Crystal Structure of Tris(tetraethylammonium)

catena-μ-Chloro-ennea-μ-chloro-heptacuprate(I),

[N(C₂H₅)₄]₃[Cu₇Cl₁₀]

MILJA ASPLUND and SUSAN JAGNER

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

The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data. $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$ crystallizes in space group $C2/c$ with $a=19.052(7)$, $b=16.296(6)$, $c=13.782(8)$ Å, $\beta=98.95(4)°$ and $Z=4$. Full-matrix least-squares refinement of 290 structural parameters gave $R=0.063$ for 2743 observed $[I>3.0\,\sigma(I)]$ reflections. The $[Cu_7Cl_{10}]^{3-}$ ion is an infinite Cl-bridged chain, the repeat unit of which contains six three-coordinated copper(I) atoms and one two-coordinated copper(I) atom. For the latter Cu−Cl=2.165(2) Å, while for the three-coordinated copper(I) atoms Cu−Cl distances range from 2.206(2) to 2.346(2) Å, the ligand configurations being approximately trigonal planar. The closest Cu···Cu distances are 2.890(2)−3.447(3) Å.

Chlorocuprate(I) ions have been encountered in the solid state as discrete $[CuCl_2]^-$ monomers,[1–9] a discrete $[Cu_5Cl_{16}]^{11-}$ ion,[10] and various types of infinite chain. The latter comprise $[CuCl_4]^{3-}$ containing two- and three-coordinated copper(I) with longer Cu···Cl contacts providing trigonal-bipyramidal ligand configurations,[11] $[CuCl_2]^-$ containing two- and four-coordinated copper(I),[3] $[CuCl_2]^-$ containing four-coordinated copper(I) only,[12,13] and $[CuCl_3]^{2-}$,[14,15] $[Cu_2Cl_3]^-$,[16] and $[Cu_3Cl_5]^{2-}$,[17] all based on shared Cu(I)−Cl tetrahedra. Both tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) contain linear monomeric anions.[7] The anion in tetraethylammonium dibromocuprate(I), on the other hand, is a centrosymmetric

$[Cu_2Br_4]^{2-}$ dimer, containing approximately trigonal-planar coordinated copper(I).[18] As part of an investigation concerning the geometry assumed by halocuprate(I) ions in the solid state as a function of the size and effective positive charge on the cation, it was of interest to investigate the chloro counterpart with the tetraethylammonium ion as cation. Crystals of composition $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$ were thus obtained.

EXPERIMENTAL

Tris(tetraethylammonium) *catena*-μ-chloro-ennea-μ-chloro-heptacuprate(I) was prepared by dissolving copper(I) chloride in a saturated solution of tetraethylammonium chloride in ethanol under nitrogen (molar ratio $N(C_2H_5)_4Cl$: $CuCl=1:1$). The pale yellow solution was allowed to stand under nitrogen, colourless prisms of $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$ being deposited after a few days.

Crystals of $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$, $M_r=1190.1$, are monoclinic, space group No. 15,[19a] $C2/c$, with $a=19.052(7)$, $b=16.296(6)$, $c=13.782(8)$ Å, $\beta=98.95(4)°$, $Z=4$, $D_c=1.87$ g cm^{-3} and $\mu(MoK\alpha)=4.23$ mm^{-1}. Diffracted intensities from a crystal, $0.20\times0.26\times0.32$ mm, were measured at approximately 290 K for $2\theta\leqslant55°$, on a Syntex $P2_1$ diffractometer, using graphite-monochromated MoKα radiation and the $\omega-2\theta$ scan mode with a variable 2θ scan rate of 2.5−25.0° min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[20] was used to calculate the intensities.[21]

Of the 4890 independent reflections thus measured, 2743 had $I > 3.0 \sigma(I)$ and were used in the subsequent calculations. Intensities were corrected for Lorentz and polarisation effects; an empirical correction[22] was made for the effects of absorption after solution of the structure. The unit-cell parameters were determined from diffractometer setting angles for 15 reflections.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved from Patterson and successive electron density maps.[23] Full-matrix least-squares refinement[23] of positional and isotropic thermal parameters for the non-hydrogen atoms gave $R = 0.16$. After an empirical correction[22] for absorption effects, $R = 0.12$. Inclusion of anisotropic thermal parameters and positional parameters for the hydrogen atoms (located from a difference map), the isotropic temperature factors of the latter being set equal to the equivalent isotropic values of the carrying carbon

atoms, yielded $R = 0.063$ (290 parameters; 2743 reflections). A comparable refinement based on the data uncorrected for absorption gave $R = 0.071$. The large temperature factor of Cu(1), $B_{eq} = 7.50(6)$ $Å^2$, suggested that there might be disorder associated with this site. Positioning Cu(1) on either side of the 2-fold axis did not, however, improve the model. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[19b] and the F_o values were weighted according to

$$w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$$

A final difference map showed a maximum electron density of 1.2 e $Å^{-3}$. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1. Structure factors, anisotropic thermal parameters, hydrogen atom coordinates and bond lengths and angles within the cations may be obtained from the authors.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms in $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$. B_{eq} is defined as $8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

| Atom	x	y	z	B_{eq}
Cu(1)	0.0000	0.26492(11)	0.2500	7.50(6)
Cu(2)	0.15341(6)	0.21921(7)	0.22452(9)	5.59(4)
Cu(3)	0.27031(5)	0.26717(6)	0.12461(8)	4.80(3)
Cu(4)	0.12710(5)	0.22734(6)	0.01251(8)	4.54(3)
Cl(1)	0.1016(1)	0.2949(1)	0.3363(2)	4.75(6)
Cl(2)	0.2660(1)	0.1819(1)	0.2530(2)	4.95(6)
Cl(3)	0.0632(1)	0.1637(1)	0.1139(2)	4.42(5)
Cl(4)	0.1901(1)	0.3452(1)	0.0286(1)	4.03(5)
Cl(5)	0.3855(1)	0.3222(1)	0.1448(1)	3.58(4)
N(1)	0.3222(2)	0.4337(3)	0.4515(4)	2.3(1)
C(1)	0.2660(4)	0.3783(4)	0.4837(6)	3.3(2)
C(2)	0.2025(4)	0.4223(6)	0.5134(7)	4.4(2)
C(3)	0.3792(4)	0.3781(4)	0.4214(6)	3.2(2)
C(4)	0.4415(4)	0.4217(6)	0.3909(7)	4.1(2)
C(5)	0.2909(4)	0.4897(4)	0.3692(5)	3.0(2)
C(6)	0.2543(4)	0.4468(6)	0.2779(6)	4.1(2)
C(7)	0.3540(4)	0.4894(4)	0.5349(5)	2.9(2)
C(8)	0.3878(5)	0.4464(5)	0.6276(6)	4.1(2)
N(2)	0.5000	0.0686(4)	0.2500	2.8(2)
C(9)	0.4737(4)	0.1226(5)	0.1609(6)	4.6(2)
C(10)	0.5312(5)	0.1760(6)	0.1288(8)	5.4(3)
C(11)	0.4370(4)	0.0172(5)	0.2661(7)	4.5(2)
C(12)	0.4505(7)	−0.0367(7)	0.3595(8)	6.2(3)
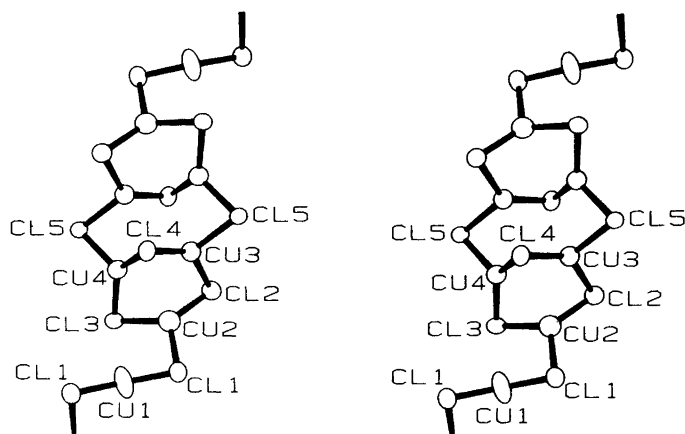
Fig. 1. Stereoscopic view[24] of part of the infinite $[Cu_7Cl_{10}]^{3-}$ chain. The thermal ellipsoids enclose 50 % probability.

DISCUSSION

Part of the infinite $[Cu_7Cl_{10}]^{3-}$ chain is shown in Fig. 1 and interatomic distances and angles within the anion are given in Table 2. Cu(2), Cu(3) and Cu(4) are approximately trigonal-planar coordinated with the copper(I) atoms displaced 0.200(2), 0.306(2) and 0.113(2) Å, respectively, from the planes (A, B and C)

through their ligand atoms. The dihedral angles between planes A and B, A and C, and B and C are 84.3(1), 115.2(1) and 111.6(1)°, respectively. Cu(3) has an additional contact of 2.980(2) Å to Cl(4^i) [symmetry code: (i):½−x,½−y,z̄], the displacement of Cu(3) from the plane through Cl(2), Cl(4) and Cl(5) being towards Cl(4^i). Cu(3) could thus be considered as having trigonal

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu_7Cl_{10}]^{3-}$ chain. Estimated standard deviations are given in parentheses. Symmetry code: (i): ½−x,½−y,z̄; (ii): x̄,y,½−z.

Cu(1)−Cl(1)	2.165(2)	Cu(3)−Cl(4)	2.253(2)
Cu(1)···Cl(3)	2.896(2)	Cu(3)−Cl(5)	2.346(2)
Cu(2)−Cl(1)	2.311(3)	Cu(3)···Cl(4^i)	2.980(2)
Cu(2)−Cl(2)	2.206(2)	Cu(4)−Cl(3)	2.245(2)
Cu(2)−Cl(3)	2.298(2)	Cu(4)−Cl(4)	2.258(2)
Cu(3)−Cl(2)	2.261(3)	Cu(4)−Cl(5^i)	2.291(2)
Cu(1)···Cu(2)	3.089(2)	Cu(3)···Cu(3^i)	3.447(3)
Cu(2)···Cu(3)	2.902(2)	Cu(3)···Cu(4)	2.990(2)
Cu(2)···Cu(4)	2.890(2)	Cu(3)···Cu(4^i)	2.924(2)
Cl(1)−Cu(1)−Cl(1^{ii})	153.9(1)	Cl(2)−Cu(3)−Cl(5)	106.8(1)
Cl(1)−Cu(1)···Cl(3)	93.3(1)	Cl(4)−Cu(3)−Cl(5)	113.0(1)
Cl(1)···Cu(1)···Cl(3^{ii})	101.5(1)	Cl(2)−Cu(3)···Cl(4^i)	102.8(1)
Cl(3)···Cu(1)···Cl(3^{ii})	110.6(1)	Cl(4)−Cu(3)···Cl(4^i)	98.9(1)
Cl(1)−Cu(2)−Cl(2)	122.2(1)	Cl(5)−Cu(3)···Cl(4^i)	89.1(1)
Cl(1)−Cu(2)−Cl(3)	107.4(1)	Cl(3)−Cu(4)−Cl(4)	131.5(1)
Cl(2)−Cu(2)−Cl(3)	128.0(1)	Cl(3)−Cu(4)−Cl(5^i)	116.1(1)
Cl(2)−Cu(3)−Cl(4)	134.6(1)	Cl(4)−Cu(4)−Cl(5^i)	111.6(1)
Cu(1)−Cl(1)−Cu(2)	87.2(1)	Cu(3)−Cl(4)−Cu(4)	83.0(1)
Cu(2)−Cl(2)−Cu(3)	81.0(1)	Cu(3)−Cl(5)−Cu(4)	78.2(1)
Cu(2)−Cl(3)−Cu(4)	79.0(1)		

pyramidal coordination geometry (Table 2), were the weak Cu$\cdots$Cl(4^i) interaction taken into account. Similarly, Cu(1) is strictly two-coordinated with a Cl(1)$-$Cu(1)$-$Cl(1^{ii}) angle of 153.9(1) ° [symmetry code: (*ii*): $\bar{x},y,\frac{1}{2}-z$)], but there are also additional contacts of 2.896(2) Å to Cl(3) and Cl(3^{ii}) forming a very distorted tetrahedron around Cu(1) (Table 2).

The Cu(1)$-$Cl(1) distance, 2.165(2) Å, is close to that in the linear CuCl$_2$ group embedded in the [CuCl$_2$]$^-$ chain in bis(2,2'-bipyridyl)copper(II) bis[dichlorocuprate(I)], *i.e.* 2.140(2) Å,[3] and that in the CuCl$_2$ group in tris[bis(1,2-diaminoethane)platinum(II)dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)], *i.e.* 2.16(1) Å.[11] All three distances are longer than the values found for isolated [CuCl$_2$]$^-$ ions.[1-9] The two-coordinated Cl$-$Cu$-$Cl units reported hitherto as part of infinite chains[3,11] or as isolated monomers[1-9] are all linear or nearly linear. In the cation radical salt of tetraselenotetracene, TSeT, with dibromocuprate(I) a bent monomeric [CuBr$_2$]$^-$ ion has, however, been observed with Br$-$Cu$-$Br=153.8(1)°, Cu$-$Br=2.267(2) and 2.282(3) Å, and a Cu$\cdots$Br contact to an adjacent anion of 2.829(2) Å.[25] The corresponding chlorocuprate(I) would appear to be isostructural with [TSeT][CuBr$_2$],[25] and would therefore be expected to have a Cl$-$Cu$-$Cl angle close to that observed for Cl(1)$-$Cu(1)$-$Cl(1^{ii}) in [Cu$_7$Cl$_{10}$]$^{3-}$.

Long Cu$\cdots$Cl distances of 3.10(1) and 3.48(1) Å are also present in tris[bis(1,2-diaminoethane)platinum(II)dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)] in which the two independent copper(I) atoms in the [CuCl$_4$]$^{3-}$ chain have linear and

trigonal-planar coordination, respectively, the long Cu$\cdots$Cl contacts leading to trigonal-bipyramidal environments for both.[11] The Cu$-$Cl distances involving three-coordinated copper(I) in [Cu$_7$Cl$_{10}$]$^{3-}$ (Table 2) are of the same order as that found in the tetrachlorocuprate(I), *i.e.* 2.291(9) Å.[11] There are no abnormally short Cu$\cdots$Cu contacts within the [Cu$_7$Cl$_{10}$]$^{3-}$ chain and the angles subtended at the bridging chloride ligands (Table 2) are similar to those found in *e.g.* chains of edge-sharing Cu(I)$-$Cl tetrahedra, *i.e.* 77,[12] and 70.8(1)°.[13] Despite the diversity of the chlorocuprate(I) chains determined hitherto,[3,11-17] there would seem to be none with geometry similar to that of [Cu$_7$Cl$_{10}$]$^{3-}$.

The packing of anions and cations is illustrated in Fig. 2. The shortest contacts between copper(I) and carbon are: Cu(2)$\cdots$C(8^i)=3.54(1) Å, Cu(3)$\cdots$C(6)=3.65(1) Å and Cu(4)$\cdots$C(10^{ii})= 3.68(1) Å. Two of these entail short Cu$\cdots$H contacts, *viz.* Cu(2)$\cdots$H(81^i)=2.5(1) Å and Cu(4)$\cdots$H(102^{ii})=2.7(1) Å. The accuracy associated with the hydrogen atom positions is not, however, expected to be high. The closest nonbonded approach distances between chlorine and carbon, *viz.* Cl(1)$\cdots$C(2)=3.54(1) Å, Cl(2)$\cdots$C(2^i)=3.61(1) Å, Cl(2)$\cdots$C(5^{iii})=3.64(1) Å, Cl(5)$\cdots$C(7^{iv})=3.44(1) Å, Cl(5)$\cdots$C(9)= 3.65(1) Å and Cl(5)$\cdots$C(10)=3.69(1) Å are appreciably shorter than the shortest such distance in tetrabutylammonium dichlorocuprate(I), 3.846(4) Å.[7] [Symmetry code: (*i*): $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$; (*ii*): $\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$; (*iii*): $\frac{1}{2}-x$, $y-\frac{1}{2},\frac{1}{2}-z$; (*iv*): x, $1-y$, $z-\frac{1}{2}$]. The tetraethylammonium ions show no anomalous features.

Whereas tetrabutylammonium seems to be effective in the suppression of $-$Cl$-$Cu$-$Cl$-$
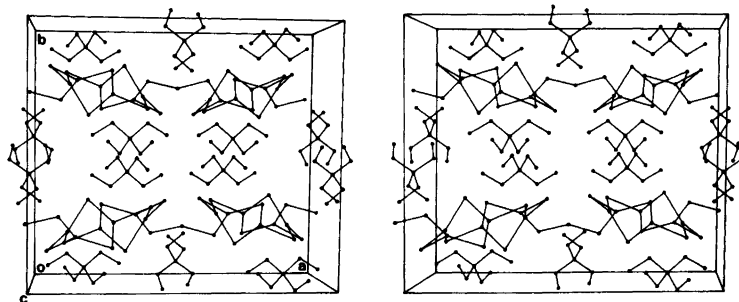

Fig. 2. Stereoscopic view[24] of the unit cell. For clarity, all atoms are represented as spheres of radius 0.05 Å.

catenation, stabilizing a monomeric $[CuCl_2]^-$ configuration in the solid state,[7] the smaller tetraethylammonium ion with less well-screened positive change appears to be insufficient for this purpose. Thus, a chain containing both two- and three-coordinated copper(I) is obtained. A similar tendency towards increased coordination number of copper(I) with decreasing size of and less well-screened positive charge on the cation has been observed for some tetraalkylammonium bromocuprates(I), copper(I) being two-coordinated in the presence of tetrabutylammonium,[7] but three-coordinated in the presence of tetrapropylammonium,[26] tetraethylammonium,[18] and tetramethylammonium.[27] The bromocuprates(I) containing three-coordinated copper(I) are, however, all discrete entities, *viz.* $[Cu_4Br_6]^{2-}$,[26] $[Cu_2Br_4]^{2-}$,[18] and $[Cu_2Br_5]^{3-}$.[27] This may indicate a greater tendency towards $-X-Cu-X-$ catenation for X=Cl as compared to X=Br.

REFERENCES

1. a. Newton, M. G., Caughman, H. D. and Taylor, R. C. *Chem. Commun.* (1970) 1227; b. *J. Chem. Soc. Dalton Trans.* (1974) 258.
2. Marsh, W. C. and Trotter, J. *J. Chem. Soc. A* (1971) 1482.
3. Kaiser, J., Brauer, G., Schröder, F. A., Taylor, I. F. and Rasmussen, S. E. *J. Chem. Soc. Dalton Trans.* (1974) 1490.
4. Siiman, O., Huber, C. P. and Post, M. L. *Inorg. Chim. Acta 25* (1977) L11.
5. Huber, C. P., Post, M. L. and Siiman, O. *Acta Crystallogr. B 34* (1978) 2629.
6. Francisco, R. H. P., de Almeida Santos, R. H., Lechat, J. R. and Massabni, A. C. *Acta Crystallogr. B 37* (1981) 232.
7. Asplund, M., Jagner, S. and Nilsson, M. *Acta Chem. Scand. A 37* (1983) 57.
8. Sakurai, T., Kobayashi, K., Masuda, H., Tsuboyama, S. and Tsuboyama, K. *Acta Crystallogr. C 39* (1983) 334.
9. Clegg, W., Garner, C. D., Nicholson, J. R. and Raithby, P. R. *Acta Crystallogr. C 39* (1983) 1007.
10. Murray-Rust, P., Day, P. and Prout, C. K. *Chem. Commun.* (1966) 277.
11. Endres, H., Keller, H. J., Martin, R. and Traeger, U. *Acta Crystallogr. B 35* (1979) 2880.
12. Prout, C. K. and Murray-Rust, P. *J. Chem. Soc. A* (1969) 1520.
13. Baglio, J. A. and Vaughan, P. A. *J. Inorg. Nucl. Chem. 32* (1970) 803.
14. Brink, C. and MacGillavry, C. H. *Acta Crystallogr. 2* (1949) 158.
15. Brink, C. and van Arkel, A. E. *Acta Crystallogr. 5* (1952) 506.
16. Brink, C., Binnendijk, N. F. and van de Linde, J. *Acta Crystallogr. 7* (1954) 176.
17. Baker, R. J., Nyburg, S. C. and Szymański, J. T. *Inorg. Chem. 10* (1971) 138.
18. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 135.
19. a. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. 1, p. 101; b. *Ibid.* 1974, Vol. 4, p. 72.
20. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr. A 30* (1974) 580.
21. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr. 12* (1979) 134.
22. Walker, N. and Stuart, D. *Acta Crystallogr. A 39* (1983) 158.
23. Lindgren, O. *An Integrated Set of Crystallographic Programs, 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.
24. Johnson, C. K. *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.
25. Shibaeva, R. P., Kaminskii, V. F., Yagubskii, E. B. and Kushch, L. A. *Kristallografiya 28* (1983) 92.
26. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 38* (1984) 725.
27. Asplund, M. and Jagner, S. *Acta Chem. Scand. A 39* (1985). *In press.*