

The Structure of Tetrakis(diethylammonium) μ_4 -Oxo-hexa- μ_2 -chloro-tetra[chlorocuprate(II)]

BY R. L. HARLOW AND S. H. SIMONSEN

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, USA

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$[(C_2H_5)_2NH_2]_4Cu_4OCl_{10}$, $M_r = 921.3$, monoclinic, $P2_1/c$ (No. 14), $Z = 4$. At 23 °C, $a = 11.099$ (1), $b = 9.744$ (1), $c = 36.977$ (2) Å, $\beta = 111.56$ (1)°, $V = 3719.2$ Å³; Cu $K\alpha_1$ radiation, $\lambda = 1.54050$ Å. $D_x = 1.645$, $D_m = 1.637$ g cm⁻³. At -30 °C, the temperature of the crystal during data collection, $a = 11.022$ (2), $b = 9.698$ (1), $c = 36.750$ (5) Å, $\beta = 111.38$ (1)°, $V = 3657.6$ Å³; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å. Full-matrix least-squares refinement of 224 variables using 4574 reflections [$I > 2\sigma(I)$] collected on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation) converged at a conventional R of 0.056. The Cu, Cl and O atoms were refined with anisotropic thermal parameters, the C and N atoms with isotropic parameters. The crystal structure consists of Cu_4OCl_{10} polynuclear anions interconnected by a three-dimensional network of $Cl \cdots H-N-H \cdots Cl$ hydrogen bonds. The anion is found to be highly distorted from ideal T_d symmetry, apparently because of interionic contacts between the bridging Cl atoms of the anion and the N atoms of the neighboring cations.

Introduction

As part of our investigations into the structural and spectral properties of chlorocuprate(II) complexes, we have begun a study of the various diethylammonium salts. We are particularly interested in the tetrachlorocuprate(II) salt which undergoes a green-to-yellow thermochromic phase transition (Willett, Haugen, Lebsack & Morrey, 1974) which may be similar to that observed for bis(*N*-methylphenethylammonium) tetrachlorocuprate(II) (Harlow, Wells, Watt & Simonsen, 1974). An attempt to prepare $(Et_2NH_2)_4CuCl_4$ by mixing warm methanol solutions containing the proper molar ratio of anhydrous $CuCl_2$ and Et_2NH_2Cl first produced garnet-red crystals; the expected $CuCl_3^-$ salt is green at room temperature. In retrospect, the $CuCl_2$ salt may have been overdried, converting some of the $CuCl_2$ into CuO (Bertrand & Kelley, 1969). Further studies showed that the red crystals would also form directly from the $CuCl_3^-$ salt if the latter were exposed to the atmosphere and allowed to deliquesce. Initial crystallographic studies indicated that the formula weight of the salt was approximately 920, for which no simple combination of Cu^{2+} , Cl and $Et_2NH_2^+$ could account. The crystal structure analysis was thus undertaken to determine the nature and composition of the salt.

Crystals of $(Et_2NH_2)_4Cu_4OCl_{10}$ were invariably found as needles with the needle axis parallel to the crystallographic b axis. One needle was segmented to produce a fragment suitable for structural analysis; the dimensions were $0.16 \times 0.18 \times 0.45$ mm perpendicular to (102), (001), and (010) respectively. Approximate unit-cell dimensions and the space group

were initially determined from oscillation and Weissenberg photographs. The crystal was mounted on a Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus which kept the crystal cooled to -35 °C. The unit-cell parameters at this temperature were refined by least squares using the Bragg angles of 44 reflections. Parameters at 23 °C were later derived from 30 reflections measured under fine conditions using a GE XRD-5 diffractometer.

Intensity data for 6444 unique reflections ($4^\circ < 2\theta < 50^\circ$) were collected on the Syntex diffractometer with the crystal cooled to -35 °C. The ω -scan technique was employed with a scan range of 1.0°. The scan rate varied from 1.5 to 5.0° min⁻¹, depending on the number of counts accumulated in a rapid preliminary scan. Background measurements were taken at both ends of the scan with ω displaced by 1.0° from the $K\alpha$ peak; each measurement was made for one-half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz, polarization and absorption effects; for the latter, the transmission coefficients ranged from 0.70 to 0.78 with $\mu = 18.7$ cm⁻¹.

Solution and refinement of the structure

The structure was solved by direct methods (*MULTAN*) which revealed the tetrahedral array of the Cu atoms and several of the Cl atoms. The remaining atoms of the Cu_4OCl_{10} ion were located in subsequent Fourier maps. Following a refinement of the positional and thermal parameters of these atoms, a difference

map readily disclosed three of the four cations. The fourth cation, containing N(20), had one clearly disordered ethyl group composed of C(21) and C(22) on the one hand and C(21)*p* and C(22)*p* on the other. Subsequent refinement of these disordered atoms yielded approximate occupation factors of 0.55 and 0.45 respectively for the two conformations.

Using only those 4574 reflections for which $I > 2\sigma(I)$, a full-matrix least-squares refinement of the 224 variables (anisotropic thermal parameters for Cu, Cl and O, isotropic for N and C) converged at $R = 0.056$ and $R_w = 0.061$. The mathematical and computational details have been reported (Harlow, Wells, Watt & Simonsen, 1975). One of the largest peaks in the

Table 1. *Final positional and isotropic thermal parameters for [(C₂H₅)₂NH₂]₄Cu₄OCl₁₀*

(a) Atomic coordinates for the Cu₄OCl₁₀⁴⁺ anion

	x	y	z
Cu(1)	0.3176 (1)	0.3763 (1)	0.11722 (3)
Cu(2)	0.6044 (1)	0.3709 (1)	0.11637 (3)
Cu(3)	0.4120 (1)	0.1332 (1)	0.07949 (3)
Cu(4)	0.5295 (1)	0.1665 (9)	0.16953 (3)
Cl(5)	0.4549 (2)	0.5593 (2)	0.09905 (6)
Cl(6)	0.2124 (2)	0.2534 (2)	0.05854 (6)
Cl(7)	0.3562 (2)	0.3175 (2)	0.18266 (6)
Cl(8)	0.6105 (2)	0.1870 (2)	0.07283 (7)
Cl(9)	0.7219 (2)	0.2980 (2)	0.18374 (6)
Cl(10)	0.4328 (3)	-0.0302 (2)	0.13298 (6)
Cl(11)	0.1508 (2)	0.5195 (2)	0.11111 (7)
Cl(12)	0.7689 (2)	0.4952 (2)	0.11160 (7)
Cl(13)	0.3536 (3)	-0.0294 (2)	0.03286 (7)
Cl(14)	0.6000 (2)	0.0569 (2)	0.22705 (5)
O	0.4644 (5)	0.2657 (5)	0.12114 (13)

(b) Atomic coordinates and isotropic thermal parameters for the (C₂H₅)₂NH₂⁺ cations

	x	y	z	U _{iso}
N(15)	0.0271 (7)	0.3662 (7)	0.1701 (2)	0.048 (2)
C(16)	0.0324 (9)	0.2089 (9)	0.1695 (3)	0.059 (2)
C(17)	0.0004 (10)	0.1624 (10)	0.1277 (3)	0.072 (3)
C(18)	0.0661 (10)	0.4179 (10)	0.2107 (3)	0.073 (3)
C(19)	0.0347 (11)	0.5738 (12)	0.2104 (3)	0.086 (3)
N(20)	0.6323 (9)	0.7905 (9)	0.0743 (3)	0.088 (3)
C(21)	0.664 (3)	0.740 (3)	0.0319 (8)	0.101 (9)
C(21) <i>p</i>	0.584 (3)	0.782 (3)	0.0320 (8)	0.084 (8)
C(22)	0.560 (3)	0.630 (3)	0.0106 (7)	0.109 (8)
C(22) <i>p</i>	0.663 (3)	0.675 (3)	0.0228 (8)	0.076 (8)
C(23)	0.7607 (11)	0.8539 (11)	0.0979 (3)	0.083 (3)
C(24)	0.7672 (12)	0.8731 (12)	0.1396 (4)	0.099 (4)
N(25)	0.1817 (7)	0.7236 (7)	0.0447 (2)	0.054 (2)
C(26)	0.1804 (11)	0.6121 (12)	0.0125 (3)	0.085 (3)
C(27)	0.1539 (12)	0.6785 (12)	-0.0264 (3)	0.090 (3)
C(28)	0.0492 (12)	0.7898 (12)	0.0348 (3)	0.094 (4)
C(29)	0.0599 (11)	0.8889 (12)	0.0675 (3)	0.084 (3)
N(30)	0.5374 (7)	0.2614 (7)	0.2867 (2)	0.055 (2)
C(31)	0.4668 (10)	0.1588 (10)	0.3016 (3)	0.070 (3)
C(32)	0.3213 (11)	0.1701 (11)	0.2780 (3)	0.083 (3)
C(33)	0.6818 (11)	0.2578 (11)	0.3107 (3)	0.081 (3)
C(34)	0.7502 (12)	0.3732 (13)	0.2959 (3)	0.100 (4)

Table 2. *Selected interatomic distances (Å) and angles (°) with estimated standard deviations*

Copper-oxygen			
Cu(1)-O	1.903 (5)	Cu(3)-O	1.919 (5)
Cu(2)-O	1.911 (5)	Cu(4)-O	1.917 (5)
Copper-chlorine (terminal)			
Cu(1)-Cl(11)	2.250 (3)	Cu(3)-Cl(13)	2.244 (3)
Cu(2)-Cl(12)	2.237 (2)	Cu(4)-Cl(14)	2.238 (2)
Copper-chlorine (bridging)			
Cu(1)-Cl(5)	2.574 (2)	Cu(3)-Cl(6)	2.358 (3)
-Cl(6)	2.365 (2)	-Cl(8)	2.347 (3)
Cl(7)	2.355 (2)	-Cl(10)	2.470 (2)
Cu(2)-Cl(5)	2.387 (2)	Cu(4)-Cl(7)	2.588 (2)
-Cl(8)	2.414 (3)	-Cl(9)	2.365 (3)
-Cl(9)	2.444 (2)	-Cl(10)	2.353 (2)
Copper...copper			
Cu(1)...Cu(2)	3.174 (1)	Cu(2)...Cu(3)	3.091 (1)
Cu(1)...Cu(3)	3.101 (1)	Cu(2)...Cu(4)	3.099 (1)
Cu(1)...Cu(4)	3.165 (1)	Cu(3)...Cu(4)	3.100 (1)
Chlorine(bridging)...chlorine(bridging)			
Cl(5)...Cl(6)	3.907 (3)	Cl(6)...Cl(10)	4.013 (3)
Cl(5)...Cl(7)	4.308 (3)	Cl(7)...Cl(9)	4.021 (3)
Cl(5)...Cl(8)	4.256 (3)	Cl(7)...Cl(10)	4.067 (3)
Cl(5)...Cl(9)	4.254 (3)	Cl(8)...Cl(9)	3.954 (3)
Cl(6)...Cl(7)	4.294 (3)	Cl(8)...Cl(10)	4.039 (3)
Cl(6)...Cl(8)	4.274 (4)	Cl(9)...Cl(10)	4.408 (3)
Probable hydrogen-bonding contacts			
N(15)...Cl(11)	3.307 (7)	*N(25)...Cl(5)	3.349 (8)
N(15)...Cl(12')	3.136 (7)	N(25)...Cl(11)	3.257 (8)
*N(20)...Cl(5)	3.314 (10)	N(25)...Cl(13')	3.181 (8)
N(20)...Cl(12)	3.294 (9)	N(30)...Cl(14)	3.212 (7)
N(20)...Cl(13')	3.376 (10)	N(30)...Cl(14')	3.194 (7)
Other N...Cl contacts less than 3.8 Å			
N(15)...Cl(7)	3.518 (8)	N(30)...Cl(7)	3.651 (7)
N(15)...Cl(9')	3.638 (8)	N(30)...Cl(10')	3.495 (7)
Copper-oxygen-copper			
Cu(1)-O-Cu(2)	112.7 (2)	Cu(2)-O-Cu(3)	107.6 (2)
Cu(1)-O-Cu(3)	108.5 (2)	Cu(2)-O-Cu(4)	108.1 (2)
Cu(1)-O-Cu(4)	111.9 (2)	Cu(3)-O-Cu(4)	107.8 (2)
Oxygen-copper-chlorine(terminal)			
O-Cu(1)-Cl(11)	175.9 (2)	O-Cu(3)-Cl(13)	177.4 (2)
O-Cu(2)-Cl(12)	179.2 (2)	O-Cu(4)-Cl(14)	177.4 (2)
Oxygen-copper-chlorine(bridging)			
O-Cu(1)-Cl(5)	81.0 (1)	O-Cu(3)-Cl(6)	84.4 (2)
-Cl(6)	84.6 (2)	-Cl(8)	85.1 (2)
-Cl(7)	87.4 (2)	-Cl(10)	83.2 (1)
O-Cu(2)-Cl(5)	86.0 (1)	O-Cu(4)-Cl(7)	80.6 (2)
-Cl(8)	83.4 (2)	-Cl(9)	86.4 (2)
-Cl(9)	84.3 (2)	-Cl(10)	86.5 (1)
Chlorine(terminal)-copper-chlorine(bridging)			
Cl(11)-Cu(1)-Cl(5)	94.9 (1)	Cl(13)-Cu(3)-Cl(6)	97.2 (1)
-Cl(6)	96.3 (1)	-Cl(8)	95.5 (1)
-Cl(7)	95.1 (1)	-Cl(10)	94.3 (1)
Cl(12)-Cu(2)-Cl(5)	93.9 (1)	Cl(14)-Cu(4)-Cl(7)	96.8 (1)
-Cl(8)	97.3 (1)	-Cl(9)	94.2 (1)
-Cl(9)	95.2 (1)	-Cl(10)	94.8 (1)

Table 2 (cont.)

Chlorine(bridging)—copper—chlorine(bridging)

Cl(5)—Cu(1)—Cl(6)	104.5 (1)	Cl(6)—Cu(3)—Cl(8)	130.6 (1)
Cl(5)—Cl(7)	121.8 (1)	Cl(6)—Cl(10)	112.5 (1)
Cl(6)—Cl(7)	131.0 (1)	Cl(8)—Cl(10)	113.9 (1)
Cl(5)—Cu(2)—Cl(8)	124.9 (1)	Cl(7)—Cu(4)—Cl(9)	108.5 (1)
Cl(5)—Cl(9)	123.4 (1)	Cl(7)—Cl(10)	110.7 (1)
Cl(8)—Cl(9)	109.0 (1)	Cl(9)—Cl(10)	138.3 (1)

Copper—chlorine(bridging)—copper

Cu(1)—Cl(5)—Cu(2)	79.5 (1)	Cu(2)—Cl(8)—Cu(3)	81.0 (1)
Cu(1)—Cl(6)—Cu(3)	82.1 (1)	Cu(2)—Cl(9)—Cu(4)	80.3 (1)
Cu(1)—Cl(7)—Cu(4)	79.5 (1)	Cu(3)—Cl(10)—Cu(4)	80.0 (1)

* N(20) and N(25) are atoms in disordered diethylammonium ions.

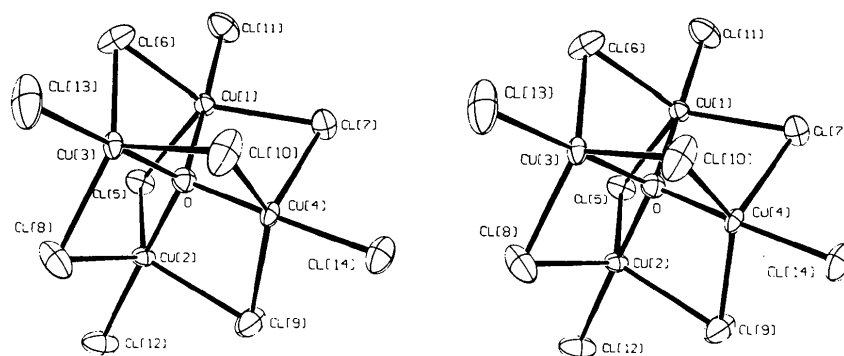
difference map at this point had a magnitude of $0.55 e \text{ \AA}^{-3}$ and was located near N(25). A careful study of the peaks in the neighborhood of this diethylammonium ion indicated that both ethyl groups were slightly disordered. These disordered atoms, which would have been labelled C(26–29)*p*, were not included in the refinement. The H atoms could not be seen in the difference map and were likewise not included in the refinement.

The final positional and isotropic thermal parameters are given in Table 1. The atom-labelling scheme for the anion is presented in Fig. 1. Table 2 lists the important bond parameters.*

Discussion

The crystal structure of $(Et_2NH_2)_4Cu_4OCl_{10}$ consists of discrete $Cu_4OCl_{10}^{4-}$ ions interconnected by a three-dimensional network of $Cl \cdots H-N-H \cdots Cl$ hydrogen

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32638 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. Stereodrawing of the $Cu_4OCl_{10}^{4-}$ anion.

bonds involving all four independent cations (Fig. 2). The probable hydrogen-bonding contacts listed in Table 2 are based on $N \cdots Cl$ distances as well as $C-N \cdots Cl$ and $N \cdots Cl-Cu$ angles. Two conclusions regarding the nature of the hydrogen-bonding scheme can be drawn. (a) Not surprisingly, the terminal Cl atoms, rather than the bridging Cl atoms, are the principal recipients. Each terminal Cl atom is associated with two short $N \cdots Cl$ distances, while only one bridging Cl atom, Cl(5), appears to play a major role in the hydrogen-bonding scheme. (b) The disorder found for the ethyl groups bonded to N(20) and N(25) is directly attributable to the fact that each of these atoms can form hydrogen bonds in two different ways; note that there are three, not just two, short $N \cdots Cl$ contacts for N(20) and N(25).

The structures of three other $Cu_4OCl_{10}^{4-}$ salts have been reported; the cations are tetramethylammonium (Bertrand & Kelley, 1969), potassium (De Boer, Bright & Helle, 1972), and *N,N,N',N'*-tetramethylethylenediammonium (Belford, Fenton & Truter, 1972). In each case, the geometry of the polynuclear anion is restricted by crystallographic site symmetry: 23 and $\bar{4}$, 2, and 2 respectively. The present structure is the first in which all fifteen atoms of the anion are crystallographically independent. In addition, of course, the arrangement of the cations around the anion is not limited by site symmetry. It is thus not surprising to find that the $Cu_4OCl_{10}^{4-}$ anion in the present structure is more distorted from ideal T_d symmetry than the anions previously studied. The distortion is, however, primarily of one type and can best be described in terms of the coordination geometry of the Cu atom. With idealized geometry, the five atoms bonded to the Cu atom form a trigonal bipyramid with three bridging Cl atoms in the equatorial plane and with the central O atom and a terminal Cl atom occupying the axial positions. Three of the four Cu atoms in the present structure have geometries in which one of the equatorial Cu—Cl(bridging) distances is considerably longer than the other two. In addition, the equatorial Cl—Cu—Cl angle opposite

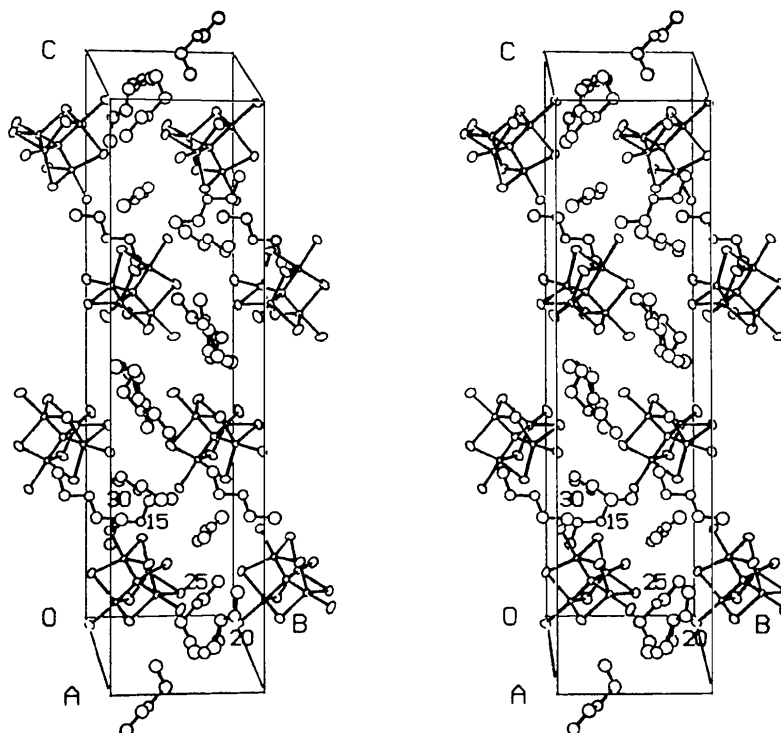


Fig. 2. Packing diagram. The N atoms of the four diethylammonium cations have been numbered.

the long bond is greater than 130° in all three cases. The coordination geometry of these three Cu atoms can thus be described as a trigonal bipyramid which is distorted toward a square pyramid in which the bridging Cl atom associated with the long Cu—Cl bond would occupy the apical position. In all other respects, the bond distances and angles of the anion agree well with those reported for the three other $\text{Cu}_4\text{OCl}_{10}^{4-}$ structures.

Can the distortion of the anion be accounted for on the basis of interionic interactions, or more precisely, do the Cl atoms which form the long Cu—Cl(bridging) bonds interact with the cations in any specific manner? A survey of the interionic bond distances and angles, in conjunction with a model of the crystal structure, has led to only one very general conclusion: those bridging Cl atoms which have elongated Cu—Cl bonds also have Cl \cdots N contacts (whether hydrogen-bonding or purely electrostatic) which are less than 3.66 \AA (see Table 2). The correlation between the lengthening of the Cu—Cl bond and the number and length of the N \cdots Cl

contacts is only qualitative. No correlation between the elongation of the Cu—Cl bond and the Cu—Cl \cdots N angle could be found.

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