Copper(I) Nitrate π-Complexes: Synthesis and Structure of [Cu(CH₂=CH–CH₂–CN)(NO₃)]

Ya. E. Filinchuk, V. V. Oliinik, and V. N. Davydov

Franko State University, ul. Lomonosova 8, Lviv, 290005 Ukraine

Received December 2, 1996

Abstract—Crystals of the $CuNO_3$ π-complex with allyl cyanide are obtained by ac electrochemical synthesis, and their structure is determined [DARCh diffractometer, MoK_α radiation, $R = 0.022$ for 902 independent reflections, $F \geq 4\sigma(F)$]. The π-complex crystallizes in space group $P2_1/b$, $a = 10.137(2)$, $b = 9.671(2)$, $c = 6.848(1)$ Å, $\alpha = 101.75(2)°$, $Z = 4$. The copper coordination polyhedron is a distorted tetrahedron formed by two O atoms, and N atom of the cyano group, and a C=C bond. The structure of the compound is compared with those of previously studied $CuNO_3$ π-complexes.

Recently, the first copper(I) nitrate π-complexes with diallylcyanamide $[Cu((C_3H_5)_2NCN)(NO_3)]$ [1] and diallylamine—molecular $[Cu((C_3H_5)_2NH)(NO_3)]$ (modifications A and B) [2, 3] and zwitterionic $[((C_3H_5)_2NH_2)Cu(NO_3)_2]$ [4]—were obtained and structurally studied. For the purpose of the systematic studies on the π-complexation of copper(I) nitrate, the $CuNO_3$–allyl cyanide π-complex of equimolar composition $[Cu(CH_2=CH–CH_2–CN)(NO_3)]$ (**I**) was synthesized, and its crystal structure was studied.

EXPERIMENTAL

Crystals **I** of prismatic habitus were prepared by the ac electrochemical reduction ($U = 0.4$ V) of a solution of copper(II) nitrate in butanol-2 in the presence of allyl cyanide. The crystals were formed at copper electrodes during one day and retained their stability for a week.

The X-ray diffraction analysis was performed at room temperature on a DARCh single-crystal diffractometer (MoK_α radiation, graphite monochromator, θ/2θ mode, $2\theta_{max} = 55°$). The crystals are monoclinic, space group $P2_1/b$, $a = 10.137(2)$, $b = 9.671(2)$, $c = 6.848(1)$ Å, $\alpha = 101.75(2)°$, $V = 657.3(4)$ Å³, $F \geq 4\sigma(F)$.

The structure was solved by the direct method, with the light atoms being located by difference Fourier syntheses. Corrections for the Lorentz, polarization, and absorption effects were applied [$\mu(MoK_\alpha) = 34.28$ cm⁻¹]. All atoms (including hydrogen) were refined by the least-squares method in the full-matrix anisotropic variant. All calculations were performed on an IBM PC/AT 486DX2 computer using the CSD suit of programs.

The coordinates and thermal parameters of the atoms in structure **I** are presented in Table 1. The interatomic distances and bond and torsion angles are presented in Table 2.

RESULTS AND DISCUSSION

A fragment of structure **I** is shown in Fig. 1. The complex is molecular, with the $Cu–O(NO_3)$ distances equal to 2.020(2) and 2.421(3) Å. The vertices of the coordination polyhedron (trigonal pyramid) of the copper atom are occupied by the nitrogen atom of the cyano group of one allyl cyanide molecule, the olefinic bond of the other C_3H_5CN molecule, and two oxygen

Table 1. Coordinates of atoms and their thermal parameters*

Atom	x	y	z	B, Å²
Cu	0.27602(4)	0.18805(4)	0.34728(5)	3.50(1)
O(1)	0.2408(2)	0.1505(2)	0.6221(3)	4.25(8)
O(2)	0.1861(3)	–0.0202(3)	0.7621(4)	6.9(1)
O(3)	0.2137(3)	–0.0571(2)	0.4446(3)	6.2(1)
N(1)	0.6084(3)	0.2905(3)	–0.2122(4)	4.1(1)
N(2)	0.2120(3)	0.0212(2)	0.6098(3)	3.40(8)
C(1)	0.4704(3)	0.1430(4)	0.2871(5)	4.7(1)
C(2)	0.4105(3)	0.1616(3)	0.1195(5)	3.5(1)
C(3)	0.4177(3)	0.2953(3)	0.0398(5)	4.2(1)
C(4)	0.5246(3)	0.2916(3)	–0.1050(4)	3.7(1)
H(11)	0.510(4)	0.218(4)	0.378(5)	6(2)
H(12)	0.477(4)	0.060(4)	0.315(5)	6(2)
H(21)	0.386(3)	0.088(3)	0.040(5)	5(1)
H(31)	0.438(4)	0.379(4)	0.156(5)	5(2)
H(32)	0.352(3)	0.307(3)	–0.015(5)	5(2)

* For all atoms, $B_{eq} = 1/3\sum_i\sum_j B_{ij}a_i^* a_j^* (\vec{a}_i\vec{a}_j)$.
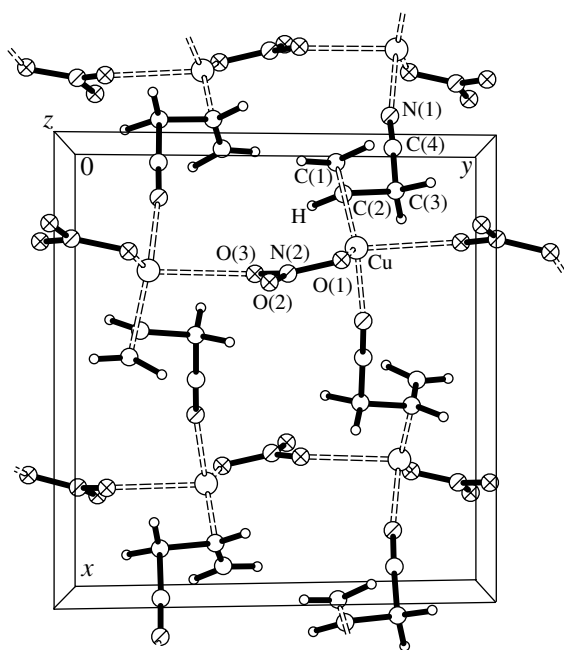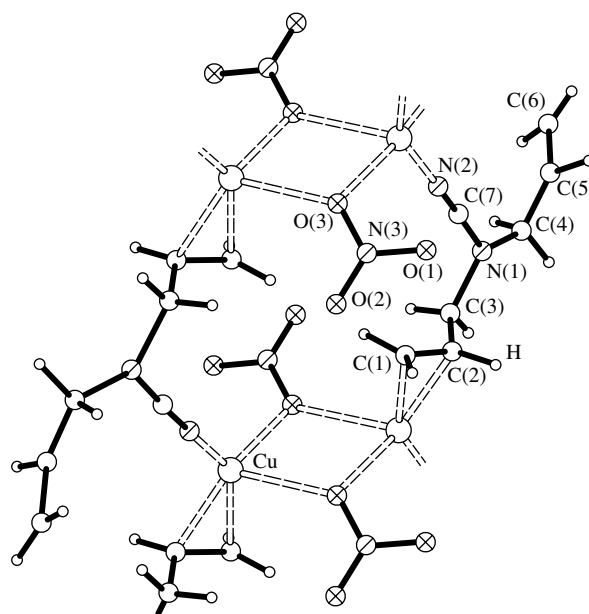
Fig. 1. Fragment of structure **I**.

Fig. 2. Fragment of structure **II**.

atoms from different nitrate groups. The $(CuNO_3)_n$ chains in the [010] direction are formed owing to the bridging character of the NO_3 groups. The bidentate allyl cyanide molecules combine the inorganic chains into ruffled layers in the (001) plane.

Structure **I** is similar to the structure of the complex $\{Cu((C_3H_5)_2NCN)(NO_3)\}$ (**II**), regarding the formation of the coordination sphere of copper(I). However, the behavior of the nitrate group in **I** differs from that in **II**. In **I**, the NO_3 group functions as a bridge by virtue of two oxygen atoms coordinated to different copper atoms, whereas in **II** only one oxygen atom fulfills the bridging function. As a result, only the $Cu_2(NO_3)_2$ dimers are formed in structure **II**, unlike the $(CuNO_3)_n$ chains in the compound with allyl cyanide. The role of the organic molecule is the same in both structures: the bidentate ligand (one of the C=C bonds in the diallylcyanamide molecule is uncoordinated) combines the inorganic fragments in one dimension. The ruffled layers are formed (Fig. 1) in the case of C_3H_5CN, and ribbons are formed in the case of $(C_3H_5)_2NCN$ (Fig. 2). In structure **I**, the $Cu–L_{ax}$ interaction is more efficient [Cu–O 2.421(3) Å] than in structure **II** [Cu–O 2.524(3) Å], while the Cu–N distance in **I** [1.966(3) Å] is somewhat longer than that in **II** [1.922(4) Å]. The copper atom is moderately shifted from the equatorial plane in **I** (by 0.16 Å), so that the C=C bond is only slightly stretched [C=C 1.342(5) Å]. The CuN(1)C(4) angle in **I** [167.2(3)°] markedly differs from 180° [the corresponding angle in structure **II** is equal to 176.9(4)°].

The three-dimensional structure **I** is formed from individual layers with the participation of hydrogen bonds: H(31)···O(3), 2.48(4) Å; H(32)···O(2), 2.51(3) Å;

and H(11)···O(1), 2.66(4) Å. The CHO angles lie within 120°–145°, which is typical of the two-center hydrogen bonds.

It is instructive to compare the conformation of the organic molecule in **I** with those in the previously studied allyl cyanide π-complexes of the compositions $2CuCl \cdot C_3H_5CN$ (modifications A and B) [6, 7] and $2CuBr \cdot C_3H_5CN$ [6]. The torsion C(1)C(2)C(3)C(4) angles in the structures of these compounds are equal to 9°, 94.1°, and 96°, respectively, while the corresponding angle in structure **I** is 93.2°. The *syn–anti*-clinal conformation of allyl cyanide in structure **I** is typical of the π-complexes of copper halides and indicates the structure-forming role of the inorganic fragment.

The ZINDO method (HYPERCHEM program package [8]) was used to calculate the charges on the atoms in the structures of π-complexes **I** and **II** (Table 3). It can be seen that the more efficient Cu–O interaction causes the smaller negative charge on the oxygen atom. Owing to the Cl–Cu $p–d_\pi$ interaction and formation of the polymeric inorganic fragments in the $2CuCl \cdot C_3H_5CN$ structure (modification B) [7], the copper atoms bear small effective charges: $q_{Cu} = 0.01\,\bar{e}$ on the copper atom coordinated by the C=C bond and $q_{Cu} = -0.04\,\bar{e}$ on the copper atom coordinated by the nitrogen atom of the cyano group. The similarity of structures **I** and **II**, as regards the formation of the inorganic fragments typical of the π-complexes of copper halides, is also manifested by the small absolute values of the effective charge on the metal atom. For compounds **I** and **II**, it is equal to $-0.19\,\bar{e}$ and $-0.16\,\bar{e}$, respectively, whereas in

Table 2. Bond lengths (*d*) and bond (ω) and torsion (φ) angles in structure **I**

Bond*	*d*, Å	Angle*	ω, deg.
Cu–O(1)	2.020(2)	O(1)CuO(3)	96.8(1)
Cu–O(3)	2.421(3)	O(1)CuN(1)	110.0(1)
Cu–N(1)	1.966(3)	O(1)Cu*m*(12)	125.5(1)
Cu–C(1)	2.042(4)	O(3)CuN(1)	88.2(1)
Cu–C(2)	2.048(4)	O(3)Cu*m*(12)	99.8(1)
Cu–*m*(12)	1.932(4)	N(1)Cu*m*(12)	122.0(1)
		C(1)CuC(2)	38.3(1)
C(1)–C(2)	1.342(5)	C(2)C(1)H(11)	122(2)
C(1)–H(11)	0.95(4)	C(2)C(1)H(12)	121(2)
C(1)–H(12)	0.87(4)	H(11)C(1)H(12)	117(3)
C(2)–C(3)	1.504(5)	C(1)C(2)C(3)	124.2(3)
C(2)–H(21)	0.84(3)	C(1)C(2)H(21)	117(2)
		C(3)C(2)H(21)	117(2)
C(3)–C(4)	1.464(5)	C(2)C(3)C(4)	112.2(3)
C(3)–H(31)	1.03(4)	C(2)C(3)H(31)	109(2)
C(3)–H(32)	0.79(3)	C(2)C(3)H(32)	111(3)
		C(4)C(3)H(31)	107(2)
		C(4)C(3)H(32)	107(3)
		H(31)C(3)H(32)	111(3)
C(4)–N(1)	1.121(5)	C(3)C(4)N(1)	178.2(4)
		CuN(1)C(4)	167.2(3)
N(2)–O(1)	1.269(4)	O(1)N(2)O(2)	118.9(3)
N(2)–O(2)	1.220(4)	O(1)N(2)O(3)	118.3(3)
N(2)–O(3)	1.227(4)	O(2)N(2)O(3)	122.9(3)
		Angle φ, deg.	
		CuO(1)N(2)O(3)	–2.0
		C(1)C(2)C(3)C(4)	93.2
		CuC(1)C(2)C(3)	100.2

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

the CuNO$_3$–diallylamine π-complexes of equimolar composition it is equal to, $q_{Cu} = -0.30\bar{e}$ and $-0.31\bar{e}$ (for modifications A and B, respectively). However, in all structures of the CuNO$_3$ π-complexes, a consider-

Table 3. Atomic charges in the inorganic fragments and coordination polyhedra of structures **I** and **II**

Atom	$q, \bar{e}$	
	I	**II**
Cu	−0.19	−0.16
C(1)*	−0.08	−0.04
C(2)*	0.08	0.05
N(1)*	−0.03	−0.01
N(2)	0.75	0.74
O(1)**	−0.35	−0.43
O(2)	−0.39	−0.47
O(3)*	−0.40	−0.33

* The atom is involved in the coordination with the copper atom in structures **I** and **II**.

** The atom is involved in the coordination with the copper atom in structure **I**.

able negative charge is concentrated on the copper atom. It is likely that this charge stabilizes the Cu(I) state in the presence of a strong oxidant such as the nitrate group.

REFERENCES

1. Oliinik, V.V., Goreshnik, E.A., Mys'kiv, M.G., *et al.*, *Zh. Strukt. Khim.*, 1994, vol. 35, no. 1, p. 95.
2. Mys'kiv, M.G., Goreshnik, E.A., Pecharskii, V.K., *et al.*, *Zh. Strukt. Khim.*, 1994, vol. 35, no. 1, p. 90.
3. Oliinik, V.V., Mys'kiv, M.G., Filinchuk, Ya.E., *et al.*, *Zh. Strukt. Khim.*, 1994, vol. 35, no. 5, p. 188.
4. Olijnik, V., Głowiak, T., and Mys'kiv, M., *J. Chem. Crystallogr.*, 1995, vol. 25, no. 10, p. 621.
5. Aksel'rud, L.G., Grin', Yu.N., Zavalii, P.Yu., *et al.*, *Paket programm dlya strukturnogo analiza kristallov CSD. Obshchee opisanie* (Program Package for Structural Analysis of Crystals CSD. General Description), Lvov: Lvov Gos. Univ., 1990.
6. Zavalii, P.Yu, Mys'kiv, M.G., and Gladyshevskii, E.I., *Kristallografiya*, 1986, vol. 31, no. 1, p. 88.
7. Mys'kiv, M.G., Zavalii, P.Yu., Oliinik, V.V., *et al.*, *Zh. Strukt. Khim.*, 1990, vol. 31, no. 4, p. 85.
8. Bearden, D.W., *Comput. Software Rev.*, 1993, vol. 33, no. 3, p. 525.