Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The low-temperature phase of diethylammonium tetrachloridocuprate(II)

Christoph E. Strasser, Stephanie Cronje and Helgard G. Raubenheimer*

Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa
Correspondence e-mail: hgr@sun.ac.za

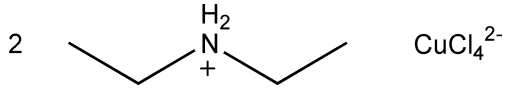
Received 17 October 2007; accepted 29 October 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.045; wR factor = 0.111; data-to-parameter ratio = 24.0.

The crystal structure of the low-temperature phase of diethylammonium tetrachloridocuprate(II), $(C_4H_{12}N)_2[CuCl_4]$, has been determined by Simonsen & Harlow [(1977). *Am. Crystallogr. Assoc. Ser. 2* Vol. 5, No. 1, Abstract HN5], but no atomic coordinates are available. We therefore redetermined the structure at 100 K. It comprises three crystallographically independent formula units linked by hydrogen bonds into a two-dimensional network. One tetrachloridocuprate(II) anion is virtually square-planar while the two others are tetrahedrally distorted.

Related literature

The compound was prepared according to Van Oort (1988). For a previous structure report of the low-temperature polymorph of diethylammonium tetrachloridocuprate(II), see: Simonsen & Harlow (1977). The high-temperature polymorph [phase transition at 323 (1) K] was determined by Bloomquist *et al.* (1988), and high- and low-temperature forms of the dipropylammonium analogue were reported by Bond *et al.* (1988).



Experimental

Crystal data

$(C_4H_{12}N)_2[CuCl_4]$
M_r = 353.63
Monoclinic, $P2_1/n$
a = 7.315 (4) Å
b = 14.843 (8) Å
c = 45.24 (2) Å
β = 90.258 (9)°
V = 4912 (5) Å^3
Z = 12
Mo $K\alpha$ radiation
μ = 1.96 mm^{-1}
T = 100 (2) K
0.45 × 0.25 × 0.15 mm

Data collection

Bruker APEX CCD area detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.421, T_{max} = 0.742
28089 measured reflections
10012 independent reflections
8231 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.111
S = 1.09
10012 reflections
418 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl13	2.2371 (12)	Cu2—Cl22	2.2764 (13)
Cu1—Cl11	2.2410 (12)	Cu2—Cl24	2.2775 (13)
Cu1—Cl14	2.2540 (12)	Cu3—Cl31	2.2372 (13)
Cu1—Cl12	2.2570 (13)	Cu3—Cl33	2.2636 (13)
Cu2—Cl23	2.2550 (13)	Cu3—Cl32	2.2683 (12)
Cu2—Cl21	2.2570 (13)	Cu3—Cl34	2.2700 (13)
Cl13—Cu1—Cl11	146.02 (4)	Cl23—Cu2—Cl24	89.24 (4)
Cl13—Cu1—Cl14	95.57 (5)	Cl21—Cu2—Cl24	90.72 (4)
Cl11—Cu1—Cl14	94.24 (5)	Cl22—Cu2—Cl24	179.32 (3)
Cl13—Cu1—Cl12	94.18 (5)	Cl31—Cu3—Cl33	159.70 (4)
Cl11—Cu1—Cl12	95.64 (5)	Cl31—Cu3—Cl32	92.64 (5)
Cl14—Cu1—Cl12	145.95 (4)	Cl33—Cu3—Cl32	91.02 (4)
Cl23—Cu2—Cl21	177.81 (4)	Cl31—Cu3—Cl34	92.80 (5)
Cl23—Cu2—Cl22	90.77 (4)	Cl33—Cu3—Cl34	90.17 (4)
Cl21—Cu2—Cl22	89.25 (4)	Cl32—Cu3—Cl34	160.99 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl11	0.92	2.31	3.214 (3)	166
N1—H1B···Cl21	0.92	2.43	3.298 (3)	158
N2—H2A···Cl12	0.92	2.29	3.197 (3)	168
N3—H3A···Cl13	0.92	2.31	3.210 (3)	166
N3—H3B···Cl23^{i}	0.92	2.44	3.298 (3)	155
N4—H4A···Cl14	0.92	2.30	3.205 (3)	169
N4—H4B···Cl22^{ii}	0.92	2.44	3.306 (3)	158
N5—H5A···Cl24	0.92	2.45	3.315 (3)	156
N5—H5B···Cl32	0.92	2.27	3.190 (3)	176
N6—H6A···Cl31^{iii}	0.92	2.49	3.320 (3)	151
N6—H6B···Cl33	0.92	2.28	3.188 (3)	172

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Atwood & Barbour, 2003; Barbour, 2001); software used to prepare material for publication: *X-SEED*.

We thank the National Research Foundation (NRF) of South Africa and Stellenbosch University for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2156).

 doi:10.1107/S1600536807054098 © 2007 International Union of Crystallography

References

Atwood, J. L. & Barbour, L. J. (2003). *Cryst. Growth Des.* **3**, 3–8.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bloomquist, D. R., Pressprich, M. R. & Willett, R. D. (1988). *J. Am. Chem. Soc.* **110**, 7391–7398.
Bond, M. R., Johnson, T. J. & Willett, R. D. (1988). *Can. J. Chem.* **66**, 963–973.
Bruker (2002). *SADABS* (Version 2.05) and *SMART* (Version 5.628). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SAINT* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Simonsen, S. H. & Harlow, R. L. (1977). *Am. Cryst. Assoc. Ser.* 2 Vol. 5, No. 1, Abstract HN5.
Van Oort, M. J. M. (1988). *J. Chem. Ed.* **65**, 84.

supplementary materials

Acta Cryst. (2007). E**63**, m2915-m2916 [**doi:10.1107/S1600536807054098**]

The low-temperature phase of diethylammonium tetrachloridocuprate(II)

C. E. Strasser, S. Cronje and H. G. Raubenheimer

Comment

In the course of an experiment in the inorganic chemistry practical at our university the thermochromic behaviour of diethylammonium tetrachloridocuprate(II) (I) is studied. Surprisingly, atomic coordinates of the low-temperature phase have only been presented at a meeting of the American Crystallographic Association (Simonsen & Harlow, 1977), but not published in a journal or deposited in a data base. However, the structure is briefly discussed in a later publication together with the high-temperature phase (Bloomquist *et al.*, 1988). Redetermination of the crystal and molecular structure was now done at 100 K from a crystal obtained at 293 K.

The molecular and crystal structures of both high- and low-temperature phases of other dialkylammonium tetrachlorocuprates(II), the anion being approximately tetrahedral and square-planar, respectively, have been determined, for example the dipropylammonium analogue (Bond *et al.*, 1988).

The asymmetric unit of (I) is shown in Figure 1. The compound consists of three crystallographically independent formula units of which the anion containing Cu2 is virtually square-planar, the others show a certain degree of distortion towards tetrahedral. The r.m.s. deviations of the atoms constituting the anions from a plane fitted to them is 0.588, 0.017 and 0.344 Å for Cu1, Cu2 and Cu3, respectively. Except for N2 which only engages in one hydrogen bond to Cl12, the other five diethylammonium cations each link two tetrachlorocuprate anions to form a two-dimensional hydrogen-bond network in the (101) plane. Likewise, all chlorine atoms of the anions are hydrogen bond acceptors with the exception of Cl34 (see Table). The connectivity of the hydrogen bonds is shown in Figure 2, a perspective view in Figure 3. Bond lengths and angles are unexceptional.

Experimental

The compound was prepared according to literature (Van Oort, 1988) and crystallized at room temperature by diffusing diethyl ether vapour into an ethanolic solution. A suitable emerald green crystal was quickly covered in oil and transferred to the cold nitrogen stream of the diffractometer.

Refinement

All H atoms were positioned geometrically (C—H = 0.98 and 0.99 Å for CH_3 and CH_2, respectively; and N—H = 0.92 Å) and constrained to ride on their parent atoms; U_{iso}(H) values were set at 1.2 times U_{eq}(C,*N*) for CH_2 or NH_2 and 1.5 times U_{eq}(C) for CH_3.

Figures

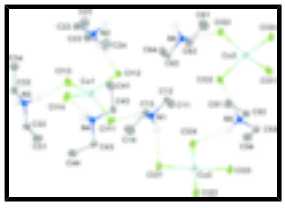


Fig. 1. Asymmetric unit of (I). Ellipsoids are shown at the 50% probability level, hydrogen bonds are shown with dashed lines. C—H hydrogen atoms are omitted for clarity.

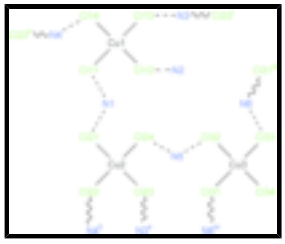


Fig. 2. Schematic representation of the hydrogen bonding network. Hydrogen bonds are shown as dashed lines and bonds to symmetry equivalent atoms as wiggled lines. Symmetry operators: (i) *x*, *y* + 1, *z*; (ii) −*x* + 1, −*y* + 1, −*z*; (iii) −*x* + 1/2, *y* + 1/2, −*z* + 1/2; (iv) −*x* + 1/2, *y* − 1/2, −*z* + 1/2; (v) *x*, *y* − 1, *z*.

Fig. 3. Perspective view of the hydrogen-bonded layer. Atoms are drawn as spheres of arbitrary radius, only N—H hydrogen atoms are shown. Symmetry operators: (iii) −*x* + 1/2, *y* + 1/2, −*z* + 1/2; (iv) −*x* + 1/2, *y* − 1/2, −*z* + 1/2; (vi) *x* − 1/2, −*y* + 1/2, *z* + 1/2; (vii) *x* − 1/2, −*y* + 3/2, *z* + 1/2; (viii) −*x*, −*y* + 1, −*z* + 1.

diethylammonium tetrachloridocuprate(II)

Crystal data

$(C_4H_{12}N)_2[CuCl_4]$	F_{000} = 2196
M_r = 353.63	D_x = 1.435 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 7081 reflections
a = 7.315 (4) Å	θ = 2.3–26.4º
b = 14.843 (8) Å	μ = 1.96 mm^{-1}
c = 45.24 (2) Å	*T* = 100 (2) K
β = 90.258 (9)º	Block, green
V = 4912 (5) Å^3	0.45 × 0.25 × 0.15 mm
Z = 12	

Data collection

Bruker APEX CCD area detector diffractometer	10012 independent reflections
Radiation source: fine-focus sealed tube	8231 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.055
T = 100(2) K	θ_{max} = 26.6º
ω–scans	θ_{min} = 0.9º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	*h* = −7→9
T_{min} = 0.421, T_{max} = 0.742	*k* = −18→18
28089 measured reflections	*l* = −56→50

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 2.1467P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
10012 reflections	$\Delta\rho_{max} = 0.78$ e Å^{-3}
418 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.50841 (5)	0.74787 (2)	0.084049 (8)	0.02153 (10)
Cu2	0.92389 (5)	0.24762 (2)	0.083225 (8)	0.01820 (10)
Cu3	0.46748 (5)	0.24221 (2)	0.255011 (8)	0.02002 (10)
Cl11	0.58990 (12)	0.62256 (5)	0.059822 (18)	0.03125 (19)
Cl12	0.42965 (12)	0.67724 (5)	0.126298 (19)	0.0324 (2)
Cl13	0.60562 (11)	0.87259 (5)	0.107010 (18)	0.03002 (19)
Cl14	0.40684 (11)	0.81893 (5)	0.043124 (19)	0.0313 (2)
Cl21	0.92291 (11)	0.38662 (5)	0.062999 (17)	0.02863 (18)
Cl22	0.91811 (11)	0.18729 (5)	0.036970 (17)	0.02770 (18)
Cl23	0.91308 (12)	0.10889 (5)	0.103458 (17)	0.02896 (19)
Cl24	0.92597 (11)	0.30808 (5)	0.129495 (17)	0.02811 (18)
Cl31	0.41369 (12)	0.11216 (5)	0.231532 (18)	0.0319 (2)
Cl32	0.60609 (13)	0.30356 (5)	0.215033 (19)	0.0367 (2)
Cl33	0.41713 (12)	0.38062 (5)	0.274342 (18)	0.0331 (2)
Cl34	0.42615 (11)	0.17926 (5)	0.300217 (17)	0.02779 (18)
N1	0.6974 (3)	0.49583 (16)	0.11481 (6)	0.0214 (5)
H1B	0.7653	0.4542	0.1046	0.026*
H1A	0.6597	0.5391	0.1016	0.026*

N2	0.3228 (3)	0.84386 (16)	0.16754 (6)	0.0224 (6)
H2A	0.3656	0.8015	0.1545	0.027*
H2B	0.2474	0.8148	0.1807	0.027*
N3	0.6853 (3)	1.00067 (16)	0.05136 (5)	0.0209 (5)
H3A	0.6517	0.9579	0.0650	0.025*
H3B	0.7567	1.0426	0.0610	0.025*
N4	0.3125 (3)	0.65577 (16)	−0.00079 (5)	0.0202 (5)
H4A	0.3491	0.6967	0.0133	0.024*
H4B	0.2415	0.6860	−0.0144	0.024*
N5	0.6930 (3)	0.15370 (16)	0.16653 (5)	0.0216 (6)
H5A	0.7597	0.1827	0.1522	0.026*
H5B	0.6629	0.1956	0.1807	0.026*
N6	0.3193 (3)	0.49932 (16)	0.21770 (6)	0.0215 (6)
H6B	0.3507	0.4604	0.2327	0.026*
H6A	0.2478	0.5441	0.2257	0.026*
C11	0.4155 (5)	0.4129 (2)	0.10258 (8)	0.0362 (8)
H11A	0.3791	0.4619	0.0893	0.054*
H11B	0.3062	0.3848	0.1110	0.054*
H11C	0.4850	0.3678	0.0915	0.054*
C12	0.5325 (4)	0.4500 (2)	0.12712 (7)	0.0254 (7)
H12A	0.4606	0.4935	0.1389	0.031*
H12B	0.5712	0.4004	0.1404	0.031*
C13	0.8173 (4)	0.5392 (2)	0.13752 (7)	0.0281 (7)
H13A	0.8636	0.4930	0.1515	0.034*
H13B	0.7460	0.5839	0.1489	0.034*
C14	0.9751 (5)	0.5849 (3)	0.12256 (9)	0.0465 (10)
H14A	1.0440	0.5405	0.1111	0.070*
H14B	1.0554	0.6119	0.1375	0.070*
H14C	0.9288	0.6321	0.1093	0.070*
C21	0.0591 (5)	0.8678 (3)	0.13455 (10)	0.0476 (10)
H21A	0.1081	0.8253	0.1200	0.071*
H21B	−0.0128	0.9141	0.1243	0.071*
H21C	−0.0191	0.8355	0.1485	0.071*
C22	0.2136 (4)	0.9113 (2)	0.15093 (7)	0.0288 (7)
H22A	0.2935	0.9431	0.1367	0.035*
H22B	0.1642	0.9565	0.1649	0.035*
C23	0.4815 (4)	0.8823 (2)	0.18419 (8)	0.0295 (8)
H23A	0.4376	0.9293	0.1979	0.035*
H23B	0.5673	0.9108	0.1702	0.035*
C24	0.5795 (5)	0.8103 (3)	0.20133 (9)	0.0491 (11)
H24A	0.4940	0.7813	0.2150	0.074*
H24B	0.6802	0.8374	0.2126	0.074*
H24C	0.6283	0.7653	0.1876	0.074*
C31	0.9615 (5)	0.9117 (3)	0.04137 (8)	0.0411 (9)
H31A	1.0374	0.9571	0.0513	0.062*
H31B	1.0326	0.8824	0.0258	0.062*
H31C	0.9221	0.8666	0.0558	0.062*
C32	0.7971 (4)	0.9564 (2)	0.02798 (7)	0.0258 (7)
H32A	0.8368	1.0020	0.0134	0.031*

H32B	0.7220	0.9109	0.0175	0.031*
C33	0.5180 (4)	1.0460 (2)	0.04010 (7)	0.0251 (7)
H33A	0.4438	1.0026	0.0286	0.030*
H33B	0.5528	1.0960	0.0268	0.030*
C34	0.4059 (5)	1.0825 (2)	0.06546 (8)	0.0357 (8)
H34A	0.3667	1.0326	0.0781	0.054*
H34B	0.2981	1.1138	0.0576	0.054*
H34C	0.4802	1.1247	0.0771	0.054*
C41	0.0368 (5)	0.6264 (3)	0.02894 (9)	0.0453 (10)
H41A	0.0792	0.6670	0.0446	0.068*
H41B	−0.0378	0.5784	0.0376	0.068*
H41C	−0.0367	0.6603	0.0146	0.068*
C42	0.1987 (4)	0.5856 (2)	0.01366 (7)	0.0272 (7)
H42A	0.2740	0.5523	0.0283	0.033*
H42B	0.1556	0.5421	−0.0014	0.033*
C43	0.4786 (4)	0.6202 (2)	−0.01612 (7)	0.0254 (7)
H43A	0.4407	0.5799	−0.0325	0.031*
H43B	0.5529	0.5846	−0.0020	0.031*
C44	0.5921 (5)	0.6961 (2)	−0.02826 (8)	0.0366 (8)
H44A	0.5201	0.7300	−0.0428	0.055*
H44B	0.7014	0.6715	−0.0378	0.055*
H44C	0.6288	0.7364	−0.0121	0.055*
C51	0.4105 (5)	0.1946 (2)	0.14004 (8)	0.0354 (8)
H51A	0.3785	0.2372	0.1557	0.053*
H51B	0.2985	0.1703	0.1311	0.053*
H51C	0.4821	0.2256	0.1249	0.053*
C52	0.5214 (4)	0.1188 (2)	0.15287 (7)	0.0247 (7)
H52A	0.4486	0.0870	0.1680	0.030*
H52B	0.5519	0.0752	0.1371	0.030*
C53	0.8102 (4)	0.0835 (2)	0.18044 (7)	0.0272 (7)
H53A	0.8341	0.0349	0.1660	0.033*
H53B	0.7458	0.0569	0.1976	0.033*
C54	0.9882 (4)	0.1238 (3)	0.19054 (8)	0.0362 (9)
H54A	1.0541	0.1478	0.1735	0.054*
H54B	1.0625	0.0773	0.2002	0.054*
H54C	0.9641	0.1726	0.2046	0.054*
C61	0.0415 (5)	0.4100 (3)	0.20903 (10)	0.0479 (10)
H61A	0.0772	0.3666	0.2243	0.072*
H61B	−0.0318	0.3796	0.1938	0.072*
H61C	−0.0307	0.4584	0.2180	0.072*
C62	0.2104 (4)	0.4494 (2)	0.19511 (7)	0.0285 (7)
H62A	0.2856	0.4005	0.1866	0.034*
H62B	0.1748	0.4909	0.1789	0.034*
C63	0.4895 (4)	0.5406 (2)	0.20549 (7)	0.0262 (7)
H63A	0.4566	0.5875	0.1908	0.031*
H63B	0.5623	0.4939	0.1953	0.031*
C64	0.6021 (5)	0.5821 (2)	0.23000 (8)	0.0366 (9)
H64A	0.5303	0.6289	0.2399	0.055*
H64B	0.7130	0.6089	0.2217	0.055*

H64C	0.6359	0.5354	0.2443	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0198 (2)	0.0189 (2)	0.0259 (2)	0.00035 (14)	0.00180 (16)	0.00107 (15)
Cu2	0.01714 (19)	0.01684 (19)	0.0206 (2)	0.00001 (14)	0.00077 (15)	0.00040 (14)
Cu3	0.0188 (2)	0.0190 (2)	0.0223 (2)	0.00079 (14)	0.00224 (15)	0.00094 (15)
Cl11	0.0407 (5)	0.0278 (4)	0.0252 (4)	0.0129 (3)	0.0024 (4)	0.0007 (3)
Cl12	0.0428 (5)	0.0199 (4)	0.0346 (5)	0.0009 (3)	0.0175 (4)	0.0015 (3)
Cl13	0.0354 (5)	0.0291 (4)	0.0256 (4)	−0.0127 (3)	−0.0006 (3)	0.0011 (3)
Cl14	0.0381 (5)	0.0198 (4)	0.0360 (5)	0.0020 (3)	−0.0144 (4)	−0.0002 (3)
Cl21	0.0430 (5)	0.0187 (4)	0.0242 (4)	0.0008 (3)	0.0026 (3)	0.0011 (3)
Cl22	0.0413 (5)	0.0202 (4)	0.0215 (4)	0.0007 (3)	0.0003 (3)	−0.0010 (3)
Cl23	0.0449 (5)	0.0184 (4)	0.0236 (4)	−0.0014 (3)	0.0007 (4)	0.0012 (3)
Cl24	0.0419 (5)	0.0205 (4)	0.0220 (4)	0.0003 (3)	0.0013 (3)	−0.0009 (3)
Cl31	0.0396 (5)	0.0295 (4)	0.0268 (4)	−0.0120 (3)	0.0053 (4)	−0.0045 (3)
Cl32	0.0499 (5)	0.0248 (4)	0.0355 (5)	−0.0058 (4)	0.0233 (4)	−0.0019 (4)
Cl33	0.0516 (5)	0.0204 (4)	0.0275 (4)	0.0072 (3)	0.0124 (4)	0.0031 (3)
Cl34	0.0397 (5)	0.0202 (4)	0.0235 (4)	0.0014 (3)	0.0037 (3)	0.0022 (3)
N1	0.0226 (13)	0.0204 (13)	0.0212 (14)	0.0021 (10)	0.0011 (11)	−0.0010 (10)
N2	0.0226 (13)	0.0171 (13)	0.0275 (15)	0.0012 (10)	0.0021 (11)	0.0013 (11)
N3	0.0218 (13)	0.0186 (13)	0.0222 (14)	−0.0012 (10)	0.0004 (11)	−0.0008 (10)
N4	0.0196 (13)	0.0180 (13)	0.0228 (14)	−0.0010 (10)	−0.0018 (10)	0.0003 (10)
N5	0.0226 (13)	0.0193 (13)	0.0231 (14)	−0.0002 (10)	0.0025 (11)	0.0019 (10)
N6	0.0208 (13)	0.0201 (13)	0.0235 (14)	0.0003 (10)	0.0029 (11)	0.0014 (11)
C11	0.0309 (19)	0.035 (2)	0.043 (2)	−0.0107 (15)	0.0002 (16)	0.0034 (17)
C12	0.0269 (17)	0.0230 (16)	0.0265 (18)	−0.0017 (13)	0.0078 (14)	0.0009 (13)
C13	0.0311 (18)	0.0268 (17)	0.0263 (18)	−0.0021 (14)	−0.0046 (14)	−0.0030 (14)
C14	0.036 (2)	0.053 (3)	0.050 (3)	−0.0169 (18)	0.0004 (19)	−0.011 (2)
C21	0.035 (2)	0.049 (2)	0.058 (3)	0.0062 (18)	−0.0163 (19)	0.005 (2)
C22	0.0315 (18)	0.0235 (17)	0.0313 (19)	0.0067 (13)	0.0047 (15)	0.0017 (14)
C23	0.0255 (17)	0.0294 (18)	0.034 (2)	−0.0055 (14)	−0.0036 (14)	−0.0018 (15)
C24	0.041 (2)	0.051 (3)	0.055 (3)	0.0009 (19)	−0.020 (2)	0.004 (2)
C31	0.038 (2)	0.048 (2)	0.038 (2)	0.0141 (17)	0.0055 (17)	−0.0007 (18)
C32	0.0262 (17)	0.0261 (17)	0.0252 (18)	−0.0011 (13)	0.0061 (14)	−0.0044 (13)
C33	0.0232 (16)	0.0216 (16)	0.0305 (18)	0.0025 (12)	−0.0042 (14)	0.0029 (13)
C34	0.0295 (19)	0.038 (2)	0.040 (2)	0.0097 (15)	0.0059 (16)	0.0069 (17)
C41	0.033 (2)	0.047 (2)	0.057 (3)	−0.0060 (17)	0.0129 (19)	0.004 (2)
C42	0.0285 (17)	0.0227 (16)	0.0304 (19)	−0.0058 (13)	0.0038 (14)	0.0041 (14)
C43	0.0252 (17)	0.0270 (17)	0.0241 (17)	0.0054 (13)	0.0021 (13)	−0.0028 (13)
C44	0.0309 (19)	0.036 (2)	0.043 (2)	0.0006 (15)	0.0079 (16)	−0.0037 (17)
C51	0.0267 (18)	0.036 (2)	0.043 (2)	0.0001 (15)	−0.0014 (16)	−0.0009 (17)
C52	0.0220 (16)	0.0248 (17)	0.0272 (18)	−0.0047 (12)	0.0029 (13)	0.0006 (13)
C53	0.0292 (18)	0.0242 (17)	0.0284 (18)	0.0043 (13)	0.0028 (14)	0.0042 (14)
C54	0.0283 (19)	0.047 (2)	0.033 (2)	0.0048 (16)	−0.0033 (16)	0.0059 (17)
C61	0.036 (2)	0.051 (2)	0.057 (3)	−0.0185 (18)	−0.0003 (19)	−0.003 (2)
C62	0.0283 (18)	0.0282 (18)	0.0291 (19)	−0.0026 (14)	−0.0022 (14)	−0.0050 (14)

C63	0.0235 (17)	0.0276 (17)	0.0276 (18)	−0.0024 (13)	0.0072 (14)	0.0029 (14)
C64	0.0328 (19)	0.037 (2)	0.040 (2)	−0.0112 (15)	−0.0024 (16)	0.0079 (17)

Geometric parameters (Å, °)

Cu1—Cl13	2.2371 (12)	C23—C24	1.500 (5)
Cu1—Cl11	2.2410 (12)	C23—H23A	0.9900
Cu1—Cl14	2.2540 (12)	C23—H23B	0.9900
Cu1—Cl12	2.2570 (13)	C24—H24A	0.9800
Cu2—Cl23	2.2550 (13)	C24—H24B	0.9800
Cu2—Cl21	2.2570 (13)	C24—H24C	0.9800
Cu2—Cl22	2.2764 (13)	C31—C32	1.498 (5)
Cu2—Cl24	2.2775 (13)	C31—H31A	0.9800
Cu3—Cl31	2.2372 (13)	C31—H31B	0.9800
Cu3—Cl33	2.2636 (13)	C31—H31C	0.9800
Cu3—Cl32	2.2683 (12)	C32—H32A	0.9900
Cu3—Cl34	2.2700 (13)	C32—H32B	0.9900
N1—C13	1.493 (4)	C33—C34	1.514 (5)
N1—C12	1.495 (4)	C33—H33A	0.9900
N1—H1B	0.9200	C33—H33B	0.9900
N1—H1A	0.9200	C34—H34A	0.9800
N2—C22	1.483 (4)	C34—H34B	0.9800
N2—C23	1.494 (4)	C34—H34C	0.9800
N2—H2A	0.9200	C41—C42	1.501 (5)
N2—H2B	0.9200	C41—H41A	0.9800
N3—C33	1.485 (4)	C41—H41B	0.9800
N3—C32	1.493 (4)	C41—H41C	0.9800
N3—H3A	0.9200	C42—H42A	0.9900
N3—H3B	0.9200	C42—H42B	0.9900
N4—C42	1.487 (4)	C43—C44	1.505 (5)
N4—C43	1.498 (4)	C43—H43A	0.9900
N4—H4A	0.9200	C43—H43B	0.9900
N4—H4B	0.9200	C44—H44A	0.9800
N5—C53	1.487 (4)	C44—H44B	0.9800
N5—C52	1.490 (4)	C44—H44C	0.9800
N5—H5A	0.9200	C51—C52	1.501 (4)
N5—H5B	0.9200	C51—H51A	0.9800
N6—C62	1.490 (4)	C51—H51B	0.9800
N6—C63	1.496 (4)	C51—H51C	0.9800
N6—H6B	0.9200	C52—H52A	0.9900
N6—H6A	0.9200	C52—H52B	0.9900
C11—C12	1.503 (4)	C53—C54	1.502 (4)
C11—H11A	0.9800	C53—H53A	0.9900
C11—H11B	0.9800	C53—H53B	0.9900
C11—H11C	0.9800	C54—H54A	0.9800
C12—H12A	0.9900	C54—H54B	0.9800
C12—H12B	0.9900	C54—H54C	0.9800
C13—C14	1.503 (5)	C61—C62	1.507 (5)
C13—H13A	0.9900	C61—H61A	0.9800

C13—H13B	0.9900	C61—H61B	0.9800
C14—H14A	0.9800	C61—H61C	0.9800
C14—H14B	0.9800	C62—H62A	0.9900
C14—H14C	0.9800	C62—H62B	0.9900
C21—C22	1.495 (5)	C63—C64	1.510 (4)
C21—H21A	0.9800	C63—H63A	0.9900
C21—H21B	0.9800	C63—H63B	0.9900
C21—H21C	0.9800	C64—H64A	0.9800
C22—H22A	0.9900	C64—H64B	0.9800
C22—H22B	0.9900	C64—H64C	0.9800
Cl13—Cu1—Cl11	146.02 (4)	C23—C24—H24C	109.5
Cl13—Cu1—Cl14	95.57 (5)	H24A—C24—H24C	109.5
Cl11—Cu1—Cl14	94.24 (5)	H24B—C24—H24C	109.5
Cl13—Cu1—Cl12	94.18 (5)	C32—C31—H31A	109.5
Cl11—Cu1—Cl12	95.64 (5)	C32—C31—H31B	109.5
Cl14—Cu1—Cl12	145.95 (4)	H31A—C31—H31B	109.5
Cl23—Cu2—Cl21	177.81 (4)	C32—C31—H31C	109.5
Cl23—Cu2—Cl22	90.77 (4)	H31A—C31—H31C	109.5
Cl21—Cu2—Cl22	89.25 (4)	H31B—C31—H31C	109.5
Cl23—Cu2—Cl24	89.24 (4)	N3—C32—C31	110.5 (3)
Cl21—Cu2—Cl24	90.72 (4)	N3—C32—H32A	109.6
Cl22—Cu2—Cl24	179.32 (3)	C31—C32—H32A	109.6
Cl31—Cu3—Cl33	159.70 (4)	N3—C32—H32B	109.6
Cl31—Cu3—Cl32	92.64 (5)	C31—C32—H32B	109.6
Cl33—Cu3—Cl32	91.02 (4)	H32A—C32—H32B	108.1
Cl31—Cu3—Cl34	92.80 (5)	N3—C33—C34	110.5 (3)
Cl33—Cu3—Cl34	90.17 (4)	N3—C33—H33A	109.5
Cl32—Cu3—Cl34	160.99 (4)	C34—C33—H33A	109.5
C13—N1—C12	114.3 (2)	N3—C33—H33B	109.5
C13—N1—H1B	108.7	C34—C33—H33B	109.5
C12—N1—H1B	108.7	H33A—C33—H33B	108.1
C13—N1—H1A	108.7	C33—C34—H34A	109.5
C12—N1—H1A	108.7	C33—C34—H34B	109.5
H1B—N1—H1A	107.6	H34A—C34—H34B	109.5
C22—N2—C23	114.4 (2)	C33—C34—H34C	109.5
C22—N2—H2A	108.7	H34A—C34—H34C	109.5
C23—N2—H2A	108.7	H34B—C34—H34C	109.5
C22—N2—H2B	108.7	C42—C41—H41A	109.5
C23—N2—H2B	108.7	C42—C41—H41B	109.5
H2A—N2—H2B	107.6	H41A—C41—H41B	109.5
C33—N3—C32	114.2 (2)	C42—C41—H41C	109.5
C33—N3—H3A	108.7	H41A—C41—H41C	109.5
C32—N3—H3A	108.7	H41B—C41—H41C	109.5
C33—N3—H3B	108.7	N4—C42—C41	111.4 (3)
C32—N3—H3B	108.7	N4—C42—H42A	109.4
H3A—N3—H3B	107.6	C41—C42—H42A	109.4
C42—N4—C43	114.5 (2)	N4—C42—H42B	109.4
C42—N4—H4A	108.6	C41—C42—H42B	109.4
C43—N4—H4A	108.6	H42A—C42—H42B	108.0

C42—N4—H4B	108.6	N4—C43—C44	110.8 (3)
C43—N4—H4B	108.6	N4—C43—H43A	109.5
H4A—N4—H4B	107.6	C44—C43—H43A	109.5
C53—N5—C52	114.6 (2)	N4—C43—H43B	109.5
C53—N5—H5A	108.6	C44—C43—H43B	109.5
C52—N5—H5A	108.6	H43A—C43—H43B	108.1
C53—N5—H5B	108.6	C43—C44—H44A	109.5
C52—N5—H5B	108.6	C43—C44—H44B	109.5
H5A—N5—H5B	107.6	H44A—C44—H44B	109.5
C62—N6—C63	113.2 (2)	C43—C44—H44C	109.5
C62—N6—H6B	108.9	H44A—C44—H44C	109.5
C63—N6—H6B	108.9	H44B—C44—H44C	109.5
C62—N6—H6A	108.9	C52—C51—H51A	109.5
C63—N6—H6A	108.9	C52—C51—H51B	109.5
H6B—N6—H6A	107.8	H51A—C51—H51B	109.5
C12—C11—H11A	109.5	C52—C51—H51C	109.5
C12—C11—H11B	109.5	H51A—C51—H51C	109.5
H11A—C11—H11B	109.5	H51B—C51—H51C	109.5
C12—C11—H11C	109.5	N5—C52—C51	110.7 (3)
H11A—C11—H11C	109.5	N5—C52—H52A	109.5
H11B—C11—H11C	109.5	C51—C52—H52A	109.5
N1—C12—C11	110.4 (3)	N5—C52—H52B	109.5
N1—C12—H12A	109.6	C51—C52—H52B	109.5
C11—C12—H12A	109.6	H52A—C52—H52B	108.1
N1—C12—H12B	109.6	N5—C53—C54	110.3 (3)
C11—C12—H12B	109.6	N5—C53—H53A	109.6
H12A—C12—H12B	108.1	C54—C53—H53A	109.6
N1—C13—C14	109.5 (3)	N5—C53—H53B	109.6
N1—C13—H13A	109.8	C54—C53—H53B	109.6
C14—C13—H13A	109.8	H53A—C53—H53B	108.1
N1—C13—H13B	109.8	C53—C54—H54A	109.5
C14—C13—H13B	109.8	C53—C54—H54B	109.5
H13A—C13—H13B	108.2	H54A—C54—H54B	109.5
C13—C14—H14A	109.5	C53—C54—H54C	109.5
C13—C14—H14B	109.5	H54A—C54—H54C	109.5
H14A—C14—H14B	109.5	H54B—C54—H54C	109.5
C13—C14—H14C	109.5	C62—C61—H61A	109.5
H14A—C14—H14C	109.5	C62—C61—H61B	109.5
H14B—C14—H14C	109.5	H61A—C61—H61B	109.5
C22—C21—H21A	109.5	C62—C61—H61C	109.5
C22—C21—H21B	109.5	H61A—C61—H61C	109.5
H21A—C21—H21B	109.5	H61B—C61—H61C	109.5
C22—C21—H21C	109.5	N6—C62—C61	110.0 (3)
H21A—C21—H21C	109.5	N6—C62—H62A	109.7
H21B—C21—H21C	109.5	C61—C62—H62A	109.7
N2—C22—C21	111.3 (3)	N6—C62—H62B	109.7
N2—C22—H22A	109.4	C61—C62—H62B	109.7
C21—C22—H22A	109.4	H62A—C62—H62B	108.2
N2—C22—H22B	109.4	N6—C63—C64	110.3 (3)

C21—C22—H22B	109.4	N6—C63—H63A	109.6
H22A—C22—H22B	108.0	C64—C63—H63A	109.6
N2—C23—C24	110.9 (3)	N6—C63—H63B	109.6
N2—C23—H23A	109.5	C64—C63—H63B	109.6
C24—C23—H23A	109.5	H63A—C63—H63B	108.1
N2—C23—H23B	109.5	C63—C64—H64A	109.5
C24—C23—H23B	109.5	C63—C64—H64B	109.5
H23A—C23—H23B	108.0	H64A—C64—H64B	109.5
C23—C24—H24A	109.5	C63—C64—H64C	109.5
C23—C24—H24B	109.5	H64A—C64—H64C	109.5
H24A—C24—H24B	109.5	H64B—C64—H64C	109.5
C13—N1—C12—C11	176.9 (3)	C43—N4—C42—C41	179.1 (3)
C12—N1—C13—C14	−178.5 (3)	C42—N4—C43—C44	−176.1 (3)
C23—N2—C22—C21	179.2 (3)	C53—N5—C52—C51	178.7 (3)
C22—N2—C23—C24	177.6 (3)	C52—N5—C53—C54	173.8 (3)
C33—N3—C32—C31	−179.4 (3)	C63—N6—C62—C61	−179.9 (3)
C32—N3—C33—C34	175.5 (3)	C62—N6—C63—C64	−174.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···Cl11	0.92	2.31	3.214 (3)	166
N1—H1B···Cl21	0.92	2.43	3.298 (3)	158
N2—H2A···Cl12	0.92	2.29	3.197 (3)	168
N3—H3A···Cl13	0.92	2.31	3.210 (3)	166
N3—H3B···Cl23^{i}	0.92	2.44	3.298 (3)	155
N4—H4A···Cl14	0.92	2.30	3.205 (3)	169
N4—H4B···Cl22^{ii}	0.92	2.44	3.306 (3)	158
N5—H5A···Cl24	0.92	2.45	3.315 (3)	156
N5—H5B···Cl32	0.92	2.27	3.190 (3)	176
N6—H6A···Cl31^{iii}	0.92	2.49	3.320 (3)	151
N6—H6B···Cl33	0.92	2.28	3.188 (3)	172

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*+1/2, *y*+1/2, −*z*+1/2.

Fig. 1

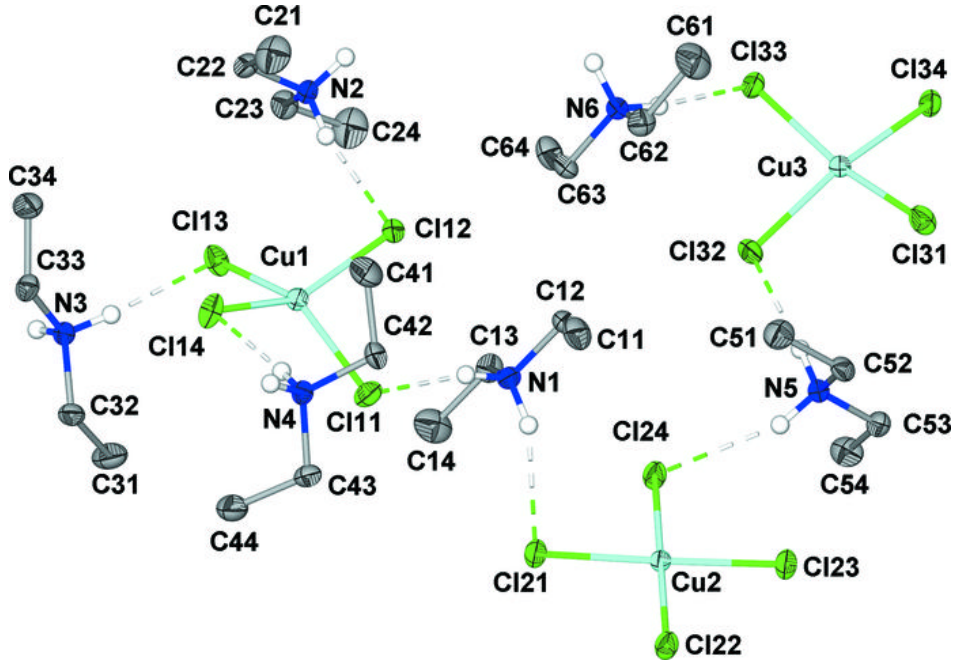

C21
C22
N2
C23
C24
C34
Cl13
Cu1
Cl12
C33
C41
N3
C42
Cl14
C32
N4
Cl11
C31
C43
C44
C12
C13
C11
N1
C14
C61
Cl33
Cl34
N6
C64
C62
Cu3
C63
Cl32
Cl31
C51
C52
N5
C53
Cl24
C54
Cl21
Cu2
Cl23
Cl22

Fig. 2

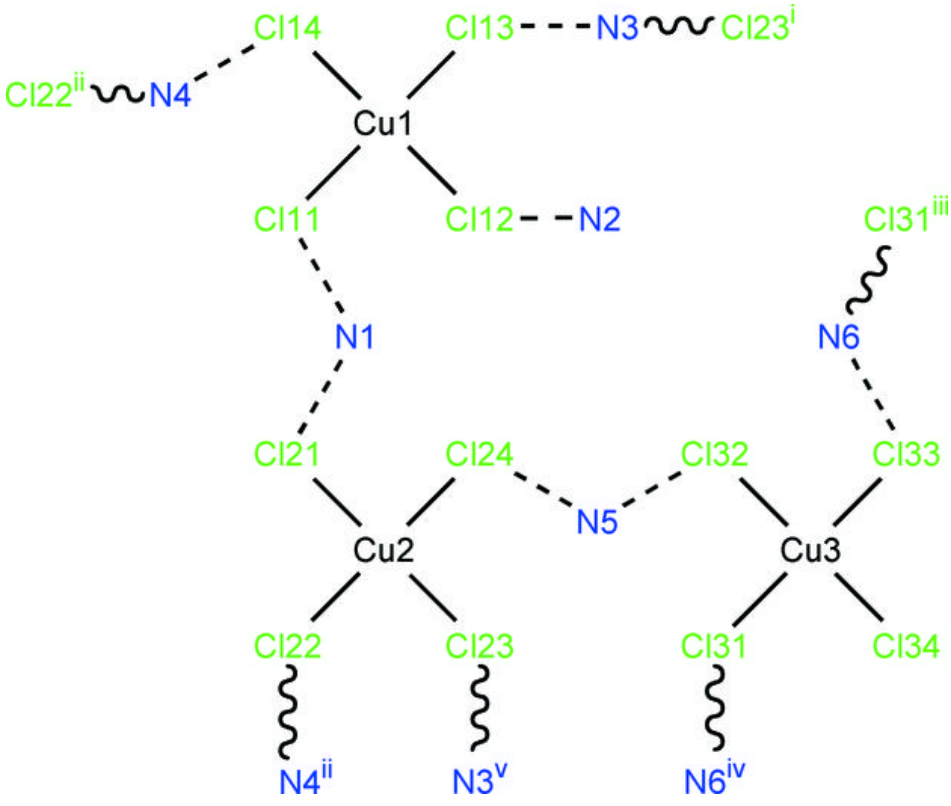
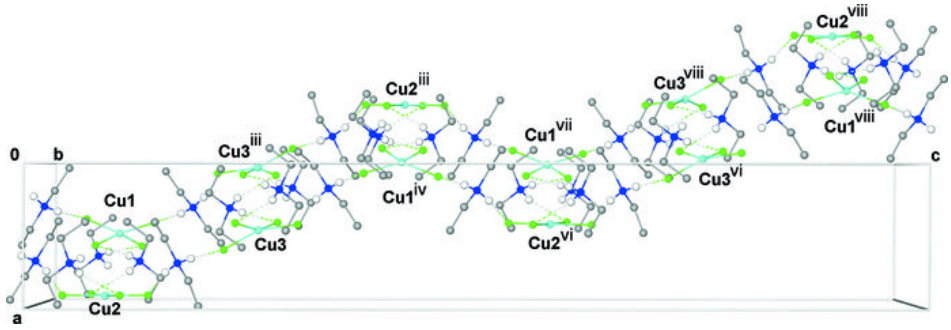

Cl14
Cl13
N3
Cl23i
Cl22ii
N4
Cu1
Cl11
Cl12
N2
Cl31iii
N1
N6
Cl21
Cl24
Cl32
Cl33
N5
Cu2
Cu3
Cl22
Cl23
Cl31
Cl34
N4ii
N3v
N6iv

Fig. 3


0
b
a
c
Cu1
Cu2
Cu3
Cu3iii
Cu2iii
Cu1iv
Cu1vii
Cu2vi
Cu3viii
Cu3vi
Cu2viii
Cu1viii