

Bis(Trimethylammonium) Decachlorotetracuprate(II)

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Abstract. $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_4\text{Cl}_{10}$ is monoclinic, space group $P2_1/c$, with $a=6.114$ (3), $b=10.253$ (4), $c=19.05$ (1) Å and $\beta=97.88$ (3)°. $\rho_{\text{calc}}=2.06$, $\rho_{\text{obs}}=2.04$ g cm⁻³, $Z=2$. The $\text{Cu}_4\text{Cl}_{10}^{2-}$ anion exists as a discrete bridged tetramer with average Cu-Cl distances of 2.28 Å. The nearly planar tetramer anions stack above each other to give either a 4+1 or a 4+1+1 coordination geometry for each copper ion.

Introduction. Dark brick-red hygroscopic needle crystals of $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_4\text{Cl}_{10}$ were prepared by slow cooling of a fivefold excess of anhydrous CuCl_2 with $(\text{CH}_3)_3\text{NHCl}$ in n-propanol. Analysis: theoretical Cu 34.85, Cl 48.64, C 9.89, N 3.84, H 2.76; experimental: Cu 35.05, Cl 47.91, C 9.82, N 3.89, H 3.28%. A small crystal (0.20 × 0.12 × 0.15 mm) was removed from the solution and immediately mounted in a Lindemann glass capillary. Systematic absences for the monoclinic crystal were $l=2n+1$ for $h0l$ reflections and $k=2n+1$ for $0k0$ reflections, indicating the unique space group $P2_1/c$. Intensity data were collected on an automated Picker full-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. A θ - 2θ step scan was utilized with scans of 2.2° and 20 steps per degree and 2.0 s per step. Background measurements of 10 s were made before and after each scan. The standard deviation in intensity was calculated by $\sigma^2(I_o) = TC - 2B + (0.03)^2 I_o^2$, where TC = total counts, B = background counts, and $I_o = TC - BC$. A total of 1544 reflections were collected in the range $2\theta \leq 45^\circ$, all of which were included in the complete data analysis. Three standards monitored every 30 reflections showed no systematic deviations from normal count-

ing statistics. Absorption corrections were made ($\mu = 4.59$ cm⁻¹) with transmission factors ranging from 0.53 to 0.58.

Copper and chlorine positions were deduced from a Patterson function based on a partial set of film data collected in 1967 when the crystal decomposed during the data collection. Carbon and nitrogen positions were obtained from an electron density map based on later film data. Full-matrix least-squares refinement of the diffractometer data with anisotropic thermal parameters [$\omega_{hkl} = 1/\sigma^2(F)$] proceeded smoothly to a conventional R value of 0.095 for all reflections and a weighted R value of 0.061. The standard error of an observation of unit weight was 1.64. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters are reported in Table 1 and pertinent distances and angles are given in Table 2.* The final difference map showed no unusual features, but did not allow unambiguous assignment of proton positions. Computer programs used were part of a local computer library (Anderson, 1971).

Discussion. The structure is characterized by the presence of discrete centrosymmetric $\text{Cu}_4\text{Cl}_{10}^{2-}$ anions as shown in Fig. 1. This is the first structure of a non-cluster copper halide tetramer which has been eluci-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31694 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final parameters for $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_4\text{Cl}_{10}$

The standard deviation on the least significant digit is given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.1981 (2)	0.4130 (1)	0.46868 (8)	0.0186 (4)	0.0088 (2)	0.00173 (5)	-0.0044 (2)	0.0013 (1)	0.0003 (1)
Cu(2)	0.6408 (2)	0.2851 (1)	0.40705 (8)	0.0200 (5)	0.0066 (2)	0.00206 (5)	0.0016 (2)	0.0020 (1)	-0.0003 (1)
Cl(1)	0.3164 (5)	0.3851 (4)	0.3623 (2)	0.0232 (9)	0.0140 (5)	0.0020 (1)	0.0069 (6)	0.0015 (2)	-0.0002 (2)
Cl(2)	0.5217 (5)	0.3196 (3)	0.5161 (1)	0.0225 (9)	0.0101 (4)	0.0019 (1)	-0.0054 (5)	0.0017 (2)	-0.0005 (2)
Cl(3)	0.6870 (5)	0.2144 (3)	0.2996 (2)	0.0306 (10)	0.0100 (4)	0.0024 (1)	-0.0017 (6)	0.0030 (3)	0.0011 (2)
Cl(4)	0.9517 (5)	0.1880 (3)	0.4607 (2)	0.0236 (10)	0.0081 (4)	0.0025 (1)	0.0045 (5)	0.0016 (3)	-0.0002 (2)
Cl(5)	-0.1097 (4)	0.5306 (3)	0.4213 (1)	0.0205 (9)	0.0079 (4)	0.0018 (1)	0.0035 (5)	0.0011 (2)	-0.0001 (2)
N	0.9103 (14)	0.4979 (9)	0.1644 (5)	0.028 (3)	0.007 (1)	0.0026 (4)	-0.002 (2)	0.0023 (9)	0.0001 (6)
C(1)	0.069 (2)	0.387 (1)	0.1683 (7)	0.040 (5)	0.011 (2)	0.0044 (6)	0.008 (3)	0.006 (1)	0.0005 (9)
C(2)	0.700 (2)	0.464 (1)	0.1155 (8)	0.028 (4)	0.011 (2)	0.0042 (6)	-0.004 (2)	0.000 (1)	-0.0018 (8)
C(3)	0.864 (2)	0.535 (1)	0.2378 (6)	0.033 (4)	0.012 (2)	0.0018 (4)	-0.005 (2)	0.004 (1)	-0.0005 (7)

dated. The Cu–Cl distances within the tetramer are all normal, ranging from 2.261 to 2.321 Å for the bridging Cu–Cl distances (average 2.294 Å) and from 2.262 Å for the terminal Cu–Cl distances (average 2.244 Å). The tetramer shows distinct deviations from planarity; the distances from the mean plane are given in Table 3. These distortions are probably induced by the bulk of the trimethylammonium ions which hydrogen bond to the terminal chloride ions. Observed C–N–Cl angles indicate that a bifurcated hydrogen

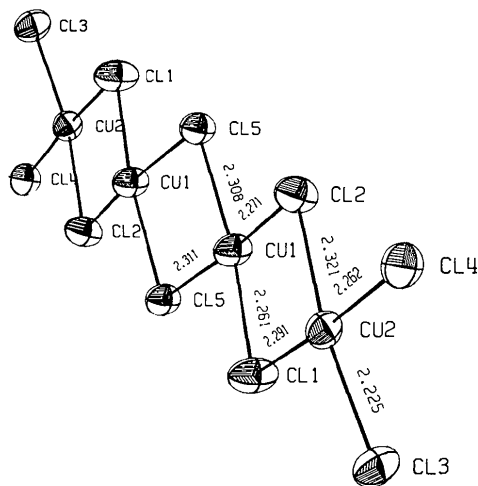


Fig. 1. The centrosymmetric tetramer, showing interatomic distances (Å).

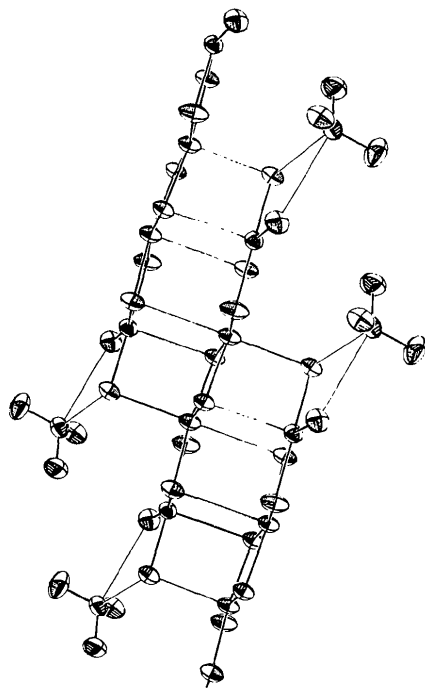


Fig. 2. Illustration of interaction between tetramers.

Table 2. Bond distances and angles in $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_4\text{Cl}_{10}$

Primes denote atoms in adjacent tetramers.

Distances (Å)		Angles (°)	
Cu(1) coordination sphere			
Cu(1)–Cl(1)	2.261 (3)	Cl(1)–Cu(1)–Cl(2)	86.3 (1)
Cu(1)–Cl(2)	2.271 (3)	Cl(1)–Cu(1)–Cl(5)	93.4 (1)
Cu(1)–Cl(5)	2.308 (3)	Cl(2)–Cu(1)–Cl(5)	92.6 (1)
Cu(1)–Cl(5)	2.311 (3)	Cl(5)–Cu(1)–Cl(5)	86.8 (1)
Cu(1)–Cl(4')	2.749 (3)	Cl(1)–Cu(1)–Cl(5)	171.4 (1)
Cu(1)–Cl(2')	3.225 (3)	Cl(2)–Cu(1)–Cl(5)	173.4 (1)
Cl(4')–Cl(1)	3.704 (4)	Cl(4')–Cu(1)–Cl(1)	94.8 (1)
Cl(4')–Cl(2)	3.751 (4)	Cl(4')–Cu(1)–Cl(2)	96.2 (1)
Cl(4')–Cl(5)	3.601 (4)	Cl(4')–Cu(1)–Cl(5)	93.8 (1)
Cl(4')–Cl(5)	3.704 (4)	Cl(4')–Cu(1)–Cl(5)	90.3 (1)
Cl(2)–Cl(1)	3.858 (4)	Cl(2)–Cu(1)–Cl(1)	87.5 (1)
Cl(2)–Cl(2)	3.754 (6)	Cl(2)–Cu(1)–Cl(2)	84.3 (1)
Cl(2)–Cl(5)	3.759 (4)	Cl(2)–Cu(1)–Cl(5)	83.8 (1)
Cl(2)–Cl(5)	3.940 (4)	Cl(2)–Cu(1)–Cl(5)	89.2 (1)
Cl(5)–Cl(3)	> 4.00	Cl(4)–Cu(1)–Cl(2)	177.6 (1)
Cu(2) coordination sphere			
Cu(2)–Cl(1)	2.291 (3)	Cl(1)–Cu(2)–Cl(2)	84.4 (1)
Cu(2)–Cl(2)	2.321 (3)	Cl(1)–Cu(2)–Cl(3)	90.9 (1)
Cu(2)–Cl(3)	2.225 (3)	Cl(2)–Cu(2)–Cl(4)	90.6 (1)
Cu(2)–Cl(4)	2.262 (3)	Cl(3)–Cu(2)–Cl(4)	93.9 (1)
Cu(2)–Cl(5')	2.936 (3)	Cl(2)–Cu(2)–Cl(3)	165.4 (1)
Cl(5')–Cl(1)	3.836 (4)	Cl(1)–Cu(2)–Cl(4)	175.0 (1)
Cl(5')–Cl(2)	3.754 (6)	Cl(5')–Cu(2)–Cu(1)	93.6 (1)
Cl(5')–Cl(4)	3.601 (4)	Cl(5')–Cu(2)–Cl(2)	90.5 (1)
		Cl(5')–Cu(2)–Cl(3)	103.6 (1)
		Cl(5')–Cu(2)–Cl(4)	86.7 (1)
Other intratetramer interactions			
Cl(1)–Cl(2)	3.098 (4)	Cu(1)–Cl(1)–Cu(2)	95.2 (1)
Cl(1)–Cl(3)	3.219 (5)	Cu(1)–Cl(2)–Cu(2)	94.1 (1)
Cl(1)–Cl(5)	3.328 (4)	Cu(1)–Cl(5)–Cu(1)	93.2 (1)
Cl(2)–Cl(4)	3.257 (4)	Cu(1)–Cu(1)–Cu(2)	170.6 (1)
Cl(2)–Cl(5)	3.309 (4)	Cl(3)–Cl(1)–Cl(5)	172.8 (1)
Cl(3)–Cl(4)	3.278 (4)	Cl(4)–Cl(2)–Cl(5)	175.8 (1)
Cl(5)–Cl(5)	3.174 (5)	Cl(1)–Cl(5)–Cl(2)	178.1 (1)
Cu(1)–Cu(1)	3.356 (3)		
Cu(1)–Cu(2)	3.361 (2)		
Trimethylammonium ion			
N–C(1)	1.48 (2)	C(1)–N–C(2)	110.3 (9)
N–C(2)	1.52 (1)	C(2)–N–C(3)	112.0 (9)
N–C(3)	1.51 (2)	C(1)–N–C(3)	110.5 (9)
N–Cl(4)	3.28 (1)		
N–Cl(3)	3.32 (1)		

bond is formed. There are two Cl–C contacts less than 3.5 Å and another two less than 3.6 Å. It is interesting to note (see Fig. 2), that despite the non-planarity, the bridging Cu_2Cl_2 moieties are planar. The non-planarity of the polymer is in sharp contrast to the $\text{Cu}_3\text{Cl}_6(\text{H}_2\text{O})_2$ trimer in $\text{Cu}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 2\text{C}_4\text{H}_8\text{SO}_2$ (Swank & Willett, 1974) and the $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$ and $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ polymers (Willett & Rundle, 1964), where very little non-planarity is observed. As is normally the case the Cl–Cl distances across the bridge (average 3.17 Å) are shorter than the Cl–Cl distances along the chain (average 3.28 Å).

As illustrated in Fig. 2, the tetramers stack on top of each other to form linear chains parallel to the *a* axis. The shortest Cl–Cl contacts between tetramers

Table 3. *Least-squares plane for the Cu₄Cl₁₀²⁻ tetramer in [(CH₃)₃NH]₂Cu₄Cl₁₀*

The equation of the plane is

$$0.4909x + 0.8712y - 0.0006z - 3.8238 = 0.$$

Atom	Distance from plane (Å)
Cu(1)	-0.142
Cu(2)	0.124
Cl(1)	0.101
Cl(2)	-0.066
Cl(3)	-0.230
Cl(4)	0.120
Cl(5)	0.046

(3.604 Å) are just equal to the sum of the van der Waals radii. The stacking is such that Cu(2) assumes a 4+1 coordination geometry, while Cu(1) takes on a 4+1+1 geometry. For the Cu(1) ion, the axial bond lengths are significantly different [Cu-Cl(4) 2.749, Cu-Cl(2) 3.225 Å] and the coordination geometry shows a pronounced square-pyramidal type distortion as indicated by the Cl(eq)-Cu(1)-Cl(ax) bond angles [average Cu(eq)-Cu(1)-Cl(4), 93.8 Å] and the *trans* Cl(eq)-Cu(1)-Cl(eq) angles (average 172.4°). For Cu(2) the distortion of the CuCl₄²⁻ moiety is more complex, with Cu(2), Cl(1), Cl(2) and Cl(4) being approximately coplanar and the Cu(2)-Cl(3) bond being tipped about 14° out of this plane away from the axial ligand.

The three unique bridging Cu-Cl-Cu bond angles average 94.2°, but are individually 93.2, 94.1 and 95.2°. Thus if, as has been proposed (Willett, 1973), this bridging angle controls the sign and magnitude of the magnetic exchange interaction, the Cu(1)-Cu(1) interaction should be ferromagnetic, but the interaction between Cu(1) and Cu(2) will probably be anti-ferromagnetic. Attempts to characterize the magnetic properties of this system have been frustrated by the difficulty of obtaining bulk samples free from CuCl₂ contamination.

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Dibenzo-1,3a,4,6a-tetraazapentalene

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Abstract. C₁₂H₈N₄, monoclinic, *C*2/*c*, *a*=12.05 (1), *b*=5.541 (5), *c*=14.71 (1) Å, β=97.69 (10)°, *Z*=4, *D*_c=1.421, *D*_x=1.425 g cm⁻³ (by flotation). The structure was determined from packing considerations by a computer search, and was refined by least squares to *R*=0.09 (photographic data). The molecule is planar and the bond distances are in good accord with the predictions of Hückel molecular orbital theory.

Introduction. Yellow needles grown from a 1:1 mixture of CHCl₃ and CCl₄ were supplied by Dr R. A. Carboni. Unit-cell dimensions were obtained from photographs

calibrated with superimposed CeO₂-powder photos (*a*=5.411 Å), taken with Cu *K*α radiation (λ=1.5418 Å). The systematic absences, *hkl* with (*h*+*k*) odd and *h0l* with *l* odd, indicated the space group to be *Cc* or *C*2/*c*; the structure analysis showed the latter to be correct. Intensities were measured visually and photometrically from integrated equi-inclination Weissenberg photographs taken with Ni-filtered Cu *K*α radiation. Of the 1027 independent reflections within the Cu *K*α sphere, 751 were observed, 182 were too weak to be measured, and 94 were inaccessible.

The approximate orientational parameters of the planar centrosymmetric molecule were found by a computer analysis of the positions of rigid assumed models situated at each of the two unique centers of symmetry of the presumed space group, *C*2/*c*, the origin and (¼, ¼, 0), very much as described earlier for an-

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