)	0.5717(2)	5.5(1)
S(2)	0.3050(1)	0.0912(3)	0.3954(2)	5.8(1)
S(3)	0.2539(1)	0.1398(3)	0.5795(2)	4.9(1)
O(1)	0.8867(3)	0.1779(7)	0.4424(6)	7.8(4)
O(2)	0.9554(3)	0.2382(9)	0.4478(7)	10.8(5)
O(3)	0.9399(4)	0.0692(9)	0.4191(8)	13.4(6)
N(1)	0.9272(3)	0.1590(9)	0.4362(7)	7.2(4)
N(11)	0.4497(3)	0.3294(8)	0.5706(6)	6.3(4)
N(12)	0.4044(3)	0.2659(8)	0.4591(6)	5.7(4)
N(21)	0.3624(4)	-0.004(1)	0.5119(7)	7.3(5)
N(22)	0.3524(4)	-0.105(1)	0.3986(7)	8.3(5)
N(31)	0.2212(3)	-0.0218(7)	0.4820(5)	5.1(4)
N(32)	0.1823(3)	-0.0069(8)	0.5828(6)	5.4(3)
C(10)	0.4062(4)	0.294(1)	0.5295(7)	5.0(4)
C(11)	0.4572(5)	0.356(1)	0.6528(8)	8.5(6)
C(12)	0.4514(7)	0.478(2)	0.669(1)	12(1)
C(13)	0.4450(8)	0.556(2)	0.624(1)	14(1)
C(14)	0.4450(5)	0.276(1)	0.4254(8)	7.8(6)
ë(15)	0.4249(8)	0.229(2)	0.348(1)	18(1)
C(16)	0.4325(8)	0.240(2)	0.297(1)	17(1)
C(20)	0.3431(4)	-0.013(1)	0.440(1)	5.9(5)
C(21)	0.3973(6)	-0.086(1)	0.552(1)	11.3(8)
C(22)	0.4381(8)	-0.032(2)	0.571(2)	23(1)
C(23)	0.4688(7)	0.008(2)	0.607(2)	20(1)
C(24)	0.3298(7)	-0.123(1)	0.317(1)	10.1(8)
C(25)	0.3641(9)	-0.118(2)	0.267(1)	12(1)
C(26)	0.4077(9)	-0.103(2)	0.286(2)	15(1)
C(30)	0.2145(3)	0.0284(8)	0.5452(7)	4.2(4)
C(31)	0.1871(5)	-0.110(1)	0.4493(9)	8.5(6)
C(32)	0.2042(7)	-0.166(2)	0.398(1)	15(1)
C(33)	0.2083(7)	-0.264(2)	0.374(1)	12.6(9)
C(34)	0.1753(5)	0.044(1)	0.6544(7)	6.6(5)
C(35)	0.2012(6)	-0.029(1)	0.7181(9)	8.1(6)
C(36)	0.1778(8)	-0.087(1)	0.761(1)	10.6(8)

$$* B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \hat{a}_i \hat{a}_j.$$

fixed in the structure, leading to a noticeable increase in the thermal parameters of the carbon atoms (Table 2) and apparent distortion of the geometry of allyl groups. For the same reason, the hydrogen atoms were not located, and the discrepancy factor was rather high.

The conjugation of the electron lone pairs of the nitrogen atoms with the double bond of the neighboring thiocarbonyl group of the DATU molecule causes planar configuration of the amido group. Accordingly, two torsion CNCS angles in each of the three independent

ligand molecules are close to 0° and 180°. The planar structure of this fragment is evidence for a considerable p, π conjugation of the amido and thiocarbonyl groups, which renders N–C(=S) bonds, in effect, sesquialternal [1.32(2)–1.39(2) Å]. The occurrence of *cis* and *trans* conformations with respect to these bonds in the DATU molecules is caused by the steric factors.

Compound **I** structurally resembles the copper(I) hexafluorosilicate complex [Cu₂(μ-ATU)₂(ATU)₄]SiF₆ (**II**) [12]. In both structures, Cu(I) is coordinated only

Table 3. Selected bond lengths and angles in structure **I**

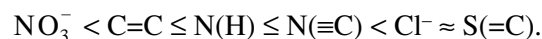
Bond	<i>d</i> , Å	Angle	ω , deg.
Cu–S(1)	2.298(5)	S(1)CuS(2)	120.8(2)
Cu–S(2)	2.288(5)	S(1)CuS(3)	97.1(2)
Cu–S(3)	2.367(5)	S(1)CuS(3)'	111.5(2)
Cu–S(3)'	2.431(4)	S(2)CuS(3)	117.2(2)
		S(2)CuS(3)'	102.4(2)
		S(3)CuS(3)'	107.6(2)
N(1)–O(1)	1.22(1)	O(1)N(1)O(2)	117(1)
N(1)–O(2)	1.23(1)	O(1)N(1)O(3)	123(1)
N(1)–O(3)	1.19(1)	O(2)N(1)O(3)	120(1)
S(1)–C(10)	1.71(1)	CuS(1)C(10)	110.0(4)
C(10)–N(11)	1.39(2)	S(1)C(10)N(11)	119.9(9)
C(10)–N(12)	1.32(2)	S(1)C(10)N(12)	123.0(9)
		N(11)C(10)N(12)	117(1)
N(11)–C(11)	1.50(2)	C(10)N(11)C(11)	122(1)
N(12)–C(14)	1.43(2)	C(10)N(12)C(14)	122(1)
S(2)–C(20)	1.74(2)	CuS(2)C(20)	104.8(5)
C(20)–N(21)	1.32(2)	S(2)C(20)N(21)	121(1)
C(20)–N(22)	1.38(2)	S(2)C(20)N(22)	119(1)
		N(21)C(20)N(22)	121(1)
N(21)–C(21)	1.48(2)	C(20)N(21)C(21)	123(1)
N(22)–C(24)	1.51(2)	C(20)N(22)C(24)	124(1)
S(3)–C(30)	1.77(1)	CuS(3)Cu'	72.4(1)
		CuS(3)C(30)	113.3(4)
		Cu'S(3)C(30)	95.6(4)
C(30)–N(31)	1.35(1)	S(3)C(30)N(31)	115.9(8)
C(30)–N(32)	1.33(1)	S(3)C(30)N(32)	121.2(8)
		N(31)C(30)N(32)	123(1)
N(31)–C(31)	1.48(2)	C(30)N(31)C(31)	117(1)
N(32)–C(34)	1.49(2)	C(30)N(32)C(34)	124(1)

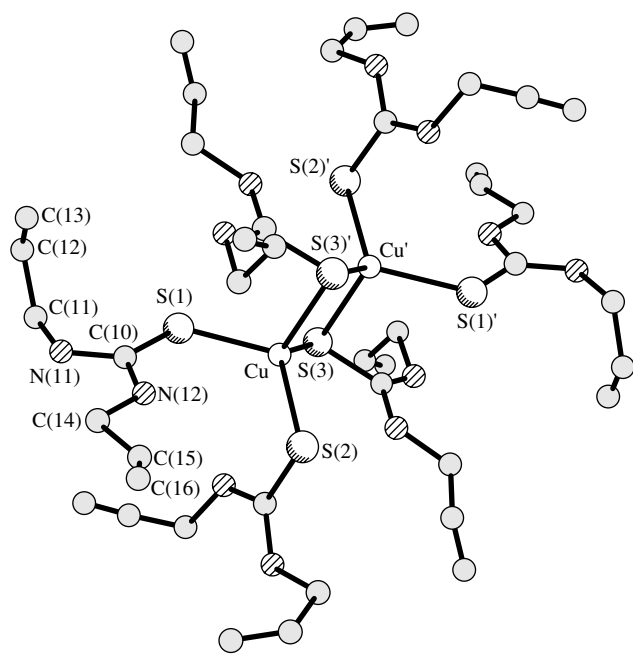
by the sulfur atoms and forms similar dimeric cations, but, in addition to the centrocymmetric $[\text{Cu}_2(\text{ATU})_6]^{2+}$ cation, **II** contains one more independent cation (on the twofold axis). The SiF_6^{2-} anion, like NO_3^- in **I**, is located in the outer coordination sphere of Cu(I), but forms a three-dimensional structural framework through the hydrogen bonds. In the $[\text{Cu}(\text{ATU})_3]\text{NO}_3$ (**III**) complex [9], the NO_3^- ion plays the same role.

These data confirm that the oxygen atoms of the NO_3^- ion are virtually incapable of being coordinated to copper(I) in the presence of the S atoms of S(=C) group. Likewise, the Cl atom in the structure of the π complex $[\text{Cu}_2\text{Cl}_2(\text{allylammonium})_2](\text{NO}_3)_2$ displaces the NO_3^- ion in the outer coordination sphere [13]. In this complex, Cu(I) is coordinated by the C=C bond and two

chlorine atoms, while the displaced nitrate ion, as in **I–III**, stabilizes the structure by the hydrogen bonds $\text{N–H}\cdots\text{ONO}_2^-$. In the presence of the less competitive ligands such as C=C or N(\equiv C), the NO_3^- ion exhibits several coordination modes (η^1 , μ - η^1 , and μ - η^2), thus adapting to the metal center. At the same time, the tendency of the amino group to form a branched system of hydrogen bonds $\text{N–H}\cdots\text{O}$ enhances the ionic character of the complex, favoring increase in the distance between the NO_3^- anion and the central atom [Cu–O 2.271(4)–2.352(3) Å] [4–8].

Thus, the ability of ligands to be coordinated to copper(I) in the copper(I) nitrate complexes increases in the order:





Dimeric cation $[\text{Cu}_2(\mu\text{-DATU})_2(\text{DATU})_4]^{2+}$ in structure I.

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