COPPER(I) NITRATE π-COMPLEXES. CRYSTAL STRUCTURE OF A NOVEL MODIFICATION OF [Cu((CH$_2$=CH–CH$_2$)$_2$NH)]NO$_3$

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Halide ligands in olefinic π-complexes CuX (X is Cl, Br) always perform the bridging function, promoting the formation of rigid Cu$_n$Cl$_n$ fragments. This frequently limits the structural variety of adducts. Polymorphism of these compounds is usually restricted by the conformational freedom of an olefinic ligand and thus occurs in CuX π-complexes mainly with allyl molecules. While possessing moderate coordination ability compared to X$^-$, the NO$_3^-$ anion is of great interest as a structure-forming agent. The interaction of CuNO$_3$ with diallylamine (DAA), for instance, results in at least two π-complexes [Cu(DAA)]NO$_3$: form A investigated in [1] and form B discussed here.

TABLE 1. Atomic Positional (for Cu$\times10^5$, H$\times10^3$, remaining atoms $\times10^4$) and Equivalent (Isotropic for H) Thermal Parameters

Atom	x/a	y/b	z/c	B(i/e)
Cu	7308(4)	20935(3)	0	2.26(1)*
O1	–676(3)	2101(3)	9447(4)	4.55(12)*
O2	–791(4)	694(3)	9578(4)	6.0(2)*
O3	–1887(3)	1482(4)	9131(6)	8.2(2)*
N1	–1128(3)	1417(3)	9382(4)	3.15(11)*
N2	1206(3)	3655(3)	1725(3)	2.26(8)*
C1	649(4)	1304(3)	1209(3)	2.97(11)*
C2	507(3)	2147(3)	1477(3)	2.36(9)*.
C3	1231(4)	2690(3)	1922(3)	2.64(10)*
C4	1338(3)	3867(3)	761(3)	2.57(10)*
C5	662(3)	3512(3)	107(4)	2.41(9)*
C6	915(3)	3259(3)	–737(3)	2.52(10)*
H11	6(5)	62(4)	107(4)	6.0(16)
H12	130(3)	105(3)	128(3)	2.4(10)
H21	–14(4)	230(4)	140(4)	5.2(15)
H31	124(3)	267(3)	245(4)	2.3(9)
H32	204(3)	249(4)	169(3)	2.7(11)
H41	120(4)	450(4)	81(5)	5.7(15)
H42	197(4)	345(4)	55(4)	5.6(16)
H51	1(4)	364(3)	26(3)	3.0(12)
H61	55(3)	311(3)	–108(3)	1.5(9)
H62	166(4)	322(4)	–98(4)	3.9(14)
Hn2	81(4)	389(4)	186(4)	3.7(13)

$$^*B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\vec{a_i}\vec{a_j}).$$
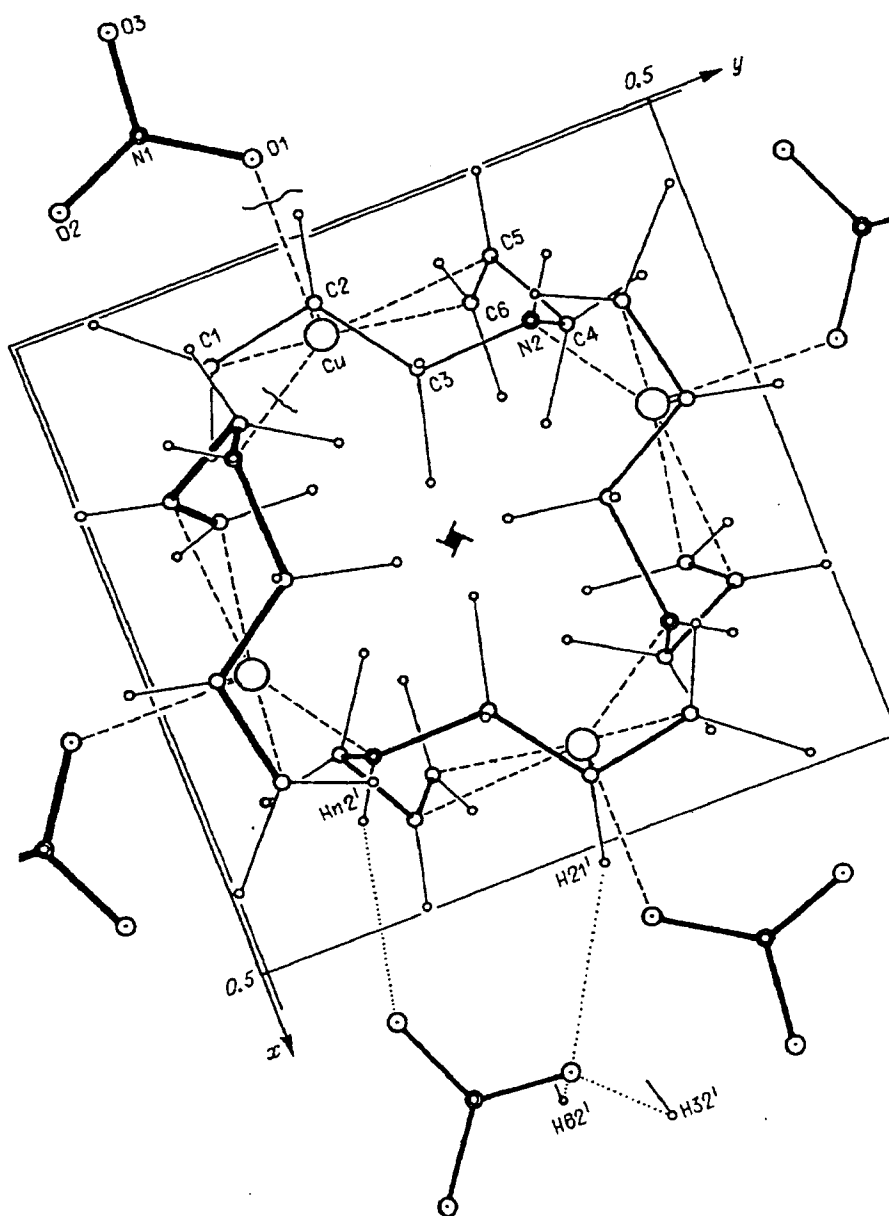
Fig. 1. The projection of the structure on the *xy* plane.

EXPERIMENTAL

Modification B of the [Cu(DAA)]NO$_3$ complex was obtained by an arbitrary transformation of crystals A placed on copper electrodes in an electrochemical container. Single crystals changed their form from octahedral (A) to tetragonal-pyramidal (B).

The diffraction study of crystals (0.2×0.2×0.7 mm in size) was carried out by the photomethod and then on an automatic DARCH diffractometer (MoK_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $2\theta \leq 55°$). Compound B, unlike A (space group $I4_1/a$, $a = 14.346(6)$, $c = 16.719(7)$ Å), crystallizes in space group $I4_1cd$ with $a = 15.083(5)$, $c = 14.694(5)$ Å, $V = 3343(3)$ Å^3, $\rho_{calc} = 1.754(2)$ g/cm^3, $Z = 16$ [Cu(C$_6$H$_{11}$N)]NO$_3$.

The structure was solved by direct methods and refined for 1122 independent reflections with $|F| \geq 4\sigma|F|$ to $R = 0.0329$. A correction for absorption ($\mu = 26.74$ cm^{-1}) was introduced by the DIFABS program. The nonhydrogen

TABLE 2. Bond Lengths d (Å), Bond Angles ω (deg), and Some Torsion Angles φ (deg) in Compound B and the Corresponding Geometric Parameters in Compound A

Bond	d		Angle	ω	
	B	A		B	A
Cu–O1	2.27(4)	2.352(3)	O1–Cu–N2	103.5(2)	103.0(1)
Cu–N2	1.987(4)	2.019(2)	O1–Cu–C(1=2)*	103.8(1)	94.36(9)
Cu–C(1=2)	2.063(5)	2.017(3)	O1–Cu–C(5=6)*	87.3(1)	92.37(9)
Cu–C(5=6)	2.005(4)	2.006(3)	N2–Cu–C(1=2)	114.8(1)	114.01(7)
Cu–C1	2.142(5)	2.100(3)	N2–Cu–C(5=6)	120.2(1)	119.27(7)
Cu–C2	2.198(4)	2.159(3)	C(1=2)–Cu–C(5=6)	119.2(2)	120.9(1)
Cu–C6	2.083(5)	2.093(3)	C1–Cu–C2	36.2(2)	37(3)
Cu–C5	2.148(4)	2.145(3)	C5–Cu–C6	37.2(2)	37.5(1)
N1–O1	1.240(6)	1.201(5)	O1–N1–O2	119.3(5)	133.0(5)
N1–O2	1.236(7)	1.190(7)	O1–N1–O3	118.5(5)	115.7(4)
N1–O3	1.207(7)	1.379(7)	O2–N1–O3	122.2(6)	99.5(5)
N1–O3′	–	1.347(11)			
C1–C2	1.350(7)	1.364(4)	C1–C2–C3	121.5(4)	122.0(3)
C2–C3	1.513(7)	1.509(4)	C2–C3–N2	115.3(4)	115.0(2)
C3–N2	1.485(6)	1.481(4)	C3–N2–C4	113.5(4)	133.3(2)
N2–C4	1.467(6)	1.468(4)	N2–C4–C5	116.7(4)	115.3(2)
C4–C5	1.500(7)	1.506(4)	C4–C5–C6	119.8(4)	122.7(3)
C5–C6	1.352(7)	1.363(4)	C3–N2–Hn2	116(4)	107(2)
N2–Hn2	0.72(6)	0.74(3)	C4–N2–Hn2	106(4)	110(2)
C–H	0.78–1.38(6)	0.77–1.07(4)	C–C–H	101–128(4)	99–123(2)
			H–C–H	104–135(5)	114–120(3)

Torsion angle	φ for B	φ for A
Cu–C1–C2–C3	101.1	103.1
Cu–C6–C5–C4	103.6	100.7
C1–C2–C3–N2	147.3	144.8
C2–C3–N2–C4	63.4	62.8
C3–N2–C4–C5	61.9	65.9
N2–C4–C5–C6	145.6	148.7

*The middle of the corresponding double bond.

atomic parameters were refined by the least-squares method in full-matrix anisotropic (hydrogen atoms in isotropic) approximation and are given in Table 1.

RESULTS AND DISCUSSION

The compound under consideration is crystallochemically related to form A of this complex studied previously. The revealed differences are, nevertheless, very informative and interesting.

The NO_3^- anion takes a more active part in coordination of the copper atom; the Cu–O distance is 2.271(4) Å, while in form A it is 2.352(3) Å (Fig. 1, Table 2). This is probably due to the ordering of the anion (in A, libration of NO_3^- is noted) with its simultaneous orientation in the (001) plane; this also explains a substantial change in the c/a ratio in the polymorphic transition. The instability of the A form seems to be a regular tendency since the reverse transformation (B→A) was not observed.
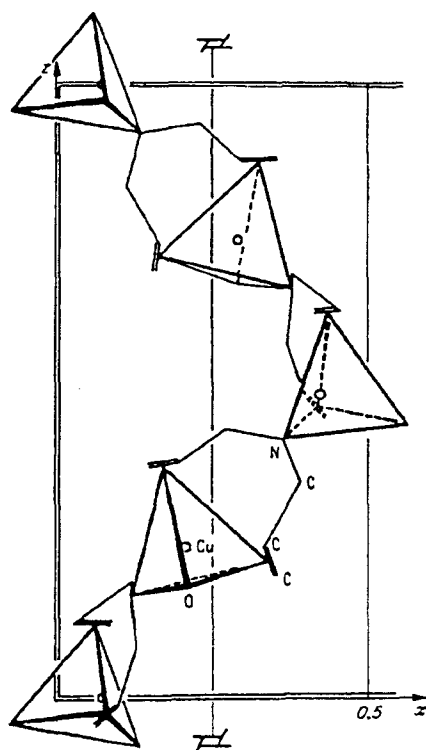
Fig. 2. The packing of the coordination tetrahedra of Cu(I) in the *xz* projection.

Apart from the stronger tetrahedral character compared to A, no substantial changes occur in the coordination sphere of Cu(I). The packing of coordination polyhedra in the structure is shown in Fig. 2 in the *xz* projection. It is interesting that the strengthening of the Cu–O bond leads to a noticeable increase of the σ-donor character of the amine nitrogen (C–N 1.987(4) Å against 2.019(2) Å in A). This compactness of the Cu(I) coordination sphere is, perhaps, partly compensated for by a weakening of the copper–olefin binding (∠Cu–Cu–C in Table 2). Only one of the two independent π-contacts, namely, Cu–(C(1) = C(2)) shows a pronounced change in geometry. In this case, the double bond is farther from the central atom, although both C = C bonds are insignificantly shorter than those in A. These observations confirm the suggestion of [1] that ionicity of the complex strengthens the metal–olefin interaction. Thus the decrease of the Co–O$_{NO_3^-}$ distance in B agrees well with the slight weakening of the Cu–(C = C) binding.

However, the (C)H...O hydrogen bonds, taking an active part in electron-exchange processes in Cu(I) ionic complexes, appeared to be somewhat stronger in the investigated compound (2.24-2.38(5) Å against 2.42-2.45(2) Å in A), while the (N)H...O bond is slightly weaker (2.34(4) and 2.22(2) Å, respectively). The absence of strong hydrogen bonds in A is, perhaps, due to the partial structural disorder of the NO$_3^-$ anion and hence changes in its geometric characteristics (the N–O distances 1.19-1.38(1) Å, the O–N–O angles 99.5-133.0(5)°). Thus the strength of the Cu...(C = C) and (= C)H...(anion) interactions may not be correlated even for such weak structural transformations as polymorphic transitions. It is especially incorrect to compare mixed-component complexes. Nevertheless, close analysis of the Cu(I) coordination sphere with several olefinic groups seems to be rather fruitful.

Polymorphism of the compound remains an interesting point for discussion. The torsion angles of the DAA molecule in A and B are virtually equal, hence the formation of the two modifications is not due to conformational flexibility of the ligand, as it occurred in Cu(I) π-complexes with nonconjugated olefins [2]. In both structures, the conformation of DAA corresponds to the same bridging-chelate function of the tridentate ligand, and the reason for polymorphism lies in redistribution of the efficiency of Cu–O, Cu–(C = C), and hydrogen bonds. Therefore, the ordered location of the NO$_3^-$ ion in structure B, resulting in the shortening of the Cu–O distance, is accompanied by a change in the strength of the copper–olefin interaction and hydrogen bonds.

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Thus, in addition to flexibility of organic ligand molecules, polymorphism is due to the presence of energetically close, weak (and hence elastic) bonds, which are capable of compensating the disadvantages of the formation of structural modifications.

REFERENCES

1. M. G. Myskiv, E. A. Goreshnik, V. K. Pecharskii, and V. V. Olijnik, *Zh. Strukt. Khim.*, 35, No. 1, 90-94 (1994).
2. M. G. Myskiv, P. Yu. Zavalii, V. V. Olijnik, and V. S. Fundamenskii, *ibid.*, 31, No. 4, 85-89 (1990).

Translated by T. Yudanova