

Coordination of Copper(I) in Two Novel Chlorocuprate(I) Anions; Structures of Tetramethylphosphonium *catena*- μ -Chloro- μ_3 -chloro- $[\mu$ -chloro-dicuprate(I)] and Bis(tetramethylphosphonium) Trichlorocuprate(I)

Staffan Andersson and Susan Jagner*

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

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The title compounds have been prepared and their structures determined from single-crystal X-ray diffraction data. $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ crystallizes in space group $P2_1/c$ with $a = 6.897(5)$, $b = 9.916(11)$, $c = 16.333(14)$ Å, $\beta = 94.20(6)^\circ$ and $Z = 4$. Full-matrix least-squares refinement of 91 structural parameters gave $R = 0.077$ for 1252 observed [$I > 3.0\sigma(I)$] independent reflections, measured at 290 K. $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$ crystallizes in space group $P2_1/m$ with $a = 7.432(4)$, $b = 9.639(6)$, $c = 12.199(7)$ Å, $\beta = 103.23(4)^\circ$ and $Z = 2$. Full-matrix least-squares refinement of 114 structural parameters gave $R = 0.046$ for 1172 observed [$I > 3.0\sigma(I)$] independent reflections measured at 290 K. The anion in $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ is an infinite chain containing three- and four-coordinated copper(I) with $\text{Cu}\cdots\text{Cu}$ distances of 2.705(3) – 3.172(4) Å. The Cu-Cl bond distances associated with the distorted trigonal-planar coordinated copper(I) centre are 2.224(4), 2.270(4) and 2.408(4) Å, while Cu-Cl distances involving the approximately tetrahedrally coordinated copper(I) atom are 2.302(4), 2.328(4), 2.411(4) and 2.636(5) Å. $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$ contains a discrete, mononuclear $[\text{CuCl}_3]^{2-}$ entity with C_{2v} symmetry, the copper(I) atom and one chloride ligand being situated in the crystallographic mirror plane; Cu-Cl bond distances are 2.214(2) and 2.232(3) Å. Trends in the coordination number of copper(I) in chlorocuprates(I) crystallizing with symmetrical tetraalkylammonium, tetraalkylphosphonium and related unipositive cations are discussed.

Structural studies on halocuprates(I) crystallizing with symmetrically substituted tetraalkylammonium and analogous unipositive cations indicate that the coordination number of copper(I) in the anion and the concentration of halide ligand in the crystalline phase increase regularly with decreasing cation size (Refs. 1–3 and references therein). This has been interpreted as suggesting that dilution of the ligand ions by the cations is of importance for the attainment of a particular copper(I) coordination number and thus for the resulting configuration of the anion in the crystal.^{1–3} In the chlorocuprate(I) series, tetrabutylammonium,⁴ tetraphenylarsonium,⁵ tetraphenylphosphonium,⁵ and tetrapropyl-

ammonium¹ have all been found to crystallize with linear, or approximately linear, monomeric anions. In $[\text{N}(\text{C}_2\text{H}_5)_4]_3[\text{Cu}_7\text{Cl}_{10}]$, the anion is an infinite chain containing one two-coordinated and six three-coordinated copper(I) centres, the former and two of the latter having additional $\text{Cu}\cdots\text{Cl}$ contacts of approximately 3 Å, such that these centres may be regarded as being (2+2) and (3+1) coordinated, respectively.⁶ In the tetramethylammonium² and ammonium⁷ compounds, copper(I) is tetrahedrally coordinated, the former containing double chains of edge-sharing tetrahedra, of stoichiometry $[\text{Cu}_2\text{Cl}_3]^{2-}$,² and the latter a single chain of vertex-sharing tetrahedra, of stoichiometry $[\text{CuCl}_3]^{2-}$.⁷ Tetramethylphosphonium, which is intermediate in size between tetraethylammonium and tetramethyl-

*To whom correspondence should be addressed.

ammonium, might be expected to crystallize with a chlorocuprate(I) anion containing three- and four-coordinated copper(I), e.g. a $[\text{Cu}_2\text{Cl}_3]^-$ chain similar to that in $[\text{S}_2\text{C}_3(\text{SCH}_3)_3][\text{Cu}_2\text{I}_3]$,⁸ a distorted version of the $[\text{Cu}_2\text{I}_3]^-$ ion first determined by Hartl and Mahdjour-Hassan-Abadi,⁹ or an isolated anion containing three- and four-coordinated copper(I), similar, for example, to the $[\text{Cu}_4\text{I}_8]^{4-}$ ion in $[\text{Co}(\text{C}_3\text{H}_5)_2]_4[\text{Cu}_4\text{I}_8]$.¹⁰ No chlorocuprate(I) analogues of these ions have been documented hitherto. The present investigation was undertaken in order to attempt to prepare such a species.

Experimental

Preparation of compounds. All operations were carried out under nitrogen. Tetramethylphosphonium chloride (0.126 g; 1.00 mmol) [Alfa (Ventron)] was dissolved in a mixture of 25 ml of ethanol and 15 ml of dichloromethane, by stirring and heating gently. Copper(I) chloride (0.099 g;

1.00 mmol) [Aldrich 99.999 % Gold Label] was added, and stirring and heating were continued until all the solid had dissolved. The resulting solution was allowed to evaporate slowly, colourless striated prisms of $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$, m.p. 227–228 °C, being obtained after approximately 2 days. On one occasion, a few colourless rectangular plates of bis(tetramethylphosphonium) trichlorocuprate(I) were deposited towards the end of the crystallisation (after approximately 4 days). Despite many attempts, it has not, however, been possible to reproduce the preparation of $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$, and thus to ascertain the exact conditions under which crystals are formed. Nor has the melting point of the compound been determined.

Crystal and experimental data for the two compounds are given in Table 1. Space groups and preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs. Diffracted intensities were measured with a Syntex P2₁ diffractometer, using graphite-

Table 1. Crystal and experimental data for $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$ and $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$.

	$[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$	$[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$
M_r	324.6	352.1
Unit cell dimensions/Å, °	$a=6.897(5)$, $b=9.916(11)$ $c=16.333(14)$, $\beta=94.20(6)$	$a=7.432(4)$, $b=9.639(6)$ $c=12.199(7)$, $\beta=103.23(4)$
Space group ^a	$P 2_1/c$	$P 2_1/m$
Z	4	2
$D_x/g \text{ cm}^{-3}$	1.94	1.37
Habit	Colourless prisms	Colourless rectangular plates
M.p./°C	227–228	—
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	4.75	1.95
Crystal size/mm	0.27×0.28×0.27	0.27×0.27×0.16
Temperature (Data collection)/K	290	290
$2\theta_{\text{max}}/^\circ$	55	50
Scan mode	ω -2 θ	ω -2 θ
2θ scan rate/ $^\circ \text{ min}^{-1}$	2.5–20.0	1.5–15.0
No. of unique reflections measured	2561	1608
No. of observed [$I > 3\sigma(I)$] reflections	1252	1172
Correction for absorption ^b	Empirical	Empirical
Method used to solve structure	Direct methods (MITHRIL, ^c DIRDIF ^d)	Direct methods (MITHRIL ^c); successive electron density calculations
No. of parameters refined	91	114
Weights calculated according to	$w=[\sigma^2(F_o)+0.00065 F_o^2]^{-1}$	$w=[\sigma^2(F_o)+0.0001 F_o^2]^{-1}$
R	0.077	0.046
R_w	0.094	0.052
Maximum residual electron density/e Å ⁻³	0.94	0.41

^aRef. 16a. ^bRef. 13. ^cRef. 14. ^dRef. 15.

monochromated MoK α radiation. A 96-step profile was recorded for each reflection, and the intensities were calculated¹¹ using the Lehmann and Larsen profile-analysis method.¹² Correction was made for Lorentz and polarisation effects; empirical corrections for the effects of absorption¹³ were made after solution of the structures. Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Structure determination and refinement

Tetramethylphosphonium catena- μ -chloro- μ_3 -chloro- $[\mu$ -chloro-dicuprate(I)]. The structure was solved by direct methods (MITHRIL,¹⁴ DIRDIF¹⁵). Full-matrix least-squares refinement of positional and isotropic thermal parameters gave

$R = 0.16$; after an empirical correction for the effects of absorption,¹³ $R = 0.14$. Inclusion of anisotropic thermal parameters gave a final $R = 0.077$ for 91 parameters and 1252 observed, independent reflections. A comparable refinement based on data uncorrected for absorption gave $R = 0.079$. It was not possible to locate the hydrogen atoms from the final difference map. Several sets of intensity data were measured for crystals from different batches; the quality of the crystals obtained, however, precluded a more complete refinement of the structure. Attempts made to measure a set of intensity data at low temperature failed owing to crystal cleavage.

Bis(tetramethylphosphonium)trichlorocuprate(I). The atomic coordinates of the anion were obtained by direct methods (MITHRIL),¹⁴ and

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-hydrogen atoms in $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$. B_{eq} is defined as $8\pi^2/3 \sum_i \Sigma_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu(1)	-0.3472(3)	0.0892(2)	-0.0265(1)	6.88(6)
Cu(2)	-0.0866(3)	-0.1075(2)	-0.0518(1)	7.61(7)
Cl(1)	-0.2168(4)	0.0268(3)	-0.1541(2)	5.32(9)
Cl(2)	-0.3262(4)	-0.1490(3)	0.0453(2)	5.76(9)
Cl(3)	-0.1662(5)	0.2471(3)	0.0488(2)	5.61(9)
P	0.2319(4)	-0.0137(3)	0.6803(2)	3.85(7)
C(1)	0.0019(18)	-0.0734(12)	0.6372(8)	5.7(4)
C(2)	0.2047(18)	0.1453(11)	0.7335(7)	5.3(4)
C(3)	0.3892(25)	0.0092(17)	0.5983(11)	9.4(6)
C(4)	0.3239(21)	-0.1348(12)	0.7540(10)	7.4(5)

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-hydrogen atoms in $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$. B_{eq} is defined as $8\pi^2/3 \sum_i \Sigma_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	0.7660(1)	0.2500	0.25757(8)	4.90(3)
Cl(1)	0.6355(3)	0.2500	0.4052(2)	6.71(8)
Cl(2)	0.8161(2)	0.4509(1)	0.1816(1)	6.22(5)
P(1)	0.2577(2)	0.2500	0.0534(2)	4.02(5)
P(2)	0.2310(3)	0.2500	0.5598(2)	4.41(6)
C(11)	0.4262(11)	0.2500	-0.0285(7)	5.2(3)
C(12)	0.0316(11)	0.2500	-0.0371(8)	5.1(3)
C(13)	0.2863(8)	0.4006(8)	0.1383(6)	6.3(2)
C(21)	0.0485(13)	0.2500	0.6321(8)	6.1(3)
C(22)	0.4472(14)	0.2500	0.6597(8)	7.5(4)
C(23)	0.2152(10)	0.3991(7)	0.4743(6)	6.7(2)

those of the cations from a subsequent electron-density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave $R = 0.099$; after an empirical correction for the effects of absorption,¹³ $R = 0.087$. In the final cycles of refinement, anisotropic thermal parameters for the non-hydrogen atoms and positional parameters for the hydrogen atoms, located from a difference map, were included, giving a final R of 0.046 for 114 parameters and 1172 observed, independent reflections. The isotropic thermal parameters for the hydrogen atoms were set equal to B_{eq} of the carrying carbon atom and were not refined.

Further details concerning the refinement of both structures are summarised in Table 1. Atomic scattering factors were taken from Ref. 16b. The computer programs employed are described in Refs. 17 and 18. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2 and 3. Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates for $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$ and connectivity relationships within the cations may be obtained from the authors on request.

Discussion

With tetramethylphosphonium as cation, two crystalline phases have been obtained, viz. $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$, which contains an infinite chain in which copper(I) is three- and four-coordinated (Fig. 1; Table 4), and $[\text{P}(\text{CH}_3)_4]_2[\text{CuCl}_3]$,

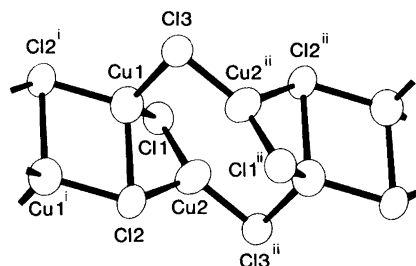


Fig. 1. The $[\text{Cu}_2\text{Cl}_3]^-$ ion in $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$, showing the crystallographic numbering. For symmetry code see Table 4. The thermal ellipsoids enclose 50% probability.¹⁹

in which the anion is an approximately trigonal-planar mononuclear species with C_{2v} symmetry (Fig. 2). The $[\text{Cu}_2\text{Cl}_3]^-$ anion is a variant of the

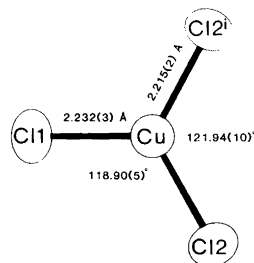


Fig. 2. The $[\text{CuCl}_3]^{2-}$ ion in $[\text{P}(\text{CH}_3)_4]_2[\text{Cu}_2\text{Cl}_3]$, showing the crystallographic numbering. Estimated standard deviations in the distances and angles are given in parentheses. The thermal ellipsoids enclose 50% probability.¹⁹

Table 4. Interatomic distances (Å) and angles ($^\circ$) within the $[\text{Cu}_2\text{Cl}_3]^-$ chain. Symmetry code: (i): $\bar{x}-1, \bar{y}, \bar{z}$; (1 $^{\#}$ 1): $\bar{x}, \bar{y}, \bar{z}$.

Cu(1)–Cl(1)	2.411(4)	Cu(2)–Cl(1)	2.270(4)
Cu(1)–Cl(2)	2.636(5)	Cu(2)–Cl(2)	2.408(4)
Cu(1)–Cl(2')	2.328(4)	Cu(2)–Cl(3 $^{\#}$)	2.224(4)
Cu(1)–Cl(3)	2.302(4)	Cu(1)⋯Cu(2 $^{\#}$)	3.172(4)
Cu(1)⋯Cu(1')	2.929(4)	Cu(2)⋯Cu(2 $^{\#}$)	2.924(4)
Cu(1)⋯Cu(2)	2.705(3)		
Cl(1)–Cu(1)–Cl(2)	98.2(1)	Cl(1)–Cu(2)–Cl(2)	109.4(1)
Cl(1)–Cu(1)–Cl(2')	111.7(2)	Cl(1)–Cu(2)–Cl(3 $^{\#}$)	130.4(2)
Cl(1)–Cu(1)–Cl(3)	114.5(1)	Cl(2)–Cu(2)–Cl(3 $^{\#}$)	117.0(2)
Cl(2)–Cu(1)–Cl(2')	108.0(1)	Cu(1')⋯Cu(1)⋯Cu(2)	96.3(1)
Cl(2)–Cu(1)–Cl(3)	111.2(3)	Cu(1)⋯Cu(2)⋯Cu(2 $^{\#}$)	68.5(1)
Cl(2')–Cu(1)–Cl(3)	112.3(2)	Cu(1)–Cl(2)–Cu(2)	64.7(1)
Cu(1)–Cl(1)–Cu(2)	70.5(1)	Cu(1')–Cl(2)–Cu(2)	125.0(2)
Cu(1)–Cl(2)–Cu(1')	72.0(1)	Cu(1)–Cl(3)–Cu(2 $^{\#}$)	89.0(1)

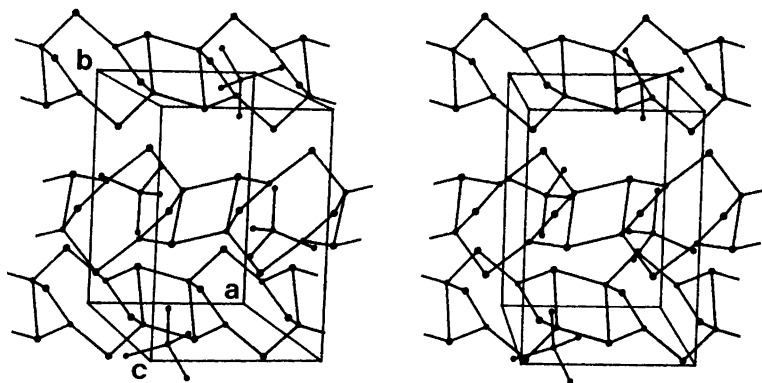


Fig. 3. Stereoscopic view¹⁹ of the structure of $[P(CH_3)_4][Cu_2Cl_3]$. The chlorine atoms are represented as spheres of radius 0.07 Å and all other atoms as spheres of radius 0.05 Å.

$[Cu_2X_3]^-$ chain of edge- and face-sharing tetrahedra first determined in the tetraethylammonium and dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium triiododicuprates(I),⁹ distorted in such a way that one of the two crystallographically independent copper(I) atoms, Cu(2), is trigonal-planar rather than tetrahedrally coordinated. The distance between Cu(2) and the nearest non-bonded chlorine atom Cl(2ⁱⁱ), is 3.814(4) Å; Cl(1ⁱⁱ) and Cl(3) are at 3.913(5) and 3.937(5) Å, respectively, (for symmetry code, see Table 4). As in apparent from Table 4, Cu(2) exhibits severely distorted trigonal-planar coordination geometry and the metal atom is displaced 0.235(3) Å from the plane through Cl(1), Cl(2) and Cl(3ⁱⁱ). The bond distances associated with the distorted tetrahedrally coordinated copper(I) centre, Cu(1), (Table 4) are similar to those determined for e.g. $[N(CH_3)_4][Cu_2Cl_3]$, viz. 2.254(2) – 2.574(2) Å,² the distances in the latter compound, which contains double chains of

edge-sharing copper(I)-chloride tetrahedra, falling into two sets, i.e. two shorter involving the μ_2 chloride ligands and two longer involving the μ_4 . In the present compound, Cu(1) exhibits one relatively long distance and one short distance to the μ_3 chloride ligand, Cl(2), there thus being no distinct correlation between the Cu-Cl distances and the type of bridging ligand. In the analogous $[Cu_2I_3]^-$ chain in $[S_2C_3(SCH_3)_3][Cu_2I_3]$, the copper(I) atoms are alternately three- and four-coordinated.⁸ In $[P(CH_3)_4][Cu_2Cl_3]$, pairs of trigonal-planar and tetrahedrally coordinated copper(I) alternate (cf. Fig. 1). Other infinite, polynuclear chlorocuprate(I) anions in which copper(I) exhibits two different coordination numbers have been documented in compounds such as bis(2,2'-bipyridyl)copper(II) bis[dichlorocuprate(I)]²⁰, tris[bis(1,2-diaminoethane)platinum(II) dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)]²¹ and $[N(C_2H_5)_4][Cu_7Cl_{10}]$.⁶

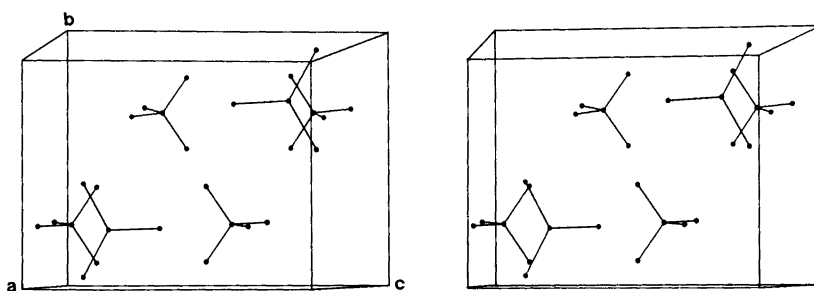


Fig. 4. Stereoscopic view¹⁹ of the structure of $[P(CH_3)_4]_2[CuCl_3]$. All atoms are represented as spheres of radius 0.05 Å.

Table 5. Coordination of copper(I) in chlorocuprates(I) crystallizing with symmetrically substituted ammonium and phosphonium cations. Infinite chain anions are denoted as such. [Cl] is the concentration (mol dm⁻³) of chloride ligand in the crystalline phase.

Cation	Anion	Coord. No. of Cu(I)	[Cl]	Ref.
N(C ₄ H ₉) ₄ ⁺	[CuCl ₂] ⁻	2	6.6	4
As(C ₆ H ₅) ₄ ⁺	[CuCl ₂] ⁻	2	6.0	5
P(C ₆ H ₅) ₄ ⁺	[CuCl ₂] ⁻	2	6.1	5
N(C ₃ H ₇) ₄ ⁺	[CuCl ₂] ⁻	2	7.8	1
N(C ₂ H ₅) ₄ ⁺	(Cu ₇ Cl ₁₀) _∞	1×(2+2) 4×3 2×(3+1)	15.7	6
P(CH ₃) ₄ ⁺	(Cu ₂ Cl ₃) _∞	1×3 1×4	17.9	This work
	[CuCl ₃] ²⁻	3	11.7	This work
N(CH ₃) ₄ ⁺	(Cu ₂ Cl ₃) _∞	4	20.3	2
NH ₄ ⁺	(CuCl ₃) _∞ ²⁻	4	30.1	7

The Cu-Cl bond lengths in the [CuCl₃]²⁻ anion (Fig. 2) are similar to those determined hitherto for trigonal-planar coordinated chlorocuprate(I) species, viz. 2.161(2), 2.224(3) and 2.427(3) Å in the discrete [Cu₂Cl₄]²⁻ dimer in [VO(SALEn)-(H₂O)]₂[Cu₂Cl₄],²² [VO(SALEn)⁺ = *N,N'*-ethylene bis(salicylideneiminato)oxovanadium(V)], 2.291(9) Å in tris[bis(1,2-diaminoethane)platinum(II) dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)],²¹ 2.206(2)–2.346(2) Å in [N(C₂H₅)₄]₃[Cu₇Cl₁₀],⁶ and 2.224(4), 2.270(4) and 2.408(4) Å in [P(CH₃)₄]₄[Cu₂Cl₃] (Table 4). Although bis(tetramethylphosphonium) tribromocuprate(I) also contains a discrete mononuclear anion, [P(CH₃)₄]₂[CuBr₃] and [P(CH₃)₄]₂[CuCl₃] are not isostructural; the tribromocuprate(I) ion has perfect *D*_{3h} symmetry, with a Cu-Br distance of 2.365(3) Å.³ In the anion in bis(methyltriphenylphosphonium) triiodocuprate(I), the first compound for which the existence of a discrete, mononuclear trigonal halocuprate(I) anion was ascertained, Cu-I distances are 2.537(2), 2.559(2) and 2.566(2) Å.²³ Bis(methyltriphenylphosphonium) tribromocuprate(I) has also been shown to contain a similar mononuclear anion.²³

The crystal structures of the two compounds are illustrated in Figs. 3 and 4. The infinite [Cu₂Cl₃]⁻ chain in [P(CH₃)₄]₄[Cu₂Cl₃] runs parallel to the *a* axis. The shortest distances between copper(I) and carbon, and between chlorine and carbon are: Cu(2)···C(2ⁱⁱⁱ) = 3.89(1) Å, and Cl(2)

···C(2^{iv}) = 3.65(1), Cl(3)···C(4^{iv}) = 3.65(2) and Cl(3)···C(1^v) = 3.70(1) Å [symmetry code: (iii): -*x*, *y* - 1/2, 1/2 - *z*; (iv): -*x*, -*y*, 1 - *z*; (v): *x*, 1/2 - *y*, *z* - 1/2]. Comparable non-bonded contacts in [P(CH₃)₄]₂[CuCl₃] are: Cu···C(11) = 3.811(9); Cu···C(13) and Cu···C(13^{iv}) = 3.816(7) Å, and Cl(1)···C(21^{vii}) = 3.63(1) Å, there being several marginally longer Cl···C distances [symmetry code: (vi): *x*, 1/2 - *y*, *z*; (vii): 1 + *x*, *y*, *z*].

Chlorocuprate(I) anions determined hitherto in compounds containing symmetrically substituted ammonium and phosphonium ions are summarised in Table 5. Copper(I) is seen to assume two, three and, finally, four coordination as the size of the cation decreases. The concentration of chloride ligand in the crystalline phase also shows a general increase with decreasing cation size. That tetraphenylarsonium and tetraphenylphosphonium yield slightly lower ligand concentrations than tetrabutylammonium is probably ascribable to the greater rigidity of the phenyl rings than the butyl chains, leading to larger effective volumes for the former cations. Similar trends have been noted for the bromocuprate(I) and iodocuprate(I) counterparts (Refs. 1–3 and references therein). Two crystalline phases have been obtained with the tetramethylphosphonium cation: the major product is [P(CH₃)₄]₄[Cu₂Cl₃], in which the anion contains trigonal-planar and tetrahedrally coordinated copper(I), as predicted from the intermediacy in cation size between tetraethylammonium and tetramethylammonium.

The Cu : Cl ratio in the $[\text{Cu}_2\text{Cl}_3]^-$ anion (1 : 1.5) implies that excess copper(I) over the total Cu : Cl molar ratio in the system (1 : 2) is consumed during formation of $[\text{P}(\text{CH}_3)_4][\text{Cu}_2\text{Cl}_3]$. That the minor crystalline product contains an anion with excess chloride over the total Cu : Cl molar ratio, viz. Cu : Cl = 1 : 3, seems not unreasonable, the situation being similar to that in the butyltriphenylphosphonium – bromocuprate(I) system.²⁴ In the latter system the second product was found to contain a two-coordinated, monomeric anion.²⁴ That a discrete, three-coordinated species was found in the present investigation would appear to be consistent with the size of the tetramethylphosphonium cation.

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