

The First π Complex of Copper(I) Sulfate: Synthesis and Crystal Structure of $[\text{Cu}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)(\text{SO}_4)]$

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Abstract—The crystals of $[\text{Cu}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)(\text{SO}_4)]$ were obtained by an ac electrochemical synthesis from *N,N'*-diallylguanidinium sulfate (which undergoes hydrolysis) and an ethanol solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The title compound was structurally characterized with the use of a twin crystal (a DARC α diffractometer, $\text{MoK}\alpha$ radiation, space group $P2_1/n$, $a = 13.288(4)$ Å, $b = 4.976(3)$ Å, $c = 9.932(2)$ Å, $\gamma = 97.47(4)^\circ$, $V = 651.1(5)$ Å 3 ; $Z = 4$, $R = 0.037$ from 761 reflections with $F \geq 2\sigma(F)$). The copper(I) atom has a trigonal-pyramidal environment made by three oxygen atoms from different sulfate groups and the C=C bond in the equatorial plane. The coordinated C=C bond length is equal to 1.38(1) Å. The structure is built from chains arranged along the [010] axis, in which the SO_4^{2-} anion coordinates with three metal atoms through two oxygen atoms. Effective charges on atoms were calculated to elucidate the role of the N–H...O hydrogen bonds in the sulfate anions functioning as acidoligands.

In coordination chemistry, the guanidinium salts are known to favor crystallization of complexes by stabilizing them via the system of strong hydrogen bonds. In its turn, the formation of hydrogen bonds is favored by hard bases (strong acid anions) present in the structure. The guanidinium salts can be used to obtain both new π complexes of copper(I) nitrate, whose numerous representatives have been described in [1], and the previously unknown π complexes of copper(I) or silver(I) sulfates. For this reason, the *N,N'*-diallylguanidinium sulfate $(\text{DAGUH}^+)_2\text{SO}_4$ was used as the starting ligand. Synthesis was carried out by the ac electrochemical method that yields crystalline π complexes with ionic copper(I) salts. However, X-ray diffraction analysis of the product showed that its π ligand is the known allyl-ammonium cation (AAH^+) [2] resulting from the hydrolysis of DAGUH^+ , while the obtained complex is the first π complex of copper(I) sulfate, $[\text{Cu}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)(\text{SO}_4)]$ (**I**). The conformational lability and the lack of large substituents in the AAH^+ cation make it possible to elucidate the ligand properties of the sulfate anion in a new group of copper(I) π complexes.

EXPERIMENTAL

The *N,N'*-diallylguanidinium sulfate $(\text{DAGUH}^+)_2\text{SO}_4$ was synthesized from the *N*-allyl-*S*-methylisothiuronium sulfate (which was preliminarily obtained from *N*-allylthiourea and dimethyl sulfate as described in [3]) and allylamine according to a modified procedure [4].

Complex **I** was obtained in the form of acicular crystals by the ac electrochemical reduction ($U = 0.4$ V, $I = 0.30$ mA) of Cu(II) to Cu(I) on copper electrodes in an ethanol solution (3 ml) containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

(~ 0.6 mmol) and $(\text{DAGUH}^+)_2\text{SO}_4$ (~ 0.4 mmol). The starting bluish suspension decolorized within six days, and colorless crystal aggregations of compound **I** were

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

Parameter	$[\text{Cu}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)(\text{SO}_4)]$
M , au	217.7
$F(000)$	440
Crystal size, mm 3	$0.15 \times 0.15 \times 0.30$
Space group	$P2_1/n$
a , Å	13.288(4)
b , Å	4.976(3)
c , Å	9.932(2)
γ , deg	97.47(4)
V , Å 3	651.1(5)
Z	4
$\rho(\text{exp})$, g/cm 3	2.19
$\rho(\text{calcd})$, g/cm 3	2.221(3)
μ_{Mo} , cm $^{-1}$	37.36
Radiation	$\text{MoK}\alpha$
Scan mode	$\theta/2\theta$
No. of reflections:	
measured	776
observed with $F \geq 2\sigma(F)$	761
independent with $F \geq 2\sigma(F)$	541
$2\theta_{\text{max}}$, deg	50
No. of the parameters to be refined	123
R/R_w	0.037/0.037
Weighting scheme	$[\sigma(F_o)^2 + 0.0008F_o^2]^{-1}$
max $\Delta\rho$, e Å $^{-3}$	0.52
GOOF	1.07

Table 2. Atomic coordinates and thermal parameters* for structure **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Cu	0.48749(7)	0.2994(2)	0.6322(1)	1.65(2)
S	0.6599(1)	0.2015(4)	0.4255(2)	1.33(5)
O(1)	0.6836(4)	0.260(1)	0.2848(6)	2.3(2)
O(2)	0.5635(4)	0.310(1)	0.4598(5)	1.9(2)
O(3)	0.3583(4)	0.098(1)	0.5569(5)	1.6(2)
O(4)	0.7414(4)	0.310(1)	0.5137(6)	2.5(2)
N	0.7110(5)	0.734(1)	0.7010(7)	1.7(2)
C(1)	0.4765(7)	0.321(3)	0.8307(9)	2.6(3)
C(2)	0.5764(6)	0.397(2)	0.7960(9)	2.2(2)
C(3)	0.6244(6)	0.688(2)	0.7951(9)	2.3(2)
H(1.1)	0.436(5)	0.44(2)	0.853(7)	1(2)
H(1.2)	0.450(5)	0.12(2)	0.858(7)	2(2)
H(2.1)	0.618(4)	0.27(1)	0.796(6)	1(1)
H(3.1)	0.570(4)	0.81(1)	0.778(5)	1(1)
H(3.2)	0.649(6)	0.76(2)	0.889(7)	4(2)
H(1 <i>n</i>)	0.750(5)	0.60(2)	0.698(7)	3(2)
H(2 <i>n</i>)	0.694(5)	0.76(1)	0.618(6)	2(2)
H(3 <i>n</i>)	0.751(5)	0.89(1)	0.727(6)	2(2)

* For non-hydrogen atoms, $B_{\text{equiv}} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\hat{a}_i \hat{a}_j)$.

formed on the electrodes. The crystals were allowed to grow for a month up to a size suitable for X-ray diffraction analysis. In the presence of atmospheric moisture, crystals **I**, even precoated with cyacrine, are unstable, being rather stable in a dry atmosphere ($T_m \geq 190^\circ\text{C}$). The crystal density measured by the flotation method in a chloroform–bromoform system is equal to 2.19 g/cm³.

Initially, structure **I** was studied by photometry. The crystals showed a tendency toward twinning; small single crystals decomposed during the experiment and produced a small set of intensities. Because of this, the structure was determined with the use of diffraction data obtained on a DARCh single-crystal diffractometer from a larger twin crystal. Continuous recording was performed by periodically centering 24 reflections with $22.5^\circ < 2\theta < 26.8^\circ$; the unit cell parameters were calculated from these 2θ values by the least-squares method. The reflection intensities were corrected for the Lorentz and polarization factors and for a slight decrease in the intensities of three reference reflections (every 97th one). The structural model was solved by direct methods, and the locations of light atoms were found from the difference Fourier syntheses. Least-squares refinement led to a high discrepancy factor ($R \sim 0.15$).

An analysis of the correlation between the random distributions of diffraction data revealed two signs of twinning; both crystal domains contribute to the intensity of only certain reflections (*non-merohedral twin*)

Table 3. Bond lengths (*d*) and bond (ω) and torsion angles (φ) in structure **I**

Bond	<i>d</i> , Å	Angle*	ω , deg	Bond	<i>d</i> , Å	Angle*	ω , deg
Cu–O(2)	1.986(5)	O(2)CuO(3)	95.2(2)	C(1)–C(2)	1.38(1)	C(2)C(1)H(1.1)	122(5)
Cu–O(3)	2.016(5)	O(2)CuO(2)'	80.9(2)	C(1)–H(1.1)	0.89(8)	C(2)C(1)H(1.2)	121(4)
Cu–O(2)'	2.328(6)	O(2)Cum(12)	133.7(3)	C(1)–H(1.2)	1.06(8)	H(1.1)C(1)H(1.2)	116(6)
Cu–C(1)	1.980(9)	O(3)CuO(2)'	87.1(2)	C(2)–C(3)	1.51(1)	C(1)C(2)C(3)	122.7(8)
Cu–C(2)	2.032(9)	O(3)Cum(12)	129.1(3)	C(2)–H(2.1)	0.89(6)	C(1)C(2)H(2.1)	118(4)
Cu– <i>m</i> (12)*	1.885(9)	O(2)'Cum(12)	110.3(3)			C(3)C(2)H(2.1)	117(4)
		C(1)CuC(2)	40.1(4)	C(3)–N	1.48(1)	C(2)C(3)N	112.0(7)
S–O(1)	1.454(6)	O(1)SO(2)	108.7(3)	C(3)–H(3.1)	1.01(5)	C(2)C(3)H(3.1)	109(3)
S–O(2)	1.492(6)	O(1)SO(3)	108.5(3)	C(3)–H(3.2)	1.04(7)	C(2)C(3)H(3.2)	114(4)
S–O(3)	1.487(6)	O(1)SO(4)	112.1(3)			NC(3)H(3.1)	114(3)
S–O(4)	1.442(6)	O(2)SO(3)	107.3(3)			NC(3)H(3.2)	108(4)
		O(2)SO(4)	111.3(3)			H(3.1)C(3)H(3.2)	99(5)
		O(3)SO(4)	108.7(3)	N–H(1 <i>n</i>)	0.90(7)	C(3)NH(1 <i>n</i>)	115(5)
		CuO(2)Cu'	99.1(2)	N–H(2 <i>n</i>)	0.87(6)	C(3)NH(2 <i>n</i>)	115(4)
		CuO(2)S	130.2(3)	N–H(3 <i>n</i>)	0.92(7)	C(3)NH(3 <i>n</i>)	108(4)
		Cu'O(2)S	124.6(3)			H(1 <i>n</i>)NH(2 <i>n</i>)	104(6)
		CuO(3)S	118.2(3)			H(1 <i>n</i>)NH(3 <i>n</i>)	109(6)
						H(2 <i>n</i>)NH(3 <i>n</i>)	107(6)
Angle	φ , deg	Angle	φ , deg	Angle	φ , deg	Angle	φ , deg
CuO(2)SO(1)	179.7(5)	CuO(3)SO(4)	165.8(5)	CuC(1)C(2)C(3)	–103(1)	C(1)C(2)C(3)N	–154(1)

* *m*(12) is the midpoint of the C(1)=C(2) bond.

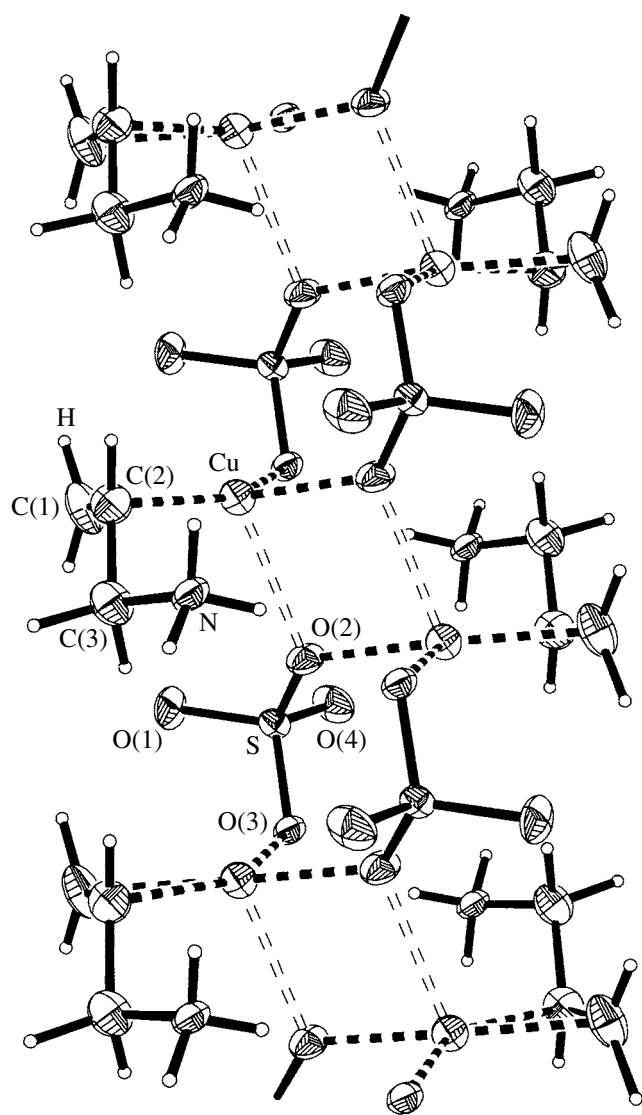


Fig. 1. Ribbon fragments along the [010] axis in structure I.

[5]: (1) reflections that increase the R factor most strongly, $F_o \gg F_c$, and (2) low-intensity reflections for which the $(F_o^2)_{av}/(F_c^2)_{av}$ ratio is mostly greater than unity. In addition, it was impossible to index all of the reflections obtained from one unit cell. To adjust the intensities of 244 reflections, $h0l$ were multiplied by 0.545 (this coefficient provides the lowest R factor). Refinement of the structural model with the use of the resulting intensity data reduced the discrepancy factor R to ~ 0.08 . The refinement did not include 84 out of 181 $h3l$ reflections with $F_o > F_c$, for which corrections for twinning were not applied. The hydrogen atoms were found from the difference Fourier syntheses. All non-hydrogen atoms were refined by a full-matrix anisotropic (isotropic for the hydrogen atoms) approximation from 761 nonaveraged reflections, and correc-

tion for absorption was applied (the DIFABS program) with the CSD programs [6].

Crystallographic data and a summary of the data collection for structure I are presented in Table 1. The atomic coordinates and thermal parameters are listed in Table 2, while the interatomic distances and bond and torsion angles are given in Table 3.

RESULTS AND DISCUSSION

The X-ray diffraction analysis of compound I showed that its crystal lattice contains the allylammonium cation (AAH⁺) which results from the hydrolysis of DAGUH⁺. The complex obtained proved to be the first π complex of copper(I) sulfate, [Cu(CH₂=CH-CH₂-NH₃)(SO₄)]. Previously, we observed the formation of π complexes of copper(I) halides with the allylammonium ligands upon the hydrolysis of the *N*-allylaldimines [7]. However, the decomposition of the guanidinium cation in such systems was noted for the first time. The nitrate anion forms with Cu(I) labile complexes and is easily replaced in the coordination sphere by the SO₄²⁻ anion. Attempts to obtain complex I by electrochemical synthesis directly from the allylammonium sulfate and copper sulfate (or nitrate) were a failure.

Compound I was found to be one of a few zwitterionic π complexes with ionic copper(I) salts [8]. The copper atom has a trigonal-pyramidal environment composed of two oxygen atoms of two sulfate groups, the equatorial C=C bond in the equatorial plane, and the axial O atom of the third SO₄²⁻ group. A rather effective Cu-(C=C) interaction (1.885(9) Å, C(1)CuC(2) 40.1(4)°) causes the C=C bond to lengthen to 1.38(1) Å. The equatorial Cu-O(2, 3) bonds in structure I (their average length is 2.001(5) Å) are comparable to those in Cu₂SO₄ (1.96 Å) with two linearly coordinated oxygen atoms [9]. Such a strong interaction makes the corresponding S-O(2, 3) bonds markedly longer (by 0.042 Å on average) than the S-O(3, 4) bonds involving the Cu-noncoordinated oxygen atoms (1.490(6) and 1.448(6) Å, respectively). In the case of mixed-cation copper(I) π complexes [Cu₂X₂(AAH⁺)(H₂O)]SO₄ (X = Cl or Br), the sulfate anion is involved only in the hydrogen bonding [10]. A slight extension (by 0.15 Å) of the metal atom from the plane of the equatorial ligands correlates well with the observed lengthening of the axial Cu-O(2)' bond (to 2.328(6) Å) and with a small angle between this plane and the C=C bond (6.5°).

A similar structure of the coordination entity was revealed earlier in the zwitterionic π complex of copper(I) hydrogen maleate [Cu(OOCCH=CHCOOH)(H₂O)] [11]. In this case, the equatorial short Cu-O bonds (each 1.999(6) Å) and very effective Cu-(C=C) interaction (1.847(8) Å, C(1)CuC(2) 41.7(3)°) are also realized, and the C=C bond is lengthened as far as

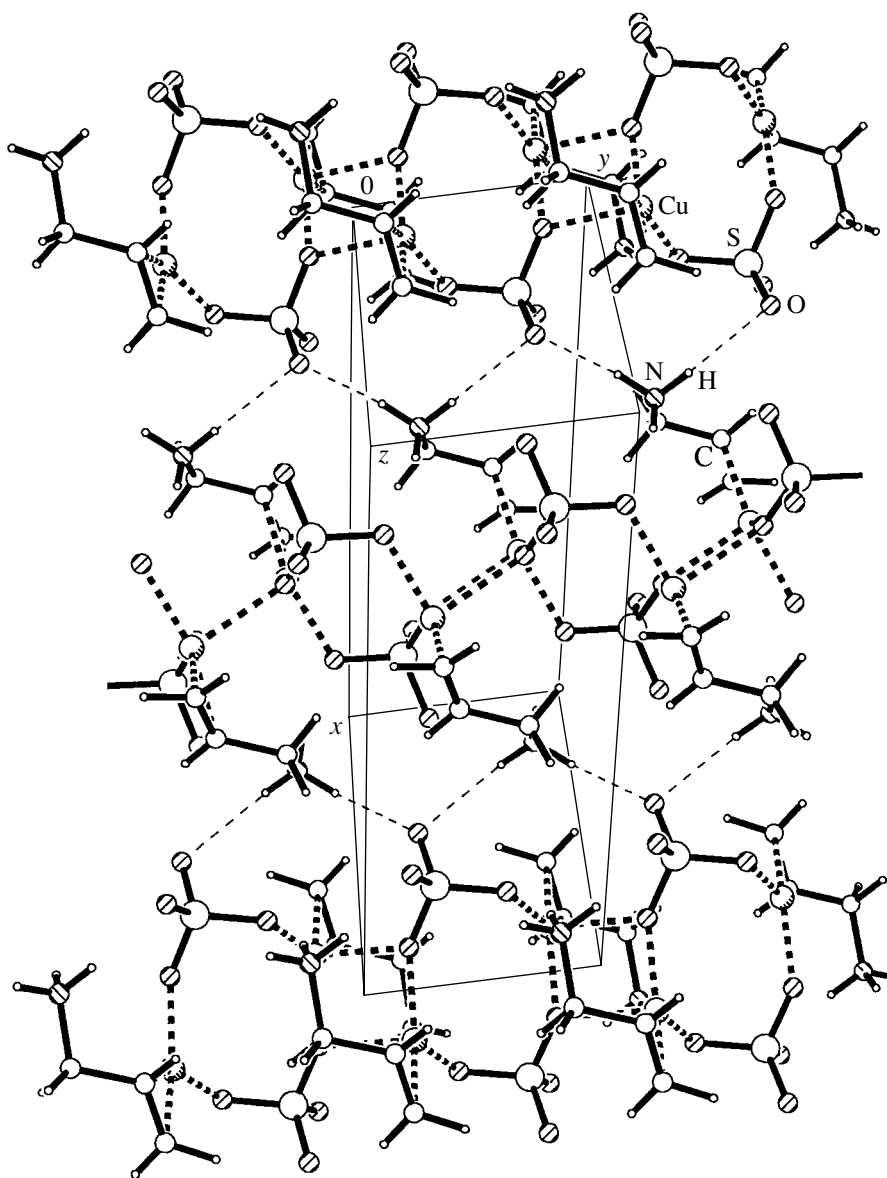


Fig. 2. Formation of structure **I** with the involvement of hydrogen bonds.

1.405(10) Å; in addition, the copper coordination sphere is also extended to be trigonal-pyramidal with a water molecule (Cu–O_w 2.31(1) Å).

Structure **I** is built from chain fragments arranged along the [010] axis (Fig. 1), in which the sulfate group is coordinated by three metal atoms through two oxygen atoms. Separate dimeric fragments join together via lengthened Cu–O contacts. The values of the torsion CuOSO angles involving the equatorial Cu–O bonds suggest a staggered conformation of an inorganic dimeric fragment. Further building of structure **I** is due to the developed system of N–H...O hydrogen bonds (Table 4). A fragment of crystal structure **I** is shown in Fig. 2. Low parameters of the atomic thermal vibrations (Table 2) are consistent both with a high

thermal stability and the low-energy structure of this compound.

Charges on the atoms in structure **I** were calculated by the HYPERCHEM program [12] using a modified version of the iterative SCF LCAO MO method in the INDO approximation (ZINDO/1). The calculation was performed for a cluster that resembles structure **I** containing 288 atoms (848 initial AOs were considered). As with the [H⁺ diallylamine]Cu(NO₃)₂ π complex having the same copper environment [13], the charge on the copper atom is $-0.19 e$. Important information was obtained from the calculated charges on the oxygen atoms (-0.74 and $-0.70 e$ for the O(1) and O(4) atoms involved in strong hydrogen bonding and -0.58 and $-0.44 e$ for the copper-coordinated O(3) and O(2)

atoms, respectively). The formation of H-bonds polarizes the $O^{\delta-}\cdots H^{\delta+}\cdots N^{\delta-}$ chain, thus concentrating a considerable portion of the negative charge of the sulfate anion on the oxygen atoms that are not coordinated to Cu(I). Becoming less hard (according to Pearson), the SO_4^{2-} anion can interact with a soft acid (Cu^+) to form the copper(I) π complex with a totally two-charge acidoligand.

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