

Crystal Structure of Tetramethylammonium *catena*- μ_4 -chloro-di- μ -chloro-dicuprate(I), $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$

Staffan Andersson and Susan Jagner*

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

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The structure of the title compound has been determined from single-crystal X-ray diffraction data. $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ crystallizes in space group *Pnma* with $a = 16.674(9)$, $b = 6.313(4)$, $c = 9.342(4)$ Å and $Z = 4$. Full-matrix least-squares refinement of 74 structural parameters gave $R = 0.056$ for 991 observed [$I > 3.0 \sigma(I)$] reflections. The $[\text{Cu}_2\text{Cl}_3]^-$ ion is an infinite double chain of edge-sharing Cu(I)-Cl tetrahedra with Cu-Cl distances of 2.254(2), 2.299(2), 2.494(2) and 2.574(2) Å. The anionic configurations of chlorocuprates(I) crystallizing with tetraalkylammonium and related unipositive cations are discussed in terms of the degree of dilution imposed on the ligands by the cations in the solid state.

In crystalline tetraalkylammonium, tetraphenylarsonium and tetraphenylphosphonium halocuprates(I), there would appear to be a trend towards increased X-Cu-X catenation and a higher coordination number of copper(I) with decreasing size of the cation. Thus, whereas the tetrabutylammonium,¹ tetraphenylarsonium,² tetraphenylphosphonium,² and tetrapropylammonium³ dichlorocuprates(I) contain discrete monomeric anions, in tris(tetraethylammonium) *catena*- μ -chloro-*ennea*- μ -chloro-heptacuprate(I),⁴ the anion is an infinite $[\text{Cu}_7\text{Cl}_{10}]^{3-}$ chain in which copper(I) is two- and three-coordinated. In the ammonium compound, copper(I) is tetrahedrally coordinated, the anion being a chain of stoichiometry $[\text{CuCl}_3]^{2-}$.⁵ Calculation of the ligand concentrations in tetraalkylammonium and related halocuprates(I) indicates that the anionic configurations assumed in the solid state are determined by the degree of dilution imposed on the ligands by the cations.³ It therefore seemed likely that tetramethylammonium would crystallize with a chlorocuprate(I) chain composed of shared Cu(I)-Cl tetrahedra. The present investi-

gation was undertaken in order to examine this hypothesis.

Experimental

Tetramethylammonium *catena*- μ_4 -chloro-di- μ -chloro-dicuprate(I) was obtained by dissolving tetramethylammonium chloride and copper(I) chloride (molar ratio 1:1) in ethanol under nitrogen and allowing the solution to evaporate slowly under nitrogen at room temperature. Colourless needles were deposited from the concentrated solution after a few days.

Crystals of $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$, $M_r = 307.6$, are orthorhombic, space group *Pnma* (No. 62)^{6a} with $a = 16.674(9)$, $b = 6.313(4)$, $c = 9.342(4)$ Å, $Z = 4$, $D_c = 2.08 \text{ g cm}^{-3}$ and $\mu (\text{MoK}\alpha) = 5.22 \text{ mm}^{-1}$. Diffracted intensities from a crystal, $0.15 \times 0.24 \times 0.19 \text{ mm}$, were measured at approximately 290 K for $2\theta \leq 60^\circ$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated MoK α radiation and the ω - 2θ scan mode with a variable 2θ scan rate of 2.5 - $29.3^\circ \text{ min}^{-1}$. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method⁷ was used to calculate the intensities.⁸ Of the 1559 in-

*To whom correspondence should be addressed.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-hydrogen atoms in $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$. B_{eq} is defined as

$$8 \pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	0.07644(6)	0.5032(1)	0.4296(1)	6.04(3)
Cl(1)	-0.0402(1)	0.2500	0.3723(2)	3.20(4)
Cl(2)	0.0953(1)	0.7500	0.2518(2)	4.59(5)
Cl(3)	0.1652(1)	0.2500	0.4915(2)	3.98(5)
N	0.1516(3)	0.2500	-0.0351(6)	2.8(1)
C(1)	0.2114(6)	0.2500	0.0824(11)	5.3(3)
C(2)	0.0694(6)	0.2500	0.0335(16)	6.6(4)
C(3)	0.1595(7)	0.0561(13)	-0.1233(10)	8.1(3)

dependent reflections measured, excluding those systematically absent, 991 had $I > 3.0 \sigma(I)$ and were considered observed. Correction was made for Lorentz and polarization effects but not for absorption. The unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Structure determination and refinement

Since the unit-cell dimensions and space group suggested structural similarity with *N*-methylpyridinium triiododicuprate(I),⁹ the atomic coordinates of the anion in the latter compound⁹ were used as starting point for solution of the structure. The cation was located by direct methods (DIRDIF).¹⁰ Full-matrix least-squares refinement¹¹ of positional, isotropic and, subsequently,

anisotropic thermal parameters for the non-hydrogen atoms gave $R = 0.065$ for 55 parameters and 991 reflections. Inclusion of positional coordinates for the hydrogen atoms, located from a difference map, gave a final $R = 0.056$ (74 parameters; 991 reflections); $R_w = 0.067$. The isotropic thermal parameters of the hydrogen atoms were set equal to the equivalent isotropic values (Table 1) of the carrying carbon atoms and not refined. Atomic scattering factors were taken from the *International Tables for x-ray Crystallography*^{6b} and weights were calculated according to $w = [\sigma^2(F_o) + 0.0008F_o^2]^{-1}$. A final difference map showed a maximum electron density of 0.46 e \AA^{-3} . Since a reasonable structural model was obtained in space group *Pnma*, no attempt was made to refine the structure in *Pna2*₁. Atomic coordinates and equivalent isotropic thermal par-

Table 2. Interatomic distances (\AA) and angles ($^\circ$) within the $[\text{Cu}_2\text{Cl}_3]^-$ anion. Estimated standard deviations are given in parentheses.

Symmetry code: (i): \bar{x} , $1-y$, $1-z$; (ii): x , $\frac{1}{2}-y$, z ; (iii): x , $1\frac{1}{2}-y$, z ; (iv): \bar{x} , $y-\frac{1}{2}$, $1-z$.

Cu—Cl(1)	2.574(2)	Cu...Cu ⁱ	2.869(2)
Cu—Cl(1')	2.494(2)	Cu...Cu ⁱⁱ	3.197(2)
Cu—Cl(2)	2.299(2)	Cu...Cu ⁱⁱⁱ	3.116(2)
Cu—Cl(3)	2.254(2)		
Cl(1)—Cu—Cl(1')	111.05(5)	Cu—Cl(1)—Cu ^{iv}	114.63(7)
Cl(1)—Cu—Cl(2)	111.99(7)	Cu—Cl(1)—Cu ⁱ	68.95(5)
Cl(1)—Cu—Cl(3)	96.28(7)	Cu—Cl(1)—Cu ⁱⁱ	76.77(7)
Cl(1')—Cu—Cl(2)	98.39(7)	Cu ^{iv} —Cl(1)—Cu ⁱ	77.34(7)
Cl(1')—Cu—Cl(3)	114.31(8)	Cu—Cl(2)—Cu ⁱⁱⁱ	85.34(9)
Cl(2)—Cu—Cl(3)	125.15(9)	Cu—Cl(3)—Cu ⁱⁱⁱ	90.32(9)

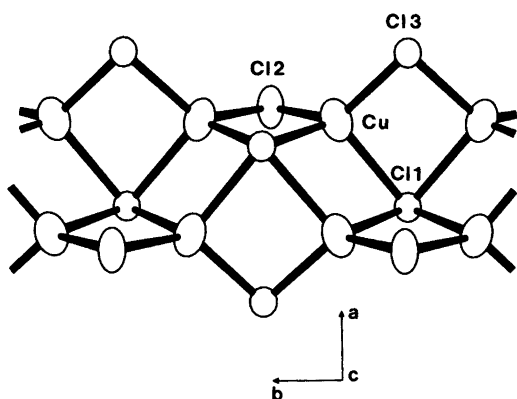


Fig. 1. Part of the infinite double $[\text{Cu}_2\text{Cl}_3]^-$ chain showing the atomic numbering. The thermal ellipsoids enclose 50% probability.¹²

ameters for the non-hydrogen atoms are listed in Table 1. Structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and carbon-hydrogen distances may be obtained from the authors.

Discussion

In tetramethylammonium *catena*- μ_4 -chloro-di- μ -chloro-dicuprate(I), the anion is an infinite double chain of edge-sharing Cu(I)–Cl tetrahedra (Fig. 1) similar to the anions in $[\text{C}_6\text{H}_8\text{N}][\text{Cu}_2\text{I}_3]$,⁹ $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$,¹³ CsCu_2Cl_3 ,¹⁴ and CsCu_2I_3 .¹⁵ As in these compounds,^{9,13–15} there are two sets of copper(I)-halide distances (Table 2), the shorter involving the μ_2 -chloride ligands and the longer the μ_4 . The $[\text{Cu}_2\text{Cl}_3]^-$ chain extends parallel to the *b* axis, the magnitude of which, 6.313(4) Å, is closely similar to that, 6.288(2) Å, in $[\text{C}_6\text{H}_8]$

$[\text{Cu}_2\text{I}_3]$,⁹ with which $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ is practically isostructural. This is also reflected in the similarity of the Cu···Cu separations along the length of the chains in the two compounds, *viz.* 3.116(2) and 3.197(2) Å in $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ and 3.136(4) and 3.144(4) Å in $[\text{C}_6\text{H}_8\text{N}][\text{Cu}_2\text{I}_3]$.⁹ The Cu···Cu separation perpendicular to the length of the chain, 2.869(2) Å, is slightly shorter than those along the length of the chain; the corresponding distance in $[\text{C}_6\text{H}_8\text{N}][\text{Cu}_2\text{I}_3]$ is 2.947(4) Å.⁹

The structure of $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ is illustrated in Fig. 2 and bond distances and angles within the cation are given in Table 3. Whereas the trimethylsulfonium cations in the compound $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$ exhibit severe orientational disorder, as a result of the unsymmetrical nature of the cation,¹³ the orientation of the cation in the tetramethylammonium chlorocuprate(I) analogue is fully ordered. As in $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$,¹³ there are no short Cu···C contacts, the shortest such distance in the present compound being Cu···C(2) = 4.03(1) Å. The shortest Cl···C distances are Cl(1)···C(2) = 3.66(1), Cl(1)···C(3') and Cl(1)···C(3ⁱⁱ) = 3.62(1), Cl(2)···C(2) and Cl(2)···C(2ⁱⁱⁱ) = 3.78(1) Å and Cl(3)···C(3^v) and Cl(3)···C(3^v) = 3.66(1) Å [symmetry code: (i): $\bar{x}, \bar{y}, \bar{z}$; (ii): $\bar{x}, \frac{1}{2}+y, \bar{z}$; (iii): $x, 1+y, z$; (iv): $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; (v): $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$].

Chlorocuprate(I) ions characterised hitherto in compounds crystallizing with symmetrical tetraalkylammonium and related cations or with alkali metal ions are summarised in Table 4. There would appear to be a trend towards increased Cl–Cu–Cl catenation and a higher coordination number of copper(I) with decreasing size of the cation. As expected, the Cu–Cl distances increase with increasing coordination number of copper(I).

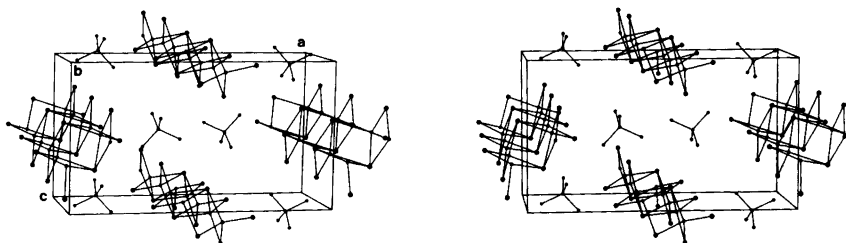


Fig. 2. Stereoscopic view¹² of the structure of $[\text{N}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$. The chlorine atoms are depicted as spheres of radius 0.075 Å and all other atoms as spheres of radius 0.05 Å. Hydrogen atoms have been omitted.

Table 3. Interatomic distances (Å) and angles (°) within the tetramethylammonium ion. Estimated standard deviations are given in parentheses. Symmetry code: (i): $x, \frac{1}{2}-y, z$.

N-C(1)	1.483(12)	C(1)-N-C(2)	107.2(7)
N-C(2)	1.513(12)	C(1)-N-C(3)	110.6(5)
N-C(3)	1.481(9)	C(2)-N-C(3)	108.4(6)
		C(3)-N-C(3')	111.5(8)

Table 4. Chlorocuprate(I) ions characterised by crystal-structure determination of compounds containing tetraalkylammonium, tetraphenylarsonium, tetraphenylphosphonium or alkali metal cations. Infinite chains are denoted as such; the remaining species are discrete entities. C.N. denotes the coordination number of copper(I). Distances are in Å and the ligand concentrations in the crystalline phases in mol dm⁻³.

Cation	Anion	C.N.	Cu-Cl	[Cl]	Ref.
N(C ₄ H ₉) ₄ ⁺	[CuCl ₂] ⁻	2	2.107(1)	6.56	1
As(C ₆ H ₅) ₄ ⁺	[CuCl ₂] ⁻	2	2.069(3), 2.072(3)	5.99	2
P(C ₆ H ₅) ₄ ⁺	[CuCl ₂] ⁻	2	2.088(2), 2.099(2)	6.05	2
N(C ₃ H ₇) ₄ ⁺	[CuCl ₂] ⁻	2	2.071(2)	7.82	3
N(C ₂ H ₅) ₄ ⁺	(Cu ₇ Cl ₁₀) _∞	2,3	2.206(2)-2.346(2)	15.7	4
N(CH ₃) ₄ ⁺	(Cu ₂ Cl ₃) _∞	4	2.299(2)-2.574(2)	20.3	present work
Cs ⁺	(Cu ₂ Cl ₃) _∞	4	2.16, 2.53	31.5	14
NH ₄ ⁺	(CuCl ₃) _∞ ²⁻	4	2.34-2.48	30.1	5
K ⁺	(CuCl ₃) _∞ ²⁻	4	2.31-2.43	31.5	16

As has been demonstrated previously,³ it is possible to rationalise the anionic configurations acquired by halocuprates(I) crystallizing with symmetrical tetraalkylammonium and related unipositive cations on the basis of the degree of dilution in the solid state imposed on the ligands by the cations. In chlorocuprates(I) containing symmetrical tetraalkylammonium and related cations or alkali metal ions (Table 4), the ligand concentration increases with decreasing size of the cation, reaching a limiting value of approximately 31 mol dm⁻³ in the cesium, ammonium and potassium compounds. That tetraphenylarsonium and tetraphenylphosphonium, both formally slightly smaller than tetrabutylammonium, yield slightly lower ligand concentrations than tetrabutylammonium can undoubtedly be ascribed to the greater rigidity of the phenyl rings as compared with the butyl chains, leading to larger effective volumes for the two former cations.

The tetramethylammonium cation permits a ligand concentration in the solid state (Table 4) sufficient for the formation of an infinite chain containing four-coordinated copper(I), of stoi-

chiometry [Cu₂Cl₃]⁻, but apparently insufficient for the formation of a species, containing four-coordinated copper (I), with a higher Cl:Cu ratio, e.g. a [CuCl₂]⁻ chain. Although the ligand concentrations calculated for the cesium, ammonium and potassium compounds differ little from one another (Table 4), the cesium compound contains a [Cu₂Cl₃]⁻ anion, whereas the ammonium and potassium compounds contain anions of stoichiometry [CuCl₃]²⁻. This suggests that the positive charge on the cation becomes determinative for the configuration of the anion in chlorocuprates(I) crystallizing with small cations, formation of a chain with a higher negative charge being favoured the smaller the cation.

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