

## Copper(I) Nitrate $\pi$ -Complexation: Synthesis and Crystal Structure of $[\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2\}\text{Cu}(\text{NO}_3)_2]$ Compound

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(Received November 29th, 1999; revised manuscript March 15th, 2000)

By alternating-current electrochemical synthesis, a crystalline  $\pi$ -complex  $[\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2\}\text{Cu}(\text{NO}_3)_2]$  (**I**) has been obtained using copper(II) nitrate and allylguanidine (AGU) in butanol-2 solution and copper-wire electrodes. A single crystal of the compound was X-ray structurally characterized. The Cu ion possesses trigonal pyramidal coordination formed by two oxygen atoms of the two nitrate anions and C=C bond of the  $\text{H}^+\text{AGU}$  cation at the equatorial plane and the oxygen atom of another nitrate anion at the apical position. Owing to the bridging function of  $\text{NO}_3$ -group, the structure **I** consists of chains connected by branched system of (N)H...O bonds of 2.19(4)–2.45(3) Å. New stereochemical features of coordinated nitrate anion in copper(I)  $\pi$ -complexes have been revealed.

**Key words:** copper(I) nitrate,  $\pi$ -complex, synthesis, crystal structure

Not long ago neither copper(I) nitrate  $\pi$ -complexes have been obtained, though some  $\text{CuNO}_3$  adducts, namely  $\sigma$ -complexes of  $[\text{Cu}(\text{L})_2]\text{NO}_3$  general composition ( $\text{L} = \text{NC}(\text{CH}_2)_2\text{CN}$ ,  $\text{NC}(\text{CH}_2)_3\text{CN}$ ,  $\text{NC}(\text{CH}_2)_4\text{CN}$ ), were commonly known [1–3]. Any oxygen atom from  $\text{NO}_3^-$  anion does not coordinate the Cu(I) atom. However, one would expect that copper(I) nitrate  $\pi$ -complexes might serve as matrices for template syntheses, because of instability of  $\text{CuNO}_3$  itself, as well as strong oxidative properties of copper(II) nitrate.

Our investigations on copper(I) nitrate  $\pi$ -complexation have shown that by simple alternating-current electrochemical technique [4], one may obtain  $\text{CuNO}_3$   $\pi$ -complexes with unsaturated ligands. Thus, we have obtained and structurally characterized first representatives of copper(I) nitrate  $\pi, \sigma$ -complexes with diallylcyanamide  $[\text{Cu}\{(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NCN}\}(\text{NO}_3)]$  [5], diallylamine  $[\text{Cu}\{(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}\}(\text{NO}_3)]$  (A and B modifications) [6,7], N-allylthiourea  $[\text{Cu}\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}-\text{C}(\text{S})-\text{NH}_2\}(\text{CH}_3-\text{CN})\text{NO}_3]$  [8] and allylcyanide  $[\text{Cu}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{CN})(\text{NO}_3)]$  [9]. It was shown that the olefinic group C=C successfully competes with *n*-donor nitrogen (of nitrile or amine type) or sulfur atoms for a place in the nearest copper(I) environment. Thus, in

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considered compounds, as in the case of  $[\text{Cu}\{\text{NC}(\text{CH}_2)_n\text{CN}\}_2]\text{NO}_3$   $\sigma$ -complexes, copper(I) nitrate is stabilized by donor atoms in the metal coordination sphere. Nevertheless, a zwitterionic  $\pi$ -complex with diallylammonium nitrate of  $[\{(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}_2\}\text{Cu}(\text{NO}_3)_2]$  composition [10] turned out to be much more interesting, being hitherto the only "pure"  $\pi$ -compound of this type: in this case copper(I) atom is surrounded by two C=C bonds and oxygen atoms from two  $\text{NO}_3^-$  groups. In this paper the synthesis and crystal structure of a second "pure" copper(I) nitrate  $\pi$ -complex with allylguanidinium nitrate  $[\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2\}\text{Cu}(\text{NO}_3)_2]$  (**I**) is reported. The choice of allylguanidinium cation is caused by its ability to form a developed system of H-bonds [11], enabling the isolation of complex **I**. Our main purposes are further investigations in stereochemistry of Cu(I)–(C=C) bonding and to reflect a behaviour of  $\text{NO}_3^-$  group acting as a ligand in copper(I)  $\pi$ -complexes.

## EXPERIMENTAL

**Synthesis of allylguanidine.** This compound (AGU) was isolated by the action of potassium hydroxide on allylguanidinium bromide in water solution. Allylguanidinium bromide was obtained starting from isothiuronium bromide (obtained starting from thiourea and bromethane [12]) and allylamine, according to a modified procedure [13].

**Preparation of complex I.** Good quality crystals of the complex have been obtained by the alternating-current electrochemical technique [4]. To 2.5 ml of a saturated solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in butanol-2, 0.2 ml of allylguanidine (2 mmol) in 3 ml of butanol-2 was added. The prepared light blue suspension was placed into a small 6-ml test-tube and copper-wire electrodes in cork (to protect against the oxidation by air) were inserted. Under alternating current (frequency 50 Hz) of 0.40 V, the needle-shaped transparent colorless crystals of compound **I** on the copper electrodes have grown over one day. To avoid decomposition, a crystal before X-ray examination was covered by a cyacryne varnish. The density of **I** was measured by flotation in  $\text{CHCl}_3/\text{CHBr}_3$  solution.

**Crystal structure of I.** Approximate unit-cell dimensions and the space group were determined from rotation and Weissenberg photographs. The intensity data were measured on a DARCH diffractometer (an automated four-circle diffractometer of the former USSR production, the analogue of a Syntex P2<sub>1</sub>) at 293 K using Zr-filtered  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) with  $\theta$ - $2\theta$  scans. The cell parameters were obtained by the least-squares refinement with regards to the angle parameters of 24 reflections in the range  $25.0 < 2\theta < 30.0^\circ$ . Structure was solved by the direct methods. All H atoms were found from difference Fourier syntheses. Absorption correction has been performed using DIFABS program. A full least-squares refinement on  $F$  was performed on the positional and thermal parameters for all atoms, anisotropically for all non H-atoms. The neutral atom scattering factors were taken from [14]. The intensities were not corrected for extinction. All the calculations (including absorption corrections) were performed using the CSD program package (Crystal Structure Determination) [15].

$\text{CuO}_6\text{N}_3\text{C}_4\text{H}_{10}$ ,  $M_w = 287.70$ , crystal size  $0.52 \times 0.13 \times 0.09 \text{ mm}$ , monoclinic,  $P2_1/n$ ,  $a = 10.085(4) \text{ \AA}$ ,  $b = 14.920(5) \text{ \AA}$ ,  $c = 6.697(4) \text{ \AA}$ ,  $\gamma = 91.96(3)^\circ$ ,  $V = 1007(1) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.898(3) \text{ g/cm}^3$ ,  $D_m = 1.86 \text{ g/cm}^3$ ,  $\mu(\text{MoK}_\alpha) = 22.81 \text{ cm}^{-1}$ ,  $2\theta_{\text{max}} = 58^\circ$ ,  $F(000) = 584$ , 975 reflections collected, 919 independent reflections with  $F_o \geq 2\sigma(F_o)$ , 185 parameters,  $w = [\sigma(F_o)^2 + 0.0007F_o^2]^{-1}$ ,  $R(F) = 0.0235$  and  $R_w(F) = 0.0252$  for all data, Goodness-of-fit  $S(F) = 1.08$ ,  $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$ ,  $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$ .

The final atomic parameters, the anisotropic thermal parameters and the list of observed and calculated structure amplitudes for **I** are available on request.\*\* The bond lengths, bond angles and the selected torsion angles in **I** are listed in Table 1.

\*\* Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK) as deposition No 140044.

**Table 1.** Bond lengths (Å), bond and torsion angles (°) (with e.s.d.'s in parentheses) for **I**.

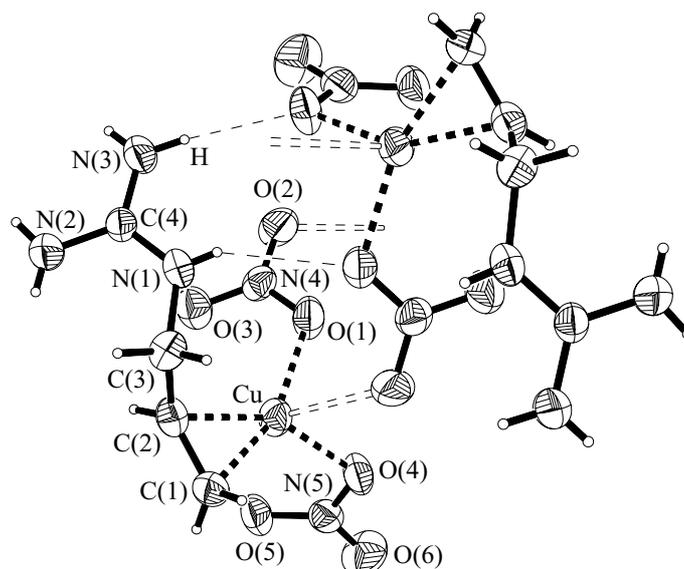
Coordination sphere			
Cu–O(1)	2.012(3)	O(1)–Cu–O(4)	90.5(1)
Cu–O(4)	2.040(3)	O(1)–Cu– <i>m</i> (12)	136.7(2)
Cu–C(1)	2.004(4)	O(4)–Cu– <i>m</i> (12)	132.6(2)
Cu–C(2)	2.023(4)	O(2) <sup>i</sup> –Cu–O(1)	83.7(1)
Cu– <i>m</i> (12) *	1.896(4)	O(2) <sup>i</sup> –Cu–O(4)	84.0(1)
Cu–O(2) <sup>i</sup>	2.566(3)	O(2) <sup>i</sup> –Cu– <i>m</i> (12)	101.2(1)
		C(1)–Cu–C(2)	39.3(2)
Anions			
N(4)–O(1)	1.270(4)	O(1)–N(4)–O(2)	119.0(3)
N(4)–O(2)	1.238(4)	O(1)–N(4)–O(3)	119.4(3)
N(4)–O(3)	1.233(4)	O(2)–N(4)–O(3)	121.6(3)
		Cu–O(1)–N(4)	117.6(2)
		Cu–O(2) <sup>i</sup> –N(4) <sup>i</sup>	122.9(3)
N(5)–O(4)	1.276(4)	O(4)–N(5)–O(5)	118.1(3)
N(5)–O(5)	1.237(4)	O(4)–N(5)–O(6)	118.7(3)
N(5)–O(6)	1.213(5)	O(5)–N(5)–O(6)	123.2(3)
		Cu–O(4)–N(5)	109.8(2)
Molecule of ligand			
C(1)–C(2)	1.353(6)	C(1)–C(2)–C(3)	124.1(4)
C(2)–C(3)	1.500(6)	C(2)–C(3)–N(1)	115.3(3)
C(3)–N(1)	1.450(5)	C(3)–N(1)–C(4)	126.3(3)
N(1)–C(4)	1.323(5)	N(1)–C(4)–N(2)	121.4(3)
C(4)–N(2)	1.318(5)	N(1)–C(4)–N(3)	119.5(3)
C(4)–N(3)	1.311(5)	N(2)–C(4)–N(3)	119.0(3)
		Cu–O(1)–N(4)–O(2)	177.8(3)
		Cu–O(2) <sup>i</sup> –N(4) <sup>i</sup> –O(1) <sup>i</sup>	–55.5(4)
		Cu–O(4)–N(5)–O(5)	–3.3(5)
		Cu–C(1)–C(2)–C(3)	–105.5(4)
		C(1)–C(2)–C(3)–N(1)	139.1(5)
		C(2)–C(3)–N(1)–C(4)	–81.9(6)
		C(3)–N(1)–C(4)–N(2)	1.0(8)
		C(3)–N(1)–C(4)–N(3)	179.8(4)

symmetry code: (i)  $-x + 1/2, -y + 1/2, z + 1/2$ ; \* *m*(12) – the mid-point of C(1)=C(2) distance.

## RESULTS AND DISCUSSION

Initial compound AGU, being a strong base, was protonated in the reaction mixture, which resulted in formation of zwitterionic  $\pi$ -complex **I**, stabilized by branched system of H-bonds. The Cu atom possesses a trigonal pyramidal coordination, formed by two oxygen atoms of two nitrate anions and C=C bond of the H<sup>+</sup>AGU cat-

ion at the equatorial plane. The oxygen atom of another nitrate anion occupies distant apical position of the copper(I) polyhedron (Cu–O(2) 2.566(3) Å). Due to the bridging function of one of NO<sub>3</sub>-groups, the structure **I** consists of chains in [001] direction (Fig. 1). The extent of pyramidal distortion of coordination sphere corresponds to a insignificant deviation (0.035 Å) of copper atom from the plane of equatorial ligands (through O(1), O(4) and the mid-point of C(1)=C(2)).



**Figure 1.** Chain in [001] direction in the structure of **I** with atom numbering scheme. Thermal ellipsoids are at the 50% probability level.

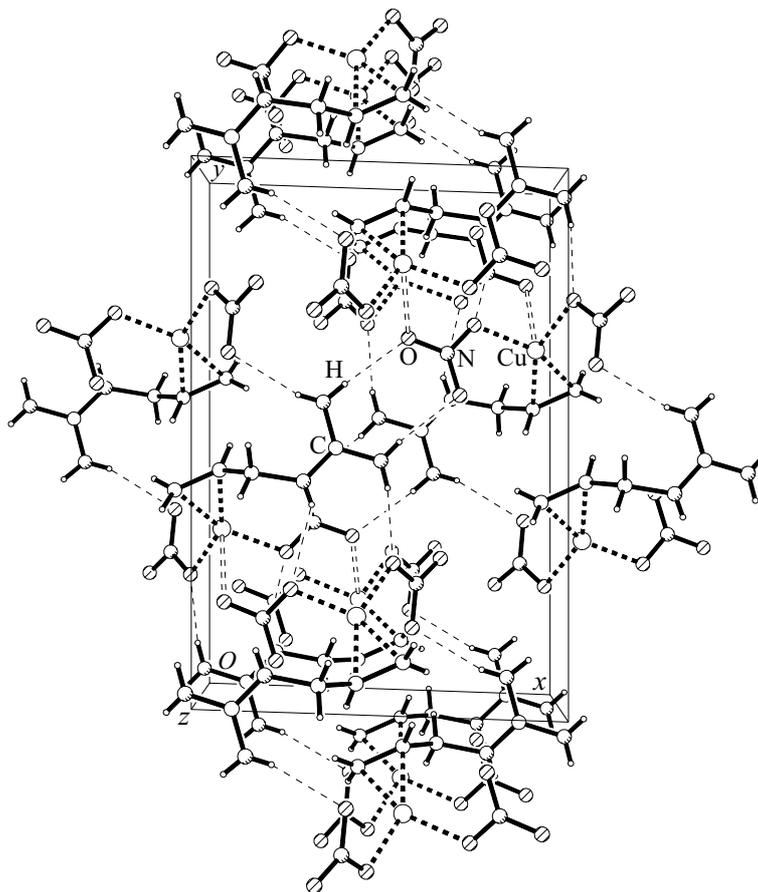
According to the model of oxidative addition, orthogonality of O–Cu–O fragment in equatorial plane of coordination sphere stabilizes  $dsp^2$ -hybridization of atomic orbitals of the central atom [16], and in this way facilitates an effective  $\pi$ -bonding Cu–(C=C) in the virtually planar trigonal coordination of Cu atom. Thus, in  $\pi$ -complexes  $[\text{Cu}_2\{(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NCN}\}(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})]\text{SiF}_6$  [17] and  $[\text{Cu}_2(\text{OOCH})_2(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)_2]\text{SiF}_6$  [18] the angles  $\omega(\text{O}-\text{Cu}-\text{O})$  equal 98.3(3) and 97.63(7)°, which imply an effective Cu–(C=C) interaction ( $\omega(\text{C}-\text{Cu}-\text{C})$  equal 39.7(5) and 40.1(1)° respectively). In the case of copper(I) hydromaleate  $[\text{Cu}(\text{OOC}-\text{CH}=\text{CH}-\text{COOH})(\text{H}_2\text{O})]$  crystal structure [19], a practically orthogonal O–Cu–O fragment (92.2(2)°) is extremely effectively  $\pi$ -bonded to C=C-group ( $\omega(\text{C}-\text{Cu}-\text{C})$  equal 41.7(3)°). According to that conformity, a nearly right angle O–Cu–O (90.5(1)°) in the structure **I** must correspond to a similar considerable C–Cu–C angle. However, this value was found to be 39.3(2)°. Furthermore, the tilt of  $\pi$ -coordinated double bond from the plane of equatorial ligands in **I** equals  $\tau = 15.5^\circ$ , in contrast to the values found for aforementioned  $\pi$ -complexes (1.8, 0.6 and 0° correspondingly). In this case it is not caused by steric hindrance in the coordination sphere or by formation of strong contacts =C–H...O. The only reason is the rigidity of H<sup>+</sup>AGU cation, caused by involvement of guani-

dinium group into a well-developed system of rather strong hydrogen bonds (Table 2), which combines chains, disposed in the [001] direction, into the three-dimensional structure (Fig. 2). Similarly, in isostructural  $\pi,\sigma$ -complexes  $3\text{CuX}\cdot(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) the diallylamine molecule is considerably stretched due to its twice-bridging function, which results in weakening of  $\text{Cu}-(\text{C}=\text{C})$  interaction (the tilt in planar trigonal coordination of  $\text{Cu}$  atom is equal to  $19^\circ$  and  $20^\circ$  respectively) [20].

**Table 2.** Hydrogen bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) (with e.s.d.'s in parentheses) in the crystals of **I**.

D-H...O	D-H ( $\text{\AA}$ )	H...O ( $\text{\AA}$ )	D...O ( $\text{\AA}$ )	D-H...O ( $^\circ$ )
N(1)-H(1)...O(1) <sup>i</sup>	0.68(3)	2.45(3)	3.017(4)	143(3)
N(2)-H(2)...O(5) <sup>ii</sup>	0.72(3)	2.27(3)	2.953(4)	158(3)
N(2)-H(3)...O(2) <sup>iii</sup>	0.80(4)	2.20(4)	2.999(4)	171(4)
N(3)-H(4)...O(4) <sup>i</sup>	0.78(3)	2.20(3)	2.951(4)	161(3)
N(3)-H(5)...O(3) <sup>iii</sup>	0.77(4)	2.19(4)	2.955(4)	170(4)

symmetry code: (i)  $-x + 1/2, -y + 1/2, z + 1/2$ , (ii)  $-x + 1, -y, -z$ , (iii)  $-x, -y, -z$ .



**Figure 2.** Formation of a three-dimensional crystal structure of **I**. H-bonds are depicted by dashes.

Strong resemblance of **I** to structure of copper(I) halide  $\pi$ -complex of  $(H^+ AGU)CuCl_{2-x}Br_x$  ( $x = 0.516$ ) composition (**II**) [11] deserves attention. The structure **II** is also formed by chains passing along screw axis  $2_1$  (sp. gr.  $Pna2_1$ ) and combined by N–H...X contacts system. Two independent nitrate anions in **I** play the same role as the halide atoms in **II**. The N–O bonds in **I**, corresponding to strongly coordinated oxygen atoms, appear to be distinctly elongated (Table 1). It should be emphasized on unnoticed before [5–7, 9, 10] structural features of  $NO_3^-$  anion, acting as equatorial ligand. Nitrate anions in the structure **I** are strictly situated in the plane with respective copper atom: torsion angles Cu–O(1)–N(4)–O(2) and Cu–O(4)–N(5)–O(5) equal  $\nu = 177.8(3)$  and  $-3.3(5)^\circ$ . Furthermore, the nitrate anions are rigidly oriented with respect to the central atom: Cu–O(1)–N(4) and Cu–O(4)–N(5) angles equal to  $\omega = 117.6(2)$  and  $109.8(2)^\circ$ . Similar features take place also in  $[Cu\{(CH_2=CH-CH_2)_2NCN\}(NO_3)]$  [5] ( $\nu = -13.1$ ,  $\omega = 112.3(2)^\circ$ ), modification A of  $[Cu\{(CH_2=CH-CH_2)_2NH\}(NO_3)]$  [6] ( $\nu = 3.9$ ,  $\omega = 122.5(4)^\circ$ ) (nitrate anion in modification B is partially disordered [7]),  $[Cu(CH_2=CH-CH_2-CN)(NO_3)]$  [9] ( $\nu = -2.0$ ,  $\omega = 109.9(2)^\circ$ ),  $[\{(CH_2=CH-CH_2)_2NH_2\}Cu(NO_3)_2]$  [10] ( $\nu = -1.5$ ,  $\omega = 108.8(2)^\circ$ ), and even in structures of silver(I) nitrate  $\pi$ -complexes, for instance in  $[Ag_2\{(CH_2=CH-CH_2)_2-S\}_2(NO_3)_2]$  [21] ( $\nu = -6.3$  and  $-13.0$ ,  $\omega = 103.4(3)$  and  $112.1(3)^\circ$  for two strong Ag–O contacts). These stereochemical peculiarities of coordinated nitrate anion are determined by its planar configuration. Shape anisotropy favours directness of electron pairs of oxygen atom and, in turn, such distinctive abilities of  $NO_3^-$  anion. Analysis of structurally investigated  $\pi$ -complexes has not revealed any preferable orientation of pseudospherical  $BF_4^-$  and  $ClO_4^-$  anions in coordination environment of Cu(I) or Ag(I).

The results obtained have revealed a remarkable capability of the Cu–(C=C) interaction to stabilize the  $CuNO_3$  moiety. Unnoticed before structural features of  $NO_3^-$  anion, acting as equatorial ligand in copper(I)  $\pi$ -complexes, are determined by directness of electron pairs of oxygen atoms. The N–H...O( $NO_2$ ) bonds stabilize the univalent-copper nitrate  $\pi$ -complexes, but their appreciable structure-forming properties may in the same cases weaken the Cu–(C=C) interaction.

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