N,N,N',N'-Tetramethylbutane-1,4-diammonium tetrachlorocuprate(II)

A. Elangovan,[a]
A. Thamaraichelvan,[a]
A. Ramu,[b] S. Athimoolam[c]* and
S. Natarajan[c]

[a]Department of Chemistry, Thiagarajar College, Madurai 625 009, India, [b]Department of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India, and [c]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail:
xrdsopmku@yahoo.com

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.042
wR factor = 0.120
Data-to-parameter ratio = 19.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_8H_{22}N_2)[CuCl_4]$, is composed of one N,N,N',N'-tetramethylbutane-1,4-diammonium cation and a tetrachlorocuprate(II) anion. The anion is mononuclear and has a flattened tetrahedral geometry. In the cation, the dimethylamino substituents are *trans* with respect to the central C—C bond of the butane. In the crystal structure, the anions and cations are linked by N—H···Cl hydrogen bonds, forming chains along the *a* axis.

Comment

The tetrachlorocuprate(II) ion exhibits a variety of interesting stereochemical features, *viz*., pseudotetrahedral D_{2d} symmetry (Helmholz & Kruh, 1952), planar and pyramidal geometry (Anderson & Willett, 1974). In general, the size of the cation strongly influences the structure of the chlorocuprate(II) anion. For very bulky organic cations, the anions exist as dimers or discrete ions with strictly four-coordinate copper (Ferguson, 1964). The geometry of the $CuCl_4{}^{2-}$ species depends on factors like the Jahn–Teller effect, electrostatic repulsion between the chlorine atoms, crystal packing forces and hydrogen bonds.

(I)
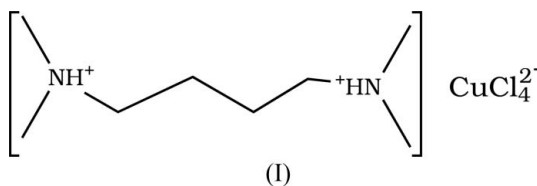
In the present structure, (I), the asymmetric unit consists of a tetrachlorocuprate(II) anion and an N,N,N',N'-tetramethylbutane-1,4-diammonium cation (Fig. 1). The structure of the $[CuCl_4]^{2-}$ anion can typically be described by the average *trans* Cl—Cu—Cl angle and the dihedral angle between $CuCl_2$ planes. This dihedral angle is 90° for tetrahedral and 0° for square-planar geometry (Bhattacharya *et al.*, 2004). In (I), the two independent *trans* Cl—Cu—Cl angles have values of 129.85 (4) and 128.08 (4)° and the dihedral angle between the $CuCl_2$ planes is 89.04 (2)°, commensurate with a flattened tetrahedral geometry for the $[CuCl_4]^{2-}$ anion. These observations are similar to those found in the structures of other chlorocuprates (Smith, 1976). As observed by Antolini *et al.* (1982), hydrogen-bonding interactions lead to longer Cu—Cl bonds for the Cl atoms involved in the hydrogen bonds. This feature is also observed in the present structure (Table 1). In the cation, the bulky –CH_2—$HN(CH_3)_2$ substituents attached to each end of the C4—C5 bond assume nearly *trans* conformations to avoid steric hindrance.
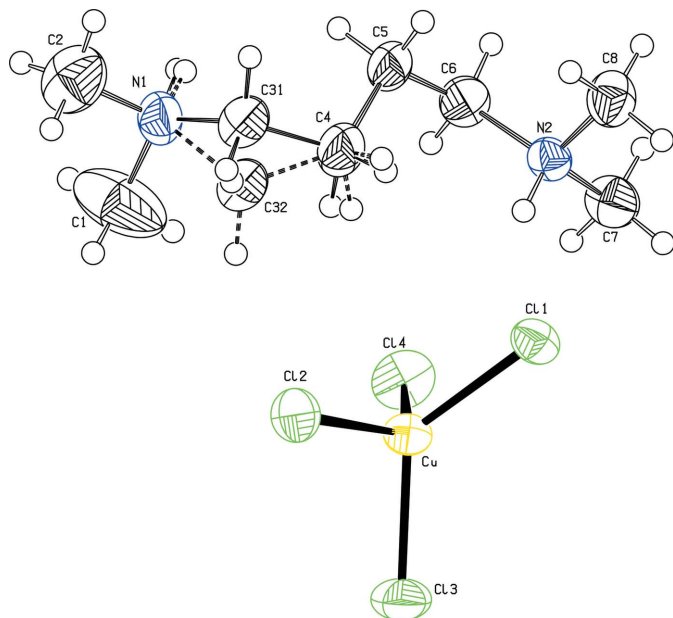
Figure 1
The asymmetric unit of the title compound, (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Both the disorder components are shown, with bonds to the minor disorder component drawn as dashed lines.
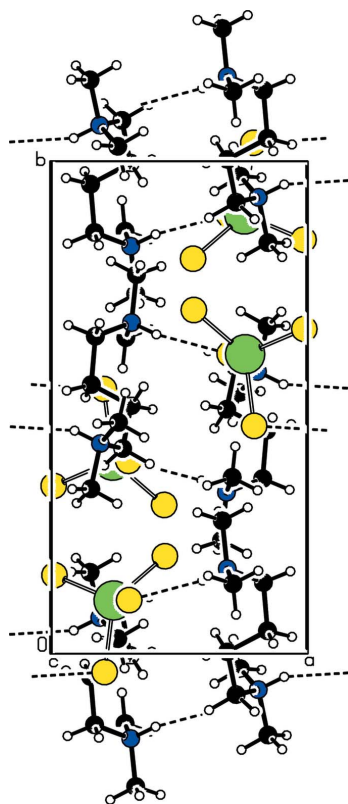

Figure 2
Packing diagram, viewed down the c axis. Hydrogen bonds are shown as dashed lines.

The crystal structure is stabilized by N—H···Cl hydrogen bonds which link the anions and cations into chains running along the a axis (Table 2, Fig. 2).

Experimental

A solution of N,N,N',N'-tetramethylbutane-1,4-diamine (20 mmol) was added to a solution (10 ml) of $CuCl_2\cdot2H_2O$ (10 mmol) in de-ionized water. This mixture was then acidified with 2 ml of hydro-chloric acid (10 N). The resulting solution was filtered and kept undisturbed. Orange-coloured single crystals were obtained after three months.

Crystal data

$(C_8H_{22}N_2)[CuCl_4]$	$Z = 4$
$M_r = 351.62$	$D_x = 1.517$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.9731$ (6) Å	$\mu = 2.09$ mm^{-1}
$b = 15.2456$ (9) Å	$T = 293$ (2) K
$c = 12.7314$ (7) Å	Block, orange
$\beta = 95.784$ (12)°	$0.21 \times 0.19 \times 0.17$ mm
$V = 1539.68$ (17) Å^3	

Data collection

Nonius MACH3 diffractometer	2700 independent reflections
ω–2θ scans	2340 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan	$R_{int} = 0.023$
(North et al., 1968)	$\theta_{max} = 25.0°$
$T_{min} = 0.586$, $T_{max} = 0.657$	3 standard reflections
(expected range = 0.625–0.701)	frequency: 60 min
3145 measured reflections	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 2.5565P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2700 reflections	$\Delta\rho_{max} = 1.06$ e Å^{-3}
139 parameters	$\Delta\rho_{min} = -1.18$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—Cl4	2.2226 (11)	Cu—Cl2	2.2623 (11)
Cu—Cl3	2.2353 (12)	Cu—Cl1	2.2691 (11)
Cl4—Cu—Cl2	129.85 (5)	Cl3—Cu—Cl1	128.08 (5)
C2—N1—C31—C4	174.3 (4)	C5—C6—N2—C7	−172.8 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl2^i	0.91	2.38	3.225 (4)	155
N1—H1'···Cl2^i	0.91	2.43	3.225 (4)	147
N2—H2···Cl1	0.91	2.35	3.191 (3)	153

Symmetry code: (i) $x + 1, y, z$.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.96/0.97 Å and N—H = 0.91 Å, with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). Atom C3 and attached H atoms of the butane chain in the cation are disordered over two positions with occupancy factors fixed at 0.75 and 0.25 in the final refinement. The occupancy-factor values are assigned by refining the occupancy using FVAR. The highest peak is located 0.77 Å from atom C32 and the deepest hole 0.13 Å from C32.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

References

Anderson, D. N. & Willett, R. D. (1974). *Inorg. Chim. Acta*, **8**, 167–175.
Antolini, L., Menabue, L., Pellacani, G. C. & Saladini, M. (1982). *Inorg. Chim. Acta*, **58**, 193–200.
Bhattacharya, R., Chanda, S., Bocelli, G., Cantoni, A. & Ghosh, A. (2004). *J. Chem. Crystallogr.* **34**, 393–400.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Ferguson, J. (1964). *J. Chem. Phys.* **40**, 11–19.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg. Germany.
Helmholz, L. & Kruh, R. F. (1952). *J. Am. Chem. Soc.* **74**, 1176–1181.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Smith, D. W. (1976). *Coord. Chem. Rev.* **21**, 93–158.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.