

Short Communications

Crystal Structure of Phenyltrimethylammonium Dichlorocuprate(I), [N(C₆H₅)(CH₃)₃][CuCl₂]

STAFFAN ANDERSSON and SUSAN JAGNER

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

The anionic configurations in crystalline tetraalkylammonium, tetraphenylarsonium and tetraphenylphosphonium halocuprates(I) would appear to be determined by the degree of dilution imposed on the ligands by the cations.¹ Cations such as tetrabutylammonium,² tetraphenylarsonium,³ tetraphenylphosphonium³ and tetrapropylammonium¹ crystallize with discrete monomeric [CuCl₂]⁻ ions in which copper(I) exhibits linear coordination geometry. In tris(tetraethylammonium) *catena-μ*-chloro-*ennea-μ*-chloro-heptacuprate(I),⁴ the anion is an infinite [Cu₇Cl₁₀]³⁻ chain containing two- and three-coordinated copper(I). No discrete chlorocuprate(I) species containing trigonal-planar coordinated copper(I), analogous to *e.g.* [Cu₄Br₆]²⁻, [Cu₂Br₄]²⁻ or [Cu₂Br₅]³⁻, obtained as the tetrapropylammonium,⁵ tetraethylammonium⁶ and tetramethylammonium⁷ compounds, respectively, has yet been isolated. With phenyltrimethylammonium as cation a centrosymmetric [Cu₂Br₄]²⁻ dimer,⁸ similar to that in bis(tetraethylammonium) di-*μ*-bromo-dibromodocuprate(I),⁶ has been obtained. Since the phenyltrimethylammonium cation might be expected to have a net volume less than that of tetrapropylammonium and similar to that of tetraethylammonium, it seemed conceivable that phenyltrimethylammonium dichlorocuprate(I) might contain a discrete [Cu₂Cl₄]²⁻ dimer. Crystals of the compound were therefore prepared and a structural investigation undertaken.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å²) for the non-hydrogen atoms in [N(C₆H₅)(CH₃)₃][CuCl₂]. 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	0.08059(8)	0.2500	0.18060(8)	4.51(3)
Cl(1)	0.3365(2)	0.2500	0.3012(2)	4.87(5)
Cl(2)	-0.1772(2)	0.2500	0.0605(2)	5.12(5)
N	0.3219(5)	0.2500	0.7865(4)	3.0(1)
C(11)	0.1378(6)	0.2500	0.7037(5)	3.0(1)
C(12)	0.0167(7)	0.2500	0.7685(7)	4.4(2)
C(13)	-0.1521(7)	0.2500	0.6878(8)	5.4(2)
C(14)	-0.1982(8)	0.2500	0.5439(8)	5.2(2)
C(15)	-0.0746(9)	0.2500	0.4792(7)	5.2(2)
C(16)	0.0930(8)	0.2500	0.5584(6)	4.0(2)
C(2)	0.4058(5)	0.0828(6)	0.7522(5)	4.3(1)
C(3)	0.3486(8)	0.2500	0.9419(7)	4.7(2)

Phenyltrimethylammonium dichlorocuprate(I) was prepared by dissolving phenyltrimethylammonium 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 prisms were deposited from the concentrated solution after approximately a week. Crystals of $[N(C_6H_5)(CH_3)_3][CuCl_2]$, $M_r=270.1$, are monoclinic, space group $P2_1/m$ (No. 11),^{9a} with $a=8.378(5)$, $b=7.360(3)$, $c=10.040(4)$ Å, $\beta=108.32(4)^\circ$, $Z=2$, $D_c=1.53$ g cm⁻³ and $\mu(MoK\alpha)=2.33$ mm⁻¹.

Diffracted intensities from a crystal, $0.28 \times 0.29 \times 0.26$ mm, were measured at approximately 290 K for $2\theta \leq 60^\circ$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated $MoK\alpha$ radiation and the ω - 2θ scan mode with a 2θ scan rate of 2.5 – 29.3 °min⁻¹. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method¹⁰ was used to calculate the intensities.¹¹ Of the 1853 independent reflections measured, excluding those systematically absent, 853 had $I > 3.0 \sigma(I)$ and were considered observed. Correction was made for Lorentz and polarisation effects; an empirical correction¹² for the effects of absorption was made after solution of the structure. The unit-cell parameters were determined from diffractometer setting angles for 15 reflections.

The atomic coordinates of the anion were determined from the Patterson map¹³ and those of the cation by direct methods (DIRDIF).¹⁴ Initially, positional and isotropic thermal parameters were refined by full-matrix least-squares¹³ in space group $P2_1$ yielding $R=0.122$ for 52 parameters and 853 reflections. Since, however, intensity statistics (MITHRIL)¹⁵ were consistent with the presence of a centre of symmetry, and correlation coefficients of the order of 0.7–0.8 were obtained between the positional and thermal parameters of the methyl carbon atoms which would be related by the mirror plane in $P2_1/m$, refinement of the structure was continued in the latter space group, all atoms other than the methyl carbon C(2) thus occupying the special position $2e$. Refinement of positional and isotropic thermal parameters gave $R=0.126$ (38 parameters; 853 reflections). After an empirical correction¹² for the effects of absorption $\bar{R}=0.071$. Inclusion of anisotropic thermal parameters gave $R=0.057$. Finally, positional parameters for the hydrogen atoms, located from a difference map,¹³ were included in the refinement, the isotropic thermal parameters of these atoms being set equal to the equivalent isotropic values of the carrying carbon atoms (see Table 1). That also the hydrogen atoms of the methyl groups could be located in chemically reasonable positions in compliance with the mirror plane indicates that space group $P2_1/m$ is preferential to $P2_1$. A final R of 0.043 was obtained for 100 parameters and 853 reflections. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*^{9b} and weights were calculated according to $w=[\sigma^2(F_o)+0.0005 F_o^2]^{-1}$. A final difference map showed a maximum electron density of 0.32 e Å⁻³. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1. Structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and carbon-hydrogen distances may be obtained from the authors.

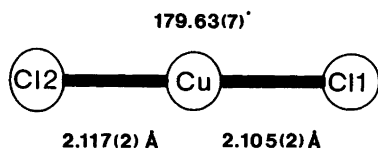


Fig. 1. The dichlorocuprate(I) ion in $[N(C_6H_5)(CH_3)_3][CuCl_2]$. Estimated standard deviations in the distances and angle are given in parentheses. The thermal ellipsoids enclose 50 % probability.¹⁶

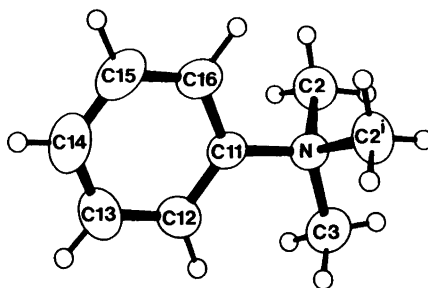


Fig. 2. The phenyltrimethylammonium ion showing the atomic numbering. The thermal ellipsoids enclose 50 % probability and hydrogen atoms are represented as spheres of radius 0.1 Å.¹⁶ Symmetry code: $i: x, \frac{1}{2}-y, z$.

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

N–C(11)	1.504(6)	C(13)–C(14)	1.373(11)
N–C(2)	1.509(5)	C(14)–C(15)	1.385(10)
N–C(3)	1.505(8)	C(15)–C(16)	1.379(9)
C(11)–C(12)	1.367(8)	C(16)–C(11)	1.388(8)
C(12)–C(13)	1.391(8)		
C(11)–N–C(2)	110.1(3)	C(16)–C(11)–C(12)	120.3(5)
C(11)–N–C(3)	111.4(4)	C(11)–C(12)–C(13)	119.6(6)
C(2)–N–C(2 ⁱ)	109.2(4)	C(12)–C(13)–C(14)	120.7(6)
C(2)–N–C(3)	108.0(3)	C(13)–C(14)–C(15)	119.3(6)
N–C(11)–C(12)	121.5(5)	C(14)–C(15)–C(16)	120.4(6)
N–C(11)–C(16)	118.2(4)	C(15)–C(16)–C(11)	119.7(6)

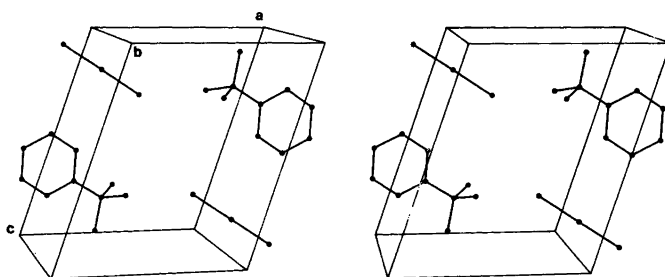


Fig. 3. Stereoscopic view¹⁶ of the unit cell. All atoms are represented as spheres of radius 0.05 Å. Hydrogen atoms have been omitted.

Discussion. The anion in phenyltrimethylammonium dichlorocuprate(I) is a linear monomer (Fig. 1) with Cu–Cl distances within the range of values determined previously for monomeric $[\text{CuCl}_2]^-$ ions (see *e.g.* Ref. 3 and references therein). The geometry of the cation (Fig. 2; Table 2) is essentially similar to that in bis(phenyltrimethylammonium) di- μ -bromo-dibromodicuprate(I).⁸ In the present compound the phenyl ring, C(11)–C(16), the nitrogen atom, and the C(3) methyl carbon lie in a crystallographic mirror plane; in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ ⁸ the dihedral angle between the least-squares plane through the phenyl group and that defined by the atoms corresponding to C(11), N and C(3) is $3.1(5)^\circ$.

The structure of phenyltrimethylammonium dichlorocuprate(I) is illustrated in Fig. 3. As in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ there are short halogen-carbon contacts involving methyl groups, *viz.* $\text{Cl}(1)\cdots\text{C}(2^i)$ and $\text{Cl}(1)\cdots\text{C}(2^{ii})=3.417(5)$ Å [symmetry code: (i): $1-x, \frac{1}{2}+y, 1-z$; (ii): $1-x, -y, 1-z$]. The closest distance between copper(I) and carbon is $\text{Cu}\cdots\text{C}(15)=3.623(7)$ Å, which is somewhat shorter than the corresponding distance, $3.829(7)$ Å, also to *meta*-carbon, in $[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_3]_2[\text{Cu}_2\text{Br}_4]$ ⁸.

Thus, although phenyltrimethylammonium yields a ligand concentration of 11.3 mol dm^{-3} in the present compound, intermediate between that in $[\text{N}(\text{C}_3\text{H}_7)_4][\text{CuCl}_2]$, 7.82 mol dm^{-3} ,¹ and that in $[\text{N}(\text{C}_2\text{H}_5)_4]_3[\text{Cu}_7\text{Cl}_{10}]$, 15.7 mol dm^{-3} ,^{1,4} this concentration would appear to be insufficient for the formation of a discrete chlorocuprate(I) species containing three-coordinated copper(I).

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1. Andersson, S. and Jagner, S. *Acta Chem. Scand. A* 40 (1986). *In press*.
2. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A* 37 (1983) 57.
3. Andersson, S. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 297.
4. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 807.
5. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 725.
6. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 38 (1984) 135.
7. Asplund, M. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 47.
8. Andersson, S. and Jagner, S. *Acta Chem. Scand. A* 39 (1985) 423.
9. a. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. 1; b. *Ibid.*, 1974, Vol. 4.
10. Lehmann, M.S. and Larsen, F.K. *Acta Crystallogr. A* 30 (1974) 580.
11. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr.* 12 (1979) 134.
12. Walker, N. and Stuart, D. *Acta Crystallogr. A* 39 (1983) 158.
13. Lindgren, O. *An Integrated Set of Crystallographic Programs*. In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*, Thesis, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg, 1977.
14. Beurskens, P.T., Bosman, W.P., Doesburg, H.M., Gould, R.O., van den Hark, T.E.M., Prick, P.A.J., Noordik, J.H., Beurskens, G. and Parthasarathi, V. *DIRDIF: Direct Methods for Difference Structures*, Technical Report 1981/2, Crystallography Laboratory, Toernooiveld, Nijmegen, Netherlands 1981.
15. Gilmore, C.J. *J. Appl. Crystallogr.* 17 (1984) 42.
16. Johnson, C.K. *ORTEP: Report ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge 1965.

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