

The Crystal Structure of Bis[iodo- μ -(2-diethylaminoethanolato- N,μ -O)copper(II)]

KIMMO SMOLANDER

Department of Chemistry, University of Joensuu, SF-80100 Joensuu 10, Finland

The title compound crystallizes in the triclinic space group $P\bar{1}$ with one dimeric unit in a cell of dimensions $a=6.297(3)$, $b=8.059(2)$, $c=10.464(4)$ Å, $\alpha=73.33(3)$, $\beta=76.84(3)$, $\gamma=71.57(3)^\circ$. The crystal structure has been determined by direct methods from 2558 independent reflections collected with an automatic four-circle diffractometer and refined by full-matrix least-squares methods to an R value of 0.062 and after extinction correction to 0.049.

The structure consists of oxygen-bridged dimers, $[\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})\text{I}]_2$. The copper(II) ion has distorted square-planar coordination with two oxygens, one nitrogen and one iodine atom in the basal plane. The distances are 1.919(3), 1.907(3), 2.045(3) and 2.554(1) Å, respectively. The Cu...Cu distance is 3.007(1) Å.

Many alkoxo-bridged Cu(II) complexes with N,N -dialkylaminoethanols as second ligands have been investigated.^{1–3} The structures have been shown to be dimeric, tetrameric, hexanuclear and polymeric in the solid state. To get more information on how the counter ions influence the structures, we have studied the structure of bis[iodo- μ -(2-diethylaminoethanolato- N,μ -O)copper(II)]. Rather few structures of copper(II) complexes with iodine ligands are known, and the present compound is the first example of an iodo-(N,N -dialkylaminoethanolato)-copper(II) complex.

EXPERIMENTAL

The compound was prepared by mixing 0.01 mol anhydrous cupric sulphate and 0.01 mol potassium iodide in methanol and adding 0.01 mol of redistilled 2-diethylaminoethanol (Fluka AG).

The solution was filtered, and when most of the solvent was removed by slow evaporation at room temperature, dark violet crystals were precipitated. The crystals were filtered off, washed with portions of ice-cold dry ether–ethanol-mixture, and dried in air at ambient temperature.

Unit cell dimensions and the orientation matrix were determined by least-squares method from 22 centered reflections measured at ambient temperature on a Syntex $P2_1$ four-circle diffractometer. The crystal used had approximate dimensions of $0.1 \times 0.2 \times 0.3$ mm. Intensities were collected ($3^\circ < 2\theta < 60^\circ$) with the ω -scan technique using a scan range of 1.0° . The scan speed varied from 1.50 to $29.3^\circ \text{ min}^{-1}$, depending on the number of counts accumulated in a preliminary scan. Background measurements were made at both ends of the scan at 1.0° from the $K\alpha$ peak. Each background was measured for half the scan time. The intensities of two standard reflections were recorded after every 100 measurements. The intensities were corrected for Lorentz and polarization effects, and for absorption from empirical ψ -scan data. Of the 2786 reflections collected, 2558 were used in subsequent calculations.

CRYSTAL DATA

$\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})\text{I}$, $FW=306.63$

Crystal system: Triclinic

Space group: $P\bar{1}$ (No. 2)

$a=6.297(3)$, $b=8.059(2)$, $c=10.464(4)$ Å

$\alpha=73.33(3)$, $\beta=76.84(3)$, $\gamma=71.57(3)^\circ$

$V=477.07$ Å³, $Z=2$, $F(000)=294$

$\mu(\text{MoK}\alpha)=55.9 \text{ cm}^{-1}$, $\lambda(\text{MoK}\alpha)=0.71069$ Å

$D_m=2.13 \text{ g cm}^{-3}$ (floatation technique)

$D_x=2.13 \text{ g cm}^{-3}$

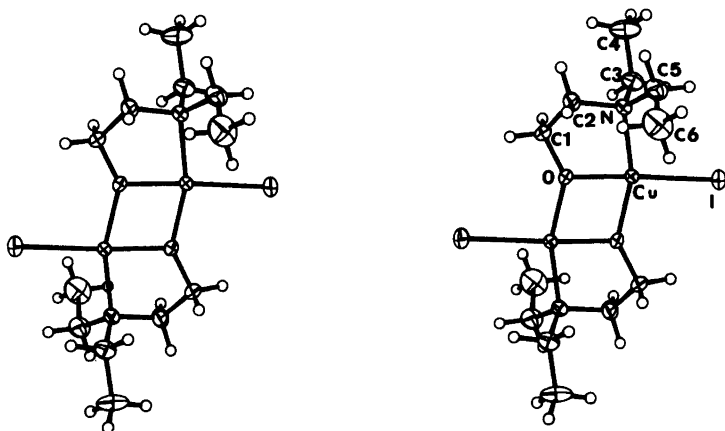


Fig. 1. Stereoview of the dimeric structure of $[\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})\text{I}]_2$. The atoms showing 50% thermal ellipsoids, hydrogen atom radii are set arbitrarily at 0.1 Å.

STRUCTURE DETERMINATION

The SHELXTL SOLV⁴ general direct method gave the positions of I and Cu atoms. The remaining non-hydrogen atoms of the structure were found from successive Fourier syntheses. The structure was refined by the blocked-cascade full-matrix least-square method⁴ with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms were placed at their calculated positions. These and the isotropic temperature factors of the hydrogen atoms were also refined. The refinement converged to conventional R and R_w values of 0.062 and 0.058 with a weighted discrepancy factor⁴ $R_w = \frac{\sum ||F_o| - |F_c||}{\sum |F_o| \sqrt{w}}$ using the weighting scheme $w = [(\sigma^2(F_o) + 0.0003F_o^2)]^{-1}$. After empirical extinction correction, the discrepancy factors were reduced to 0.049 and 0.049, respectively. The neutral atom scattering factors were those of *International Tables for X-Ray Crystallography*.⁵

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL software for minicomputer. The figures were drawn by the ORTEP (Fig. 1) and by the SHELXTL (Fig. 2) programs. The final atomic positional and thermal parameters with their standard deviations are given in Tables 1 and 2.

DISCUSSION

The crystal structure is built up from centrosymmetric oxygen bridged dimers. The coordination around copper(II) ion is distorted square-planar with two oxygen atoms, one nitrogen atom and one iodine atom in the basal plane. The interatomic distances Cu–O 1.919(3) and 1.907(3) Å, and Cu–N 2.045(3) Å are typical for coordination bonds.^{1–3}

The Cu–I distance of 2.554(1) Å is somewhat

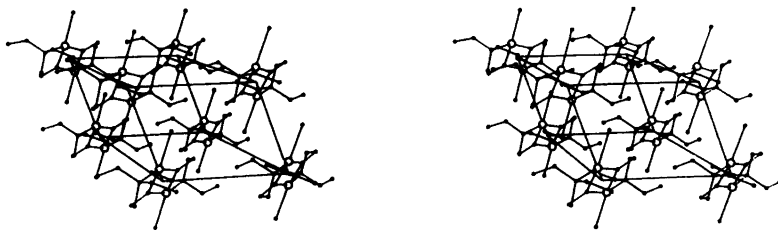


Fig. 2. Stereoview of the molecular packing.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters^a ($\times 10^3$) for non-hydrogen atoms. Estimated standard deviations are in parentheses.

	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
I	6095(1)	-1260(1)	-1723(1)	33(1)	38(1)	46(1)	8(1)	9(1)	-1(1)	44(1)
Cu	1953(1)	361(1)	-1069(1)	28(1)	24(1)	32(1)	-4(1)	6(1)	-5(1)	31(1)
O	-953(6)	1551(4)	-228(4)	36(2)	23(1)	50(2)	1(1)	15(1)	-1(1)	44(1)
N	1609(6)	2724(5)	-2509(4)	30(2)	30(6)	29(2)	-5(1)	1(1)	-9(1)	31(1)
C1	-1756(8)	3372(6)	-804(5)	33(2)	25(2)	40(2)	-4(2)	3(2)	-1(2)	37(1)
C2	-875(7)	3654(7)	-2300(5)	31(2)	36(2)	38(2)	-1(2)	-5(2)	-5(2)	38(2)
C3	2980(9)	3749(7)	-2204(6)	41(2)	38(2)	52(3)	-8(2)	-5(2)	-17(2)	43(2)
C4	2825(15)	5641(9)	-3082(10)	69(4)	37(3)	102(6)	-1(3)	-14(4)	-26(3)	70(3)
C5	2356(10)	2449(7)	-3910(5)	52(3)	46(3)	29(2)	-4(2)	1(2)	-12(2)	45(2)
C6	1448(16)	1087(12)	-4174(8)	85(5)	76(5)	51(4)	-29(3)	-8(4)	-24(4)	67(3)

^aThe anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots 2hka^*b^*U_{12} + \dots)]$. Equivalent isotropic U values were calculated from the anisotropic U_{ij} components.

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^2$) for hydrogen atoms.

Atom	X	Y	Z	U
H1(C2)	-120(11)	485(10)	-283(7)	5(2)
H2(C2)	-164(9)	305(7)	-258(5)	2(1)
H1(C3)	226(10)	385(8)	-124(7)	4(1)
H2(C3)	447(10)	296(8)	-209(6)	3(1)
H1(C1)	-346(13)	389(10)	-58(8)	7(2)
H2(C1)	-109(14)	407(12)	-43(9)	8(2)
H1(C5)	157(21)	332(18)	-413(14)	12(4)
H2(C5)	409(10)	195(7)	-401(6)	3(1)
H1(C4)	398(17)	571(14)	-291(11)	9(3)
H2(C4)	143(11)	644(11)	-308(6)	4(1)
H3(C4)	368(23)	557(19)	-435(17)	18(4)
H1(C6)	232(24)	42(19)	-479(17)	18(4)
H2(C6)	-12(17)	143(14)	-404(12)	10(3)
H3(C6)	172(15)	-8(12)	-338(10)	7(2)

shorter than usually found in copper(II) complexes. In five-coordinated trigonal bipyramidal complexes, where the iodine occupies on the equatorial position, the Cu-I distances are 2.70 Å in iodo-bis(2,2'-bipyridyl)-copper(II) iodide,⁶ 2.679 and 2.717 Å in di[iodo-bis(2,2'-bipyridyl)amine]copper(II) iodide perchlorate⁷ and 2.672 Å in iodo-bis(1,10-phenanthroline)copper(II) iodide octasulfur,⁸ respectively. In the square-pyramidal complex of catena- μ -iodo-bis{ μ -{[2-(3-aminopropyl)amino]ethanolato- $N,N',\mu-O$ }copper(II)}iodide dihydrate⁹ the apical Cu-I distances are elongated to 2.996 and 3.026 Å.

In alkoxo-bridged Cu(II) complexes with N,N' -

dialkylaminoethanols and halogenides X^- one would expect increasing Cu-X distances in the anion order $Cl < Br < I$ according to the ionic radii. The ranges of the Cu-X distances are 2.222–2.249 Å^{10–16} for Cu-Cl and 2.239–2.395 Å^{10–16} for Cu-Br. This work provides the first example of a Cu-I distance (2.554 Å).

In the coordination sphere there is some tetrahedral distortion. The oxygen and iodine atoms lie 0.27 and 0.14 Å above and nitrogen and oxygen atoms 0.18 and 0.22 Å below the basal plane. The dihedral angle between the CuOO' and CuNI planes is 17.4°.

Table 3. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses.

The copper(II) environment			
Cu—N	2.045(3)	N—Cu—O	84.5(1)
Cu—O	1.919(3)	N—Cu—I	101.4(1)
Cu—O ⁱ	1.907(3)	O—Cu—O ⁱ	76.4(1)
Cu—I	2.554(1)	I—Cu—O ⁱ	100.3(1)
Cu...Cu	3.007(1)	N—Cu—O ⁱ	155.9(1)
Cu...I ⁱⁱ	3.739(1)	O—Cu—I	167.8(1)
		Cu—O—Cu ⁱ	103.6(1)
The 2-diethylaminoethanolato ligand			
O—C1	1.391(5)	Cu—N—C2	104.4(2)
C1—C2	1.513(7)	Cu—N—C3	106.5(3)
N—C2	1.501(5)	Cu—N—C5	112.9(3)
N—C3	1.502(8)	C2—N—C3	111.2(4)
N—C5	1.492(6)	C2—N—C5	110.5(4)
C3—C4	1.523(8)	C3—N—C5	111.0(4)
C5—C6	1.500(14)	N—C2—C1	109.5(4)
		N—C3—C4	116.1(6)
		N—C5—C6	113.6(5)
Symmetry code:		O—C1—C2	107.2(4)
i —x, —y, —z		C1—O—Cu	115.6(3)
ii 1—x, —y, —z		C1—O—Cu ⁱ	140.2(3)

The bridging oxygen atoms and the copper(II) ions form a centrosymmetric planar Cu₂O₂ core. The Cu...Cu distance 3.007(1) Å agrees well with the dimeric alkoxo-bridged Cu(II) complexes with *N,N*-dialkylaminoethanols where the distances vary from 2.950 to 3.026 Å. Also the Cu—O—Cu' and O—Cu—O' angles of 103.6(1) and 76.4(1)° are very similar to those of the other dimers.^{11,12,14-20} The deviations from the Cu₂O₂ plane are for the iodine and the nitrogen atoms 0.52 Å above and 0.52 Å below, respectively.

The bond distances and angles of the 2-diethylaminoethanolato ligand are as expected. The five-membered aminoethanolato chelate ring has the *gauche* form. In the ring C1 and C2 lie 0.18 Å above and 0.45 Å below the plane defined by OCuN. The nitrogen atom has sp³ hybridization with a mean bond angle of 109.4°. The C—H bond lengths vary from 0.73 to 1.32 Å with an average value of 0.97 Å.

The dimers are connected to each other so that iodine (1—x, —y, —z) occupies the apical position of the copper. The distance Cu...I 3.739(1) Å is somewhat longer than the sum of the van der Waals radii of these atoms (3.56 Å).²¹ The structure is very similar to the bis[bromo- μ -(2-diethylaminoethanolato-*N*, μ -O)copper(II)]¹⁶ where the Cu...Br distance is 3.660 Å.

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