Crystal Structure of Tristrimethylammonium *catena*-Tri-μ-chlorocuprate(1−) Tetrachlorocuprate(2−)

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The crystal structure of the title compound has been determined from photographic X-ray data. Crystals are monoclinic, space group Cc, with cell dimensions a = 1430, b = 2467, c = 630 pm, β = 92·52° and Z = 4. The structure was solved by Patterson and Fourier methods and refined by least squares to R 0·101 for 1480 observed reflections. The compound is unusual in having two types of copper-containing anion, a $[CuCl_3^-]_n$ chain and a $[CuCl_4]^{2-}$ tetrahedron. The symmetry of the crystal lattice is almost hexagonal, and the distortion from hexagonal symmetry is attributed to the Jahn–Teller effect in the $[CuCl_3^-]_n$ chains. The distortion of the tetrahedron differs from that usually found in tetrahedral tetrachlorocuprate(II) complexes in that it approximates to C_{3v} rather than D_{2d} symmetry.

PREVIOUS determinations of the crystal structures of a number of chlorocuprate(II) complexes have shown that there is more than one possible co-ordination geometry about the Cu^{2+} ion for each of the stoicheiometries $ACuCl_3$, A_2CuCl_4, and A_3CuCl_5.[1] The situation is summarised in Table 1. The structure of $(Me_3NH)Cu_2Cl_5$ has also been reported,[2] and contains the polymeric $[Cu_4Cl_{10}]^{2-}$ anion.

TABLE 1

The stoicheiometries and structures of various chlorocuprates(II)

Anion type	Co-ordn. geometry	Example
(*a*) Stoicheiometry $ACuCl_3$		
$[CuCl_3^-]_n$ chains	Distorted octahedral	$CsCuCl_3$
$[Cu_2Cl_6]^{2-}$ dimer	Distorted octahedral	$KCuCl_3$
$[Cu_2Cl_6]^{2-}$ dimer	Square pyramidal	$Me_2NH_2CuCl_3$
(*b*) Stoicheiometry A_2CuCl_4		
Square planar $[CuCl_4]^{2-}$	Distorted octahedral	$(NH_4)_2CuCl_4$
Tetrahedral $[CuCl_4]^{2-}$	Distorted tetrahedral	Cs_2CuCl_4
(*c*) Stoicheiometry A_3CuCl_5		
$[CuCl_5]^{3-}$	Trigonal bipyramidal	$Co(NH_3)_6CuCl_5$
$[CuCl_4]^{2-}$ + Cl^-	Distorted octahedral	$(dienH_3)CuCl_5$
$[CuCl_4]^{2-}$ + Cl^-	Distorted tetrahedral	Cs_3CuCl_5

The known trimethylammonium chlorocuprates(II) [3] are $(Me_3NH)CuCl_3$, $(Me_3NH)CuCl_3,2H_2O$, $(Me_3NH)_2CuCl_4$, $(Me_3NH)_3CuCl_5$, and $(Me_3NH)_3Cu_2Cl_7$. A greater number of chlorocuprate(II) anions is formed with $[Me_3NH]^+$ than with any other cation, and it is considered that this is probably due to a combination of size and hydrogen-bonding effects in the solid state and the effect of $[Me_3NH]^+$ on the chlorocuprate species present in solution.

$(Me_3NH)_3Cu_2Cl_7$ is the only known anhydrous chlorocuprate(II) with this anion stoicheiometry. (A hydrated compound $Cs_3Cu_2Cl_7,2H_2O$ has also been reported [4] and its structure determined.[5] It contains discrete binuclear $[Cu_2Cl_7(H_2O)_2]^{3+}$ anions.) There are various chemically reasonable arrangements of two Cu^{2+} and seven Cl^- ions, based on the structural units of Table 1, and as it was impossible to distinguish between them spectroscopically an X-ray structure determination was undertaken.

EXPERIMENTAL

The compound was prepared by the method of ref. 3 as orange needles.

Crystal Data.—$C_9H_{30}Cl_7Cu_2N_3$, M = 555·59, Monoclinic, a = 1430(3), b = 2467(4), c = 630(2) pm, β = 92·52°, U = 2220 × 10^6 pm^3, D_m(flotation) = 1·65, D_c = 1·65, Z = 4. Space group Cc (No. 9). Cu-K_α radiation λ = 154·18 pm; μ(Cu-K_α) = 97·46 cm^{-1}. Crystal dimensions 0·1 × 0·1 × 0·2 mm.

Structure Determination and Refinement.—The compound is hygroscopic, and each crystal examined was sealed into a thin-walled glass capillary tube together with a small amount of P_2O_5. Oscillation photographs (Cu-K_α radiation) about the needle axis c showed a repeat distance of 630 pm, and the $hk0$ Weissenberg photograph had $6mm$ symmetry, with a 1430 pm. However the $hk1$ photograph showed that each spot had six components of unequal intensity, arranged in a small hexagon. This crystal was therefore a six-fold twin about c and examination of further specimens confirmed that this was a common phenomenon. When a single untwinned crystal was found, it was monoclinic, and systematic absences: hkl $h + k = 2n + 1$, $h0l$ $l = 2n + 1$ $(h = 2n + 1)$, and $0k0$ $k = 2n + 1$, indicated space groups Cc (No. 9) or $C2/c$ (No. 15).[6a] Lattice parameters were obtained from precession photographs (Cu-K_α radiation).

The ease with which twinning occurs can be explained in terms of the closeness of the lattice parameters to those for a hexagonal cell, *i.e.* b is approximately equal to $\sqrt{3}a$ and β is almost equal to 90°; this twinning is of pseudo-merohedral type.[7] The intensity distribution on $hk0$ for the monoclinic individual is still very similar to that for a hexagonal crystal, and there is a pseudo-mirror plane perpendicular to c, so that the symmetry of the diffraction pattern approximates to the Laue group $6/mmm$. These two points are further discussed later.

Layers $hk0$—5 were collected by use of equi-inclination Weissenberg geometry and a multiple-film multiple-exposure technique; $h0$—$2l$ were collected by precession photography. The intensities of the Weissenberg photographs were estimated visually, and those of the precession photographs by use of a Joyce–Loebl flying spot microdensitometer. Lorentz and polarization, but not absorption or spot-shape, corrections were applied. No correction was made for anomalous dispersion. The cross-level data from the precession photographs were used to determine

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[1] R. Colton and J. H. Canterford, ' Halides of the First-row Transition Elements,' Wiley–Interscience, New York, 1969.

[2] R. Caputo and R. D. Willett, personal communication.

[3] H. Remy and G. Laves, *Ber.*, 1933, **66**, 571.

[4] H. L. Wells and L. C. Dupee, *Z. anorg. Chem.*, 1894, **5**, 300.

[5] W. Vogt and H. Haas, *Acta Cryst.*, 1971, **B27**, 1528.

[6] (*a*) International Tables for X-Ray Crystallography, vol. I, Kynoch Press, Birmingham, 1952; (*b*) vol. III, 1962.

[7] R. W. Cahn, *Adv. Phys.*, 1954, **3**, 363.

approximate layer scale-factors for the Weissenberg data, and those were later included in the least-squares refinement. In this way 1480 independent reflections were obtained. Atomic form factors used in subsequent calculations were taken from ref. 6(*b*).

Because the intensity distribution of the diffraction pattern approximates to $6/mmm$ symmetry, attempts were made to assign the unit cell to a hexagonal space group. Space groups $P6_3/mmm$ or $P6_3mc$ fit the data very well, reflections required to be absent by these space groups being either systematically absent or very weak. The overall atomic arrangement must therefore be very close to that required by these space groups, at least for the heavy atoms. It was also noticed that *c* is approximately equal to twice the Cu · · · Cu distance for the chains in $\mathrm{CsCuCl_3}$.[8] These two facts suggested that the structure probably contains $[\mathrm{CuCl_3}^-]_n$ chains of 6_3 symmetry parallel to *c*, and it was therefore postulated that the anion was composed of these chains and isolated chloride ions.

Data reduction was followed by a two-dimensional Patterson synthesis, and a sharpened *hk*0 projection was calculated, assuming *cmm* symmetry. This was interpreted in terms of $[\mathrm{CuCl_3}^-]_n$ chains and Cl^- ions. A two-dimensional Fourier synthesis phased on this model produced a map indicating that the structure in fact contains $[\mathrm{CuCl_4}]^{2-}$ tetrahedra and $[\mathrm{CuCl_3}^-]_n$ chains. A difference-Fourier map gave more accurate heavy-atom positions, and a two-dimensional synthesis phased on these also showed the three trimethylammonium cations. The location of the central copper atom [Cu(1)] of the $\mathrm{CuCl_4}^{2-}$ tetrahedron was found to be almost exactly in the *bc* plane with *z ca.* 2/3. This corresponds to Wyckoff position (*b*) in $P6_3mc$ (non-centrosymmetric) or Wyckoff position (*c*) in $P6_3/mmc$ (centrosymmetric). The symmetry of the $\mathrm{CuCl_4}^{2-}$ ion must therefore be either $3m$ (C_{3v}) in $P6_3mc$ (corresponding to *Cc*) or $6m2$ (D_{3h}) in $P6_3/mmc$ (corresponding to $C2/c$). Since there is no chemically reasonable way of arranging a $\mathrm{CuCl_4}^{2-}$ group to have D_{3h} symmetry, the structure was assumed to be non-centrosymmetric, and the space group *Cc* was confirmed by the structure analysis. The remaining positional parameters were determined by a combination of trial-and-error and three-dimensional Fourier techniques. Nine cycles of block-diagonal[9] least-squares refinement of positional and isotropic thermal parameters reduced *R* to 0·186 for all observed reflections. Ten cycles of full-matrix refinement[10] of positional parameters, with isotropic thermal parameters for carbon and nitrogen, and anisotropic thermal parameters for copper and chlorine [including a weighting scheme with $w = 1$ for $F < F^*$ and $w = 1/\{1 + [(F - F^*)/G^*]^2\}$ for $F \geqslant F^*$ with $F^* = 25$ and $G^* = 35$] gave a final *R* of 0·101. Refinement was considered complete when the shifts in parameters were all $< \sigma$. Positional and thermal parameters with their standard deviations are given in Table 2, and bond distances and angles in Table 3. Structure factors are deposited in Supplementary Publication No. SUP 20589 (20 pp., 1 microfiche).* The unit cell is illustrated in Figure 1.

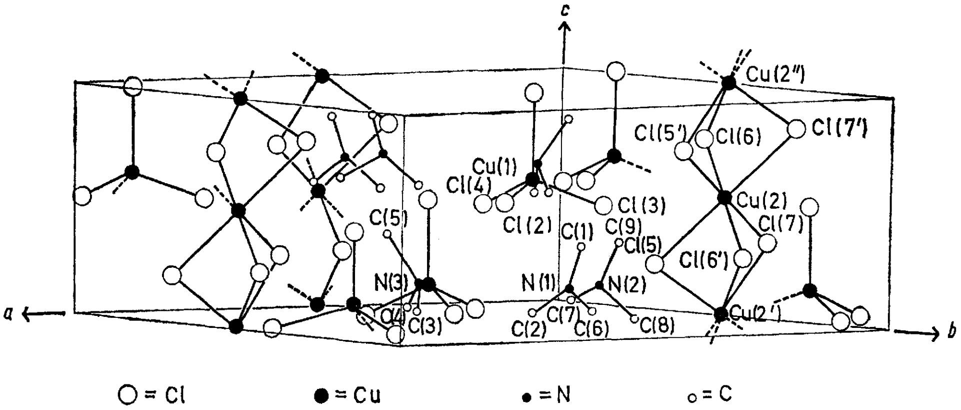

FIGURE 1 The unit cell; one $[\mathrm{CuCl_3}^-]_n$ chain and some of the light-atom groups have been omitted for the sake of clarity

DISCUSSION

This compound is particularly interesting in that it is the only chlorocuprate(II) complex having two separate and different types of copper containing anion, $[\mathrm{CuCl_3}^-]_n$ chains and $[\mathrm{CuCl_4}]^{2-}$ tetrahedra, together with $[\mathrm{Me_3NH}]^+$ cations. Each type of anion is predicted to show Jahn–Teller distortion,[11] and the copper atoms do not have regular octahedral and tetrahedral environments.

An underlying feature of this structure is its almost hexagonal symmetry about *c*, which is illustrated in the *ab* projection (Figure 2). This pseudosymmetry is strongly evident in the diffraction pattern on *hk*0 (see earlier), and also facilitates the growth of twinned crystals.

The hexagonality of the atomic arrangement is chiefly a function of the $[\mathrm{CuCl_3}^-]_n$ chains, which are very similar to those in $\mathrm{CsCuCl_3}$. The latter structure can be thought of in several ways, *e.g.* as a close-packed array of Cl^- ions with Cu^{2+} and Cs^+ ions in the interstices, as containing linked $\mathrm{CuCl_4}^{2-}$ ions, or as containing face-linked $\mathrm{CuCl_6}$ octahedra; these various aspects are helpful in considering the chains in the title compound. Examples

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[8] A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, 1966, **2**, 277.

[9] University of Dundee, CRYPTIC, suite of crystallographic programs.

[10] M. T. G. Powell and A. Griffiths, Portsmouth Polytechnic, 'Crystal '69,' suite of crystallographic programs.

[11] B. N. Figgis, 'An Introduction to Ligand Fields,' Wiley-Interscience, New York, 1966.

of other closely related structures are those of $CsNiCl_3$ [12] and $RbCoCl_3$,[13] both of which contain chains of slightly distorted face-linked octahedra; the chains have 6_3 symmetry. The $[CuCl_3^-]_n$ chains (Figure 3) are of less

TABLE 2

(*a*) Positional parameters (×10^4) with standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Cu(1)	15(3)	1669(1)	6382(8)
Cu(2)	0 *	4999(1)	5000 *
Cl(1)	27(5)	1672(2)	31(17)
Cl(2)	5(6)	814(3)	5229(15)
Cl(3)	−1254(6)	2090(3)	5117(15)
Cl(4)	1294(5)	2098(3)	5402(14)
Cl(5)	1164(5)	4605(2)	2116(12)
Cl(6)	−2(5)	4266(2)	7519(13)
Cl(7)	−1151(4)	4607(2)	2953(12)
N(1)	25(12)	2920(6)	1846(24)
N(2)	−1864(14)	1043(8)	1576(34)
N(3)	1884(11)	1054(7)	1974(27)
C(1)	−6(19)	3269(10)	3722(45)
C(2)	850(27)	3003(15)	681(65)
C(3)	1623(20)	607(11)	662(50)
C(4)	2421(21)	1426(12)	792(54)
C(5)	2468(19)	859(11)	3933(47)
C(6)	−766(23)	3019(12)	376(56)
C(7)	−1566(23)	561(13)	509(58)
C(8)	−2404(19)	1421(11)	254(48)
C(9)	−2367(18)	874(11)	3506(45)

* Fixed to determine the origin, σ therefore is zero.

(*b*) Isotropic thermal parameters ($pm^2 \times 10^5$) with standard deviations in parentheses

	T *		*T*
N(1)	29(3)	C(4)	59(7)
N(2)	43(4)	C(5)	54(7)
N(3)	31(3)	C(6)	62(8)
C(1)	52(6)	C(7)	66(8)
C(2)	76(9)	C(8)	52(6)
C(3)	53(6)	C(9)	49(6)

* *T* is the coefficient in the expression for the isotropic temperature factor: $\exp-(T\sin^2\theta/\lambda^2)$.

(*c*) Anisotropic thermal parameters * (×10^4) with standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	55(2)	18(1)	260(8)	−1(1)	1(2)	1(2)
Cu(2)	42(1)	15(1)	183(8)	1(1)	−6(2)	2(1)
Cl(1)	48(3)	17(1)	227(17)	−2(1)	−9(5)	−3(4)
Cl(2)	77(4)	16(1)	398(23)	1(2)	8(7)	−21(4)
Cl(3)	57(3)	23(1)	454(27)	7(2)	−29(7)	15(4)
Cl(4)	55(3)	23(1)	398(24)	−6(2)	24(7)	7(4)
Cl(5)	47(3)	16(1)	249(19)	−1(1)	−20(5)	5(3)
Cl(6)	47(2)	17(1)	288(17)	−1(2)	−1(5)	−2(4)
Cl(7)	40(2)	15(1)	225(17)	−3(1)	−22(5)	−9(3)

* β_{ij} are coefficients in the expression:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta kl)].$$

TABLE 3

Selected bond distances and angles with estimated standard deviations in parentheses

(*a*) Bond distances (pm)

Cu(1)–Cl(1)	230(1)	N(1)–C(1)	146(4)
Cu(1)–Cl(2)	223(1)	N(1)–C(2)	142(5)
Cu(1)–Cl(3)	220(1)	N(1)–C(6)	141(5)
Cu(1)–Cl(4)	223(1)	N(2)–C(7)	148(5)
Cu(2)–Cl(5)	270(1)	N(2)–C(8)	140(5)
Cu(2)–Cl(6)	241(1)	N(2)–C(9)	154(4)
Cu(2)–Cl(7)	226(1)	N(3)–C(3)	140(4)
Cu(2)–Cl(5′)	230(1)	N(3)–C(4)	145(5)
Cu(2)–Cl(6′)	239(1)	N(3)–C(5)	157(4)
Cu(2)–Cl(7′)	272(1)		

TABLE 3 (*Continued*)

(*b*) Bond angles (°)

Cl(1)–Cu(1)–Cl(2)	109·2(0·4)	Cl(6)–Cu(2)–Cl(7′)	78·4(0·5)
Cl(1)–Cu(1)–Cl(3)	109·2(0·4)	Cl(6′)–Cu(2)–Cl(7)	88·3(0·5)
Cl(1)–Cu(1)–Cl(4)	107·8(0·4)	Cl(6′)–Cu(2)–Cl(7′)	101·1(0·3)
Cl(2)–Cu(1)–Cl(3)	109·5(0·4)	Cl(7)–Cu(2)–Cl(7′)	95·6(0·5)
Cl(2)–Cu(1)–Cl(4)	110·7(0·4)	C(1)–N(1)–C(2)	112(3)
Cl(3)–Cu(1)–Cl(4)	110·4(0·4)	C(1)–N(1)–C(6)	111(3)
Cl(5)–Cu(2)–Cl(5′)	95·2(0·5)	C(2)–N(1)–C(6)	106(3)
Cl(5)–Cu(2)–Cl(6)	101·1(0·3)	C(3)–N(3)–C(4)	109(3)
Cl(5)–Cu(2)–Cl(6′)	79·4(0·5)	C(3)–N(3)–C(5)	110(3)
Cl(5)–Cu(2)–Cl(7)	85·2(0·3)	C(4)–N(3)–C(5)	110(2)
Cl(5)–Cu(2)–Cl(7′)	179·1(0·5)	C(7)–N(2)–C(8)	115(3)
Cl(5′)–Cu(2)–Cl(6)	87·6(0·5)	C(7)–N(2)–C(9)	108(3)
Cl(5′)–Cu(2)–Cl(6′)	92·1(0·5)	C(8)–N(2)–C(9)	113(3)
Cl(5′)–Cu(2)–Cl(7)	179·4(0·5)	Cu(2)–Cl(5)–Cu(2′)	77·6(0·5)
Cl(5′)–Cu(2)–Cl(7′)	84·0(0·5)	Cu(2)–Cl(6′)–Cu(2′)	82·0(0·5)
Cl(6)–Cu(2)–Cl(6′)	179·5(0·5)	Cu(2)–Cl(7)–Cu(2′)	77·9(0·5)
Cl(6)–Cu(2)–Cl(7′)	91·9(0·3)		

(*c*) Angles between Cl · · · Cu · · · Cl vectors in the $CuCl_5$ octahedron (°)

Between Cl(5) · · · Cu(2) · · · Cl(7′) and Cl(6) · · · Cu(6) · · · Cl(6′) 101·1(0·5)

Between Cl(5′) · · · Cu(2) · · · Cl(7) and Cl(6′) · · · Cu(2) · · · Cl(6) 91·9(0·5)

Between Cl(5′) · · · Cu(2) · · · Cl(7) and Cl(5) · · · Cu(2) · · · Cl(7′) 95·5(0·5)

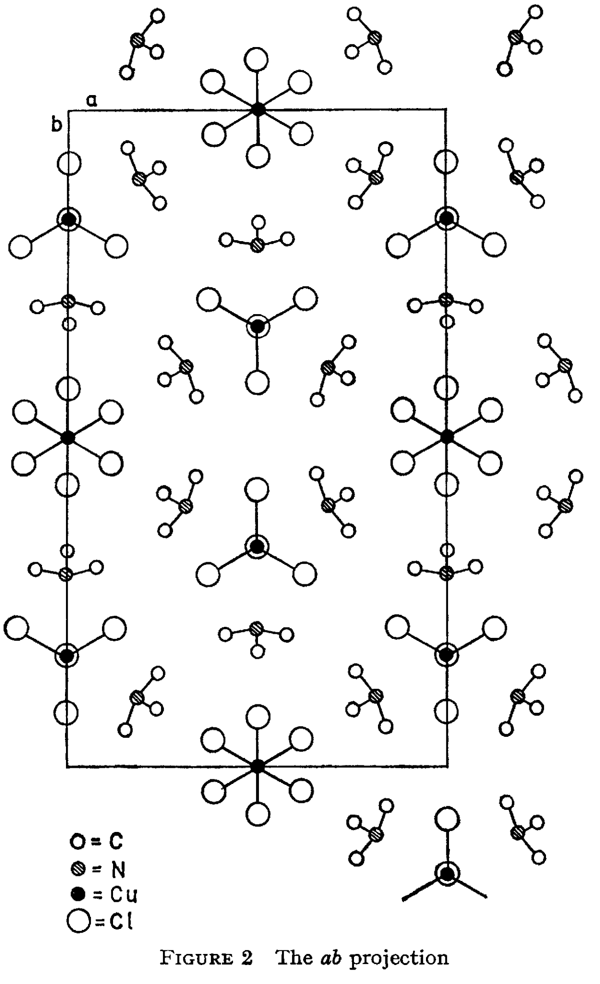

FIGURE 2 The *ab* projection

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[12] G. Stucky, S. D'Agostino, and G. McPherson, *J. Amer. Chem. Soc.*, 1966, **88**, 4828.

[13] A. Engberg and H. Soling, *Acta Chem. Scand.*, 1967, **21**, 168.

than 6_3 symmetry ($CsCuCl_3$ was originally described[14] as containing chains of square planar $CuCl_4^{2-}$ ions joined by one-chloride bridges), but the detailed geometry of the chain differs between $(Me_3NH)_3Cu_2Cl_7$ and $CsCuCl_3$. In the former the system of copper atoms is linear and parallel to *c*, whereas in the latter the copper atoms are displaced by *ca.* 42 pm from the unique axis, resulting in a spiral arrangement with 6_1 symmetry. The system of bridging between adjacent copper atoms is similar in each case, with one symmetrical Cu–Cl–Cu bridge formed with two bonds of medium length and two unsymmetrical bridges with one long and one short bond. In each $CuCl_6$ octahedron there are two long (270 and 277 pm), two medium (241 and 235 pm), and two short (226 and 228 pm) bonds, but the arrangement of these around the central atom is not identical in the two compounds.

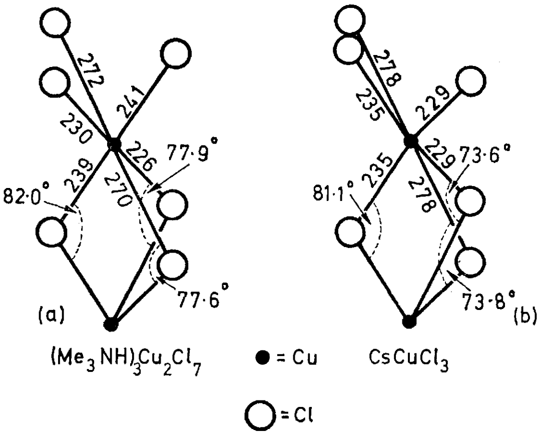

FIGURE 3 The $[CuCl_3^-]_n$ chains in (*a*) $(Me_3NH)_3Cu_2Cl_7$ and (*b*) $CsCuCl_3$

In each case the two long bonds are mutually *trans*, but whereas in $(Me_3NH)_3Cu_2Cl_7$ the short bonds are mutually *trans*, in $CsCuCl_3$ they are *cis*, and are related by the two-fold axis through the central copper atom. In $(Me_3NH)_3Cu_2Cl_7$ the Cl–Cu–Cl axes of the octahedron are straight (179·1, 179·4, and 179·5°), whereas in $CsCuCl_3$ they deviate significantly from linearity (178·3, 178·3, and 171·2°). The $CuCl_6$ octahedron in $(Me_3NH)_3Cu_2Cl_7$ has an approximate centre of symmetry, but is distorted not only by bond lengthening but by angle distortions, so that it can be described in terms of three triclinic vectors. If the three planes containing the central atom and four chlorine ligands are considered, the greatest angular distortions are found where the Cu–Cl distances are longest, and *vice versa*. The angles between the Cl ··· Cu vectors are given in Table 3(*c*). It is suggested that this represents an increase in the ease of distortion with Cu–Cl distance, *i.e.* with weakening of the Cu–Cl bond. In $CsCuCl_3$ the situation is less clear, since no group of four chlorine ligands is exactly coplanar, but qualitatively the relationship between distortion and bond distance appears similar.

Despite the distortions, the atomic arrangement in the chains of $(Me_3NH)_3Cu_2Cl_7$ tends towards hexagonal symmetry. Another effect contributing to the hexagonality of the lattice is the packing of the chains in the cell. $CsCuCl_3$ has been regarded as a close-packed structure of individual ions,[8] but it can also be considered as a close-packed arrangement of roughly cylindrical $[CuCl_3^-]_n$ chains with Cs^+ ions in the interstices. The model seems relevant to the present structure, in which the hexagonal packing of the chains leaves holes for the cations and $CuCl_4^{2-}$ ions (Figure 2).

The $CuCl_4^{2-}$ tetrahedron is slightly unusual. MCl_4^{2-} tetrahedra (M = Cu, Co, Ni, and Zn) in the compounds $(Me_4N)_2MCl_4$ all show some degree of distortion from T_d symmetry,[15] but this is very much more marked for Cu^{2+} than for the other metal ions, an effect usually attributed to Jahn–Teller distortion of the d^9 ion. In each instance the distortion can be described as a 'flattening' of the tetrahedron towards D_{2d} symmetry; this is also true of the $CuCl_4^{2-}$ ion in other tetrahedral tetrachlorocuprates, *e.g.* trimethyl(benzyl)ammonium tetrachlorocuprate,[16] caesium tetrachlorocuprate,[17] and tetramethylammonium tetrachlorocuprate[18] (Table 4).

TABLE 4

Bond distances (pm) and angles (°) in some chlorocuprates

	Cu–Cl		Cl–Cu–Cl	
$(Me_3PhN)CuCl_4$	222·9	226·3	99·1	132·1
	226·6	226·3	98·3	132·8
			99·7	100·3
$CsCuCl_4$	218	225	124·9	102·5
			123·3	102·9
$(Me_4N)_2CuCl_4$	225	221	132·1	101·1
	223		126·6	100·8
$CuCl_4$ in $(Me_3NH)_3Cu_2Cl_7$	230	223	109·2	109·5
	223	220	109·2	110·7
			107·8	110·4

In contrast, in the lattice of $(Me_3NH)_3Cu_2Cl_7$ the holes left for the $CuCl_4^{2-}$ ions have approximate three-fold symmetry. There are no crystallographic symmetry restrictions on the shape of the $CuCl_4^{2-}$ ion, and it adopts an arrangement with approximate trigonal (C_{3v}) symmetry, in which all the bond angles are close to 109·5°. In an isolated crystal structure it is difficult to distinguish between the effects of crystal packing on the shape of the ions and the influence of the ions on their environments, but there seems to be sufficient evidence that tetrahedral $CuCl_4^{2-}$ ions usually adopt a D_{2d} configuration, so that the C_{3v} configuration in $(Me_3NH)_3Cu_2Cl_7$ must be explained in terms of crystal packing. Not only is the ion placed in a hole with approximate three-fold symmetry, but this is reinforced by interaction with the cations. If a model is constructed of the $CuCl_4^{2-}$ tetrahedron and its surrounding Me_3NH^+ groups, with hydrogen atoms being introduced to complete the tetrahedral

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[14] A. F. Wells, *J. Chem. Soc.*, 1947, 1662.

[15] J. R. Wiesner, R. C. Srivastava, C. H. L. Kennard, M. DiVaira, and E. C. Lingafelter, *Acta Cryst.*, 1967, **B23**, 565.

[16] M. Bonamico, G. Dessy, and A. Vaciago, *Theor. Chim. Acta*, 1967, **7**, 367.

[17] B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, 1961, **65**, 50.

[18] P. Murray-Rust and J. Murray-Rust, unpublished work.

co-ordination of the nitrogen atoms, the N $\cdots$ H vectors are directed approximately towards Cu(1), and the N $\cdots$ Cl(2), N $\cdots$ Cl(3), and N $\cdots$ Cl(4) distances are all *ca.* 350 ± 2 pm. No specific hydrogen-bonding interaction is postulated, but electrostatic interactions between $CuCl_4^{2-}$ and the N–H groups will provide additional stabilization for the C_{3v} configuration. It may be argued that the Jahn–Teller effect is still operative in this ion, since the Cu(1)–Cl(1) bond is significantly longer than the bonds to Cl(2), Cl(3), and Cl(4), although the bond angles are all close to 109·5°; however, Cl(1) is the only one of the four chloride ligands which does not interact with the cations, so that its bond with Cu(1) might be expected to differ from the other three. [It is improbable that Cl(1′), at 400 pm from Cu(1), can be regarded as a fifth ligand.] It is impossible, therefore, to confirm the existence of Jahn–Teller distortion in the $CuCl_4^{2-}$ tetrahedron.

An interesting property of this compound concerns the possibility of replacing the copper ions either in the chain, or the tetrahedra, or in both, with other metal ions. In practice it is possible to replace the $CuCl_4^{2-}$ tetrahedron with $CoCl_4^{2-}$ and $ZnCl_4^{2-}$, but not to replace any of the Cu^{2+} in the chain. Preliminary *X*-ray data[19] show that $(Me_3NH)_3CuCoCl_7$ [or $(Me_3NH)_3CuCl_3,CoCl_4$] has a diffraction pattern almost identical with $(Me_3NH)_3Cu_2Cl_7$, although the cell dimensions differ slightly. The diffuse reflectance spectrum (350—700 nm) confirmed the presence of tetrahedral $CoCl_4^{2-}$.

It is, however, difficult to prepare a pure specimen of $(Me_3NH)_3CuCoCl_7$, since it forms a continuous series of solid solutions with $(Me_3NH)_3Cu_2Cl_7$. This had led to a more general interest in the formation of solid solutions between compounds containing ions predicted to show Jahn–Teller distortion and those which do not.

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[19] J. Murray-Rust, unpublished work.