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Bis(diethylammonium) tetrachloridocuprate(II)

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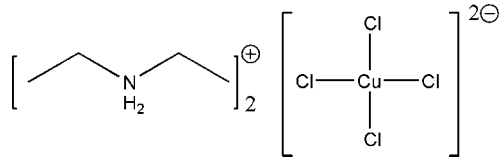
Key indicators: single-crystal X-ray study; T = 84 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.069; data-to-parameter ratio = 26.7.

The structure of the title compound, $(C_4H_{12}N)_2[CuCl_4]$ or $[DEA]_2[CuCl_4]$ (DEA is diethylammonium), at 84 (2) K has three crystallographically independent $[CuCl_4]^{2-}$ anions in the asymmetric unit, each with a different geometry. These geometries range from essentially square-planar to compressed tetrahedral geometry. The low-temperature structure reported here is the same as the room-temperature structure [Harlow & Simonsen (1976). *Am. Crystallogr. Assoc. Ser. 2 Program Abstr.* **4**, Abstract PBlO], thereby confirming the absence of a low-temperature phase transition.

Related literature

For related literature, see Bloomquist & Willett (1982); Halvorson *et al.* (1990); Harlow & Simonsen (1976); Kapustianik *et al.* (1994); Landee *et al.* (1978); Willett *et al.* (1974).



Experimental

Crystal data

$(C_4H_{12}N)_2[CuCl_4]$
M_r = 353.63
Monoclinic, $P2_1/n$
a = 7.2936 (15) Å
b = 14.881 (3) Å
c = 44.751 (9) Å
β = 90.12 (3)°
V = 4857.1 (17) Å^3
Z = 12
Mo $K\alpha$ radiation
μ = 1.99 mm^{-1}
T = 84 (2) K
0.35 × 0.31 × 0.30 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.510, T_{max} = 0.551
63568 measured reflections
11170 independent reflections
9931 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.069
S = 1.15
11170 reflections
418 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···Cl2	0.92	2.53	3.3754 (19)	153
N3—H3A···Cl1	0.92	2.55	3.192 (2)	127
N3—H3B···Cl10^{i}	0.92	2.30	3.1986 (18)	167
N3—H3B···Cl9^{i}	0.92	2.92	3.421 (2)	116
N8—H8A···Cl1	0.92	2.27	3.1835 (18)	172
N8—H8B···Cl3^{ii}	0.92	2.47	3.3076 (19)	151
N8—H8B···Cl2^{ii}	0.92	2.64	3.3148 (18)	130
N13—H13A···Cl5	0.92	2.45	3.3116 (18)	155
N13—H13A···Cl6	0.92	2.67	3.312 (2)	127
N13—H13B···Cl4	0.92	2.28	3.1948 (18)	176
N18—H18A···Cl11	0.92	2.31	3.2095 (18)	166
N18—H18A···Cl10	0.92	2.88	3.3683 (18)	115
N18—H18B···Cl8	0.92	2.41	3.2833 (19)	158
N18—H18B···Cl5	0.92	2.70	3.3128 (18)	124
N23—H23A···Cl7^{iii}	0.92	2.44	3.3079 (18)	157
N23—H23A···Cl8^{iii}	0.92	2.69	3.3229 (19)	126
N23—H23B···Cl12	0.92	2.31	3.2135 (18)	168
N23—H23B···Cl11	0.92	2.93	3.413 (2)	114
N28—H28A···Cl9^{iv}	0.92	2.30	3.2012 (18)	167
N28—H28A···Cl12^{iv}	0.92	2.90	3.3997 (18)	115
N28—H28B···Cl6	0.92	2.43	3.2874 (18)	155
N28—H28B···Cl7	0.92	2.67	3.3101 (18)	127

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y+1, z$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* (Bruker, 2003); program(s) used to refine structure: *XL* (Bruker, 2003); molecular graphics: *XP* (Bruker, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2513).

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supplementary materials

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Bis(diethylammonium) tetrachloridocuprate(II)

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Comment

The room temperature structure of $(DEA)_2CuCl_4$ was originally reported by Simonsen (Harlow & Simonsen, 1976), but full details were never published. Nevertheless, the compound has been the subject of several investigations, including thermochromism (Willett *et al.*, 1974; Bloomquist & Willett, 1982; Kapustianik *et al.*, 1994) and magnetism (Landee *et al.*, 1978). The compound undergoes a first order phase transition at 323 K, changing color from green to yellow. In the high temperature phase, there are two independent $CuCl_4^{2-}$ anions, both with compressed tetrahedral geometry (Bloomquist & Willett, 1982) in the asymmetric unit. The unique feature of both the room and low temperature structures is the existence of three crystallographic independent $CuCl_4^{2-}$ anions in the asymmetric unit, each with different geometries, ranging from essentially square planar coordination to compressed tetrahedral geometry.

The stucture of the title compound, (I), is shown below. Dimensions are available in the archived CIF. The distortions of the $CuCl_4^{2-}$ anions may be characterized by the average of the two larger *trans* Cl—Cu—Cl angles. For the square planar anion (containing Cu2), the average *trans* angle is 178.6°. In the anions containing Cu1 and Cu3, these values are 161.9° and 146.2 ° respectively, indicating increasing distortion towards tetrahedral geometry. The differences in distortion can be traced to the hydrogen bonding interactions, with stronger hydrogen bonding interactions favoring the square planar geometry over the compressed tetrahedral geometry (Halvorson *et al.*, 1990). All three $CuCl_4^{2-}$ anions participate in four bifurcated N—H···Cl hydrogen bonds. However, the nature of the bonding interactions is different for the three anions. For the square planar anion, all four of the bifurcated hydrogen bonds are nearly symmetric. In contrast, the anion containing Cu1 has two nearly symmetric hydrogen bonds and two very asymmetric ones, while for the anion closest to tetrahedral geometry, all of the hydrogen bonds are very asymmetric. These hydrogen bonds tie the anions together into layers that lie parallel to the (101) planes, producing short Cl···Cl contacts, that are presumably responsible for the observed two-dimensional magnetic behavior (Landee *et al.*, 1978).

Experimental

The compound was prepared following the published method (Willett *et al.*, 1974).

Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atom with C—H distances of 0.99 (CH_3), 0.98 (CH_2), and 0.92 (NH_2) Å with $U_{iso}(H) = 1.2U_{eq}(C)$, ($CH_2$, NH_2) and $1.5U_{eq}(C)$ (CH_3).

Figures

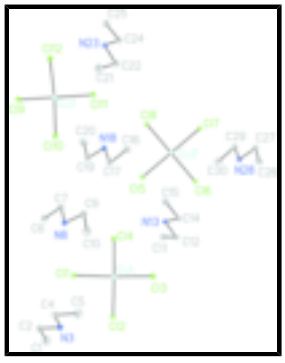

Fig. 1. Structure of $[DEA]_2[CuCl_4]$ (thermal displacement 30%) showing the asymmetric unit. Hydrogen atoms omitted for clarity.

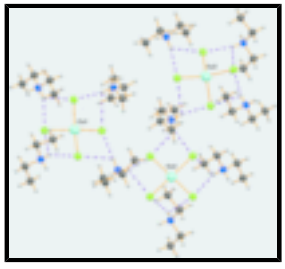

Fig. 2. Ball and stick H bonding diagram of $[DEA]_2[CuCl_4]$ (H bonding indicated by dashed lines).

Bis(diethylammonium) tetrachloridocuprate(II)

Crystal data

$(C_4H_{12}N)_2[CuCl_4]$	F_{000} = 2196
M_r = 353.63	D_x = 1.451 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 7583 reflections
a = 7.2936 (15) Å	θ = 2.3–30.0º
b = 14.881 (3) Å	μ = 1.99 mm^{-1}
c = 44.751 (9) Å	T = 84 (2) K
β = 90.12 (3)º	Block, green
V = 4857.1 (17) Å^3	0.35 × 0.31 × 0.30 mm
Z = 12	

Data collection

Bruker SMART APEX diffractometer	11170 independent reflections
Monochromator: graphite	9931 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3 pixels mm^{-1}	R_{int} = 0.031
T = 84(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 0.9º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −9→9

T_{min} = 0.510, T_{max} = 0.551
63568 measured reflections
k = −19→19
l = −58→58

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.069
S = 1.15
11170 reflections
418 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 4.0209P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
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}
C1	0.5586 (3)	0.63100 (17)	0.13404 (6)	0.0294 (5)
H1A	0.4869	0.5851	0.1235	0.044*
H1B	0.6083	0.6739	0.1195	0.044*
H1C	0.4794	0.6628	0.1482	0.044*
C2	0.7141 (3)	0.58671 (14)	0.15075 (5)	0.0182 (4)
H2A	0.6641	0.5419	0.1649	0.022*
H2B	0.7944	0.5549	0.1364	0.022*
C4	0.9816 (3)	0.61610 (14)	0.18455 (5)	0.0184 (4)
H4A	1.0688	0.5879	0.1705	0.022*
H4B	0.9367	0.5690	0.1983	0.022*
C5	1.0784 (3)	0.68851 (16)	0.20216 (6)	0.0292 (5)
H5A	1.1782	0.6617	0.2138	0.044*
H5B	0.9911	0.7175	0.2157	0.044*
H5C	1.1287	0.7334	0.1884	0.044*
C6	0.3953 (3)	0.41620 (15)	0.26985 (5)	0.0224 (5)
H6A	0.2855	0.3882	0.2784	0.034*

H6B	0.4680	0.3705	0.2595	0.034*
H6C	0.3589	0.4631	0.2557	0.034*
C7	0.5088 (3)	0.45737 (14)	0.29464 (5)	0.0166 (4)
H7A	0.4356	0.5037	0.3051	0.020*
H7B	0.5420	0.4104	0.3093	0.020*
C9	0.7894 (3)	0.54954 (14)	0.30513 (5)	0.0183 (4)
H9A	0.8255	0.5084	0.3215	0.022*
H9B	0.7137	0.5982	0.3138	0.022*
C10	0.9588 (3)	0.58930 (17)	0.29112 (5)	0.0273 (5)
H10A	1.0290	0.6220	0.3063	0.041*
H10B	0.9230	0.6308	0.2751	0.041*
H10C	1.0345	0.5410	0.2828	0.041*
C11	0.0105 (3)	0.87563 (15)	0.30933 (5)	0.0216 (5)
H11A	−0.0626	0.9208	0.2987	0.032*
H11B	−0.0575	0.8542	0.3268	0.032*
H11C	0.0356	0.8250	0.2959	0.032*
C12	0.1892 (3)	0.91698 (14)	0.31938 (5)	0.0162 (4)
H12A	0.2535	0.9433	0.3020	0.019*
H12B	0.1648	0.9657	0.3339	0.019*
C14	0.4795 (3)	0.88164 (14)	0.34734 (4)	0.0156 (4)
H14A	0.4490	0.9253	0.3633	0.019*
H14B	0.5530	0.9132	0.3320	0.019*
C15	0.5903 (3)	0.80499 (15)	0.36044 (5)	0.0210 (4)
H15A	0.7013	0.8289	0.3699	0.032*
H15B	0.6248	0.7632	0.3445	0.032*
H15C	0.5166	0.7733	0.3754	0.032*
C16	0.5854 (3)	0.58761 (15)	0.39748 (5)	0.0214 (5)
H16A	0.6931	0.6177	0.3890	0.032*
H16B	0.6254	0.5383	0.4105	0.032*
H16C	0.5139	0.6309	0.4092	0.032*
C17	0.4681 (3)	0.55059 (14)	0.37244 (5)	0.0165 (4)
H17A	0.4290	0.6002	0.3591	0.020*
H17B	0.5406	0.5075	0.3605	0.020*
C19	0.1829 (3)	0.46044 (14)	0.36214 (5)	0.0183 (4)
H19A	0.2547	0.4155	0.3508	0.022*
H19B	0.1371	0.5061	0.3479	0.022*
C20	0.0231 (3)	0.41500 (17)	0.37722 (5)	0.0276 (5)
H20A	−0.0543	0.3861	0.3621	0.041*
H20B	−0.0490	0.4598	0.3881	0.041*
H20C	0.0688	0.3696	0.3912	0.041*
C21	0.9643 (3)	0.37423 (16)	0.47100 (6)	0.0272 (5)
H21A	1.0376	0.4216	0.4616	0.041*
H21B	0.9222	0.3319	0.4557	0.041*
H21C	1.0393	0.3422	0.4858	0.041*
C22	0.8012 (3)	0.41546 (14)	0.48626 (5)	0.0176 (4)
H22A	0.8437	0.4591	0.5015	0.021*
H22B	0.7260	0.4482	0.4714	0.021*
C24	0.5207 (3)	0.38035 (14)	0.51631 (5)	0.0163 (4)
H24A	0.4462	0.4157	0.5020	0.020*

H24B	0.5581	0.4206	0.5328	0.020*
C25	0.4070 (3)	0.30393 (15)	0.52858 (5)	0.0222 (5)
H25A	0.2983	0.3282	0.5386	0.033*
H25B	0.4803	0.2695	0.5430	0.033*
H25C	0.3689	0.2645	0.5122	0.033*
C26	0.0372 (3)	1.08848 (16)	0.45872 (5)	0.0254 (5)
H26A	−0.0344	1.1176	0.4745	0.038*
H26B	−0.0388	1.0433	0.4486	0.038*
H26C	0.0770	1.1337	0.4442	0.038*
C27	0.2031 (3)	1.04349 (14)	0.47231 (4)	0.0163 (4)
H27A	0.2789	1.0889	0.4828	0.020*
H27B	0.1630	0.9984	0.4872	0.020*
C29	0.4826 (3)	0.95297 (14)	0.46020 (4)	0.0158 (4)
H29A	0.4470	0.9029	0.4735	0.019*
H29B	0.5567	0.9961	0.4720	0.019*
C30	0.5962 (3)	0.91688 (15)	0.43456 (5)	0.0220 (5)
H30A	0.7057	0.8870	0.4425	0.033*
H30B	0.6332	0.9667	0.4216	0.033*
H30C	0.5233	0.8737	0.4230	0.033*
Cl1	0.57998 (8)	0.61712 (3)	0.225343 (11)	0.01953 (11)
Cl2	0.57444 (7)	0.81973 (3)	0.199561 (11)	0.01711 (10)
Cl3	0.58550 (7)	0.88706 (3)	0.268534 (11)	0.01901 (11)
Cl4	0.39458 (8)	0.69435 (3)	0.285299 (11)	0.02130 (11)
Cl5	0.07286 (7)	0.69125 (3)	0.370252 (10)	0.01695 (10)
Cl6	0.08622 (7)	0.89147 (3)	0.396389 (11)	0.01752 (10)
Cl7	0.08134 (7)	0.81295 (3)	0.463214 (10)	0.01704 (10)
Cl8	0.07654 (7)	0.61251 (3)	0.437103 (11)	0.01732 (10)
Cl9	0.39456 (7)	0.12640 (3)	0.392757 (11)	0.01813 (10)
Cl10	0.56943 (7)	0.32285 (3)	0.373451 (11)	0.01938 (11)
Cl11	0.41007 (7)	0.37771 (3)	0.440331 (11)	0.01867 (11)
Cl12	0.59301 (7)	0.18030 (3)	0.457060 (11)	0.01874 (11)
Cu1	0.53186 (3)	0.756216 (16)	0.244934 (5)	0.01262 (6)
Cu2	0.07544 (3)	0.752143 (16)	0.416740 (5)	0.01178 (6)
Cu3	0.49144 (3)	0.251794 (16)	0.415907 (5)	0.01350 (6)
N3	0.8235 (2)	0.65478 (11)	0.16751 (4)	0.0137 (3)
H3A	0.7474	0.6841	0.1807	0.016*
H3B	0.8674	0.6967	0.1542	0.016*
N8	0.6793 (2)	0.49902 (11)	0.28244 (4)	0.0142 (3)
H8A	0.6475	0.5377	0.2672	0.017*
H8B	0.7513	0.4545	0.2744	0.017*
N13	0.3071 (2)	0.84654 (11)	0.33356 (4)	0.0136 (3)
H13A	0.2401	0.8177	0.3481	0.016*
H13B	0.3375	0.8046	0.3193	0.016*
N18	0.3031 (2)	0.50445 (11)	0.38495 (4)	0.0136 (3)
H18A	0.3414	0.4615	0.3984	0.016*
H18B	0.2345	0.5459	0.3953	0.016*
N23	0.6875 (2)	0.34506 (11)	0.50089 (4)	0.0134 (3)
H23A	0.7587	0.3151	0.5146	0.016*
H23B	0.6513	0.3041	0.4866	0.016*

N28	0.3147 (2)	0.99868 (11)	0.44880 (4)	0.0135 (3)
H28A	0.3490	1.0410	0.4349	0.016*
H28B	0.2427	0.9569	0.4392	0.016*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0247 (13)	0.0299 (13)	0.0338 (13)	−0.0032 (10)	−0.0113 (10)	−0.0055 (11)
C2	0.0196 (11)	0.0153 (10)	0.0198 (10)	−0.0040 (8)	−0.0001 (8)	−0.0029 (8)
C4	0.0178 (11)	0.0188 (10)	0.0187 (10)	0.0050 (8)	−0.0040 (8)	0.0014 (8)
C5	0.0264 (13)	0.0285 (13)	0.0327 (13)	−0.0002 (10)	−0.0108 (10)	−0.0036 (11)
C6	0.0212 (11)	0.0239 (11)	0.0221 (11)	−0.0061 (9)	−0.0016 (9)	0.0027 (9)
C7	0.0162 (10)	0.0174 (10)	0.0163 (10)	−0.0023 (8)	0.0033 (8)	0.0024 (8)
C9	0.0196 (11)	0.0191 (10)	0.0164 (10)	−0.0012 (8)	−0.0007 (8)	−0.0018 (8)
C10	0.0222 (12)	0.0302 (13)	0.0296 (13)	−0.0091 (10)	−0.0014 (10)	−0.0008 (10)
C11	0.0188 (11)	0.0260 (11)	0.0199 (11)	0.0022 (9)	−0.0016 (9)	0.0018 (9)
C12	0.0177 (10)	0.0155 (10)	0.0153 (10)	0.0029 (8)	0.0003 (8)	0.0028 (8)
C14	0.0149 (10)	0.0179 (10)	0.0140 (9)	−0.0016 (8)	0.0005 (8)	−0.0009 (8)
C15	0.0195 (11)	0.0228 (11)	0.0207 (11)	0.0011 (9)	−0.0023 (9)	−0.0001 (9)
C16	0.0217 (11)	0.0216 (11)	0.0210 (11)	−0.0054 (9)	−0.0014 (9)	0.0030 (9)
C17	0.0186 (11)	0.0149 (10)	0.0160 (10)	−0.0008 (8)	0.0031 (8)	0.0021 (8)
C19	0.0197 (11)	0.0195 (10)	0.0157 (10)	−0.0006 (8)	−0.0031 (8)	−0.0020 (8)
C20	0.0220 (12)	0.0347 (13)	0.0263 (12)	−0.0109 (10)	−0.0005 (10)	−0.0057 (10)
C21	0.0242 (12)	0.0267 (12)	0.0308 (13)	−0.0030 (10)	0.0092 (10)	0.0031 (10)
C22	0.0188 (11)	0.0165 (10)	0.0174 (10)	−0.0040 (8)	−0.0006 (8)	0.0019 (8)
C24	0.0169 (10)	0.0172 (10)	0.0149 (10)	0.0033 (8)	0.0018 (8)	−0.0018 (8)
C25	0.0202 (11)	0.0230 (11)	0.0234 (11)	−0.0027 (9)	0.0056 (9)	−0.0026 (9)
C26	0.0225 (12)	0.0308 (13)	0.0230 (11)	0.0086 (10)	0.0024 (9)	−0.0024 (10)
C27	0.0187 (10)	0.0171 (10)	0.0131 (9)	0.0013 (8)	0.0022 (8)	−0.0017 (8)
C29	0.0154 (10)	0.0158 (10)	0.0163 (10)	0.0014 (8)	−0.0021 (8)	0.0008 (8)
C30	0.0195 (11)	0.0245 (11)	0.0220 (11)	0.0059 (9)	0.0033 (9)	0.0016 (9)
Cl1	0.0298 (3)	0.0133 (2)	0.0155 (2)	0.0035 (2)	0.0058 (2)	0.00167 (18)
Cl2	0.0242 (3)	0.0140 (2)	0.0131 (2)	0.00066 (19)	0.00172 (19)	0.00114 (18)
Cl3	0.0235 (3)	0.0185 (2)	0.0151 (2)	−0.0063 (2)	0.00214 (19)	−0.00279 (19)
Cl4	0.0291 (3)	0.0156 (2)	0.0193 (2)	−0.0031 (2)	0.0114 (2)	−0.00083 (19)
Cl5	0.0246 (3)	0.0140 (2)	0.0123 (2)	−0.00008 (19)	−0.00015 (19)	−0.00072 (18)
Cl6	0.0272 (3)	0.0124 (2)	0.0129 (2)	−0.00079 (19)	−0.00031 (19)	0.00069 (18)
Cl7	0.0254 (3)	0.0137 (2)	0.0120 (2)	0.00022 (19)	0.00019 (19)	−0.00032 (18)
Cl8	0.0253 (3)	0.0125 (2)	0.0141 (2)	0.00020 (19)	0.00095 (19)	0.00078 (18)
Cl9	0.0221 (3)	0.0180 (2)	0.0144 (2)	−0.00639 (19)	−0.00049 (19)	0.00048 (19)
Cl10	0.0254 (3)	0.0136 (2)	0.0192 (2)	0.00087 (19)	0.0089 (2)	0.00093 (19)
Cl11	0.0242 (3)	0.0176 (2)	0.0142 (2)	0.0067 (2)	0.00078 (19)	0.00003 (19)
Cl12	0.0234 (3)	0.0135 (2)	0.0193 (2)	0.00086 (19)	−0.0075 (2)	0.00020 (19)
Cu1	0.01308 (12)	0.01246 (12)	0.01232 (11)	0.00018 (9)	0.00094 (9)	0.00059 (9)
Cu2	0.01240 (12)	0.01158 (11)	0.01136 (11)	−0.00023 (9)	0.00032 (9)	0.00019 (9)
Cu3	0.01362 (12)	0.01268 (12)	0.01420 (12)	0.00028 (9)	0.00068 (9)	0.00071 (9)
N3	0.0135 (8)	0.0131 (8)	0.0146 (8)	−0.0009 (6)	0.0015 (7)	0.0005 (7)
N8	0.0149 (9)	0.0139 (8)	0.0137 (8)	0.0000 (7)	0.0017 (7)	0.0005 (7)

N13	0.0151 (9)	0.0138 (8)	0.0119 (8)	−0.0001 (7)	0.0011 (6)	0.0003 (6)
N18	0.0144 (8)	0.0136 (8)	0.0127 (8)	0.0016 (7)	−0.0008 (6)	−0.0002 (6)
N23	0.0145 (8)	0.0131 (8)	0.0125 (8)	0.0000 (7)	0.0000 (6)	0.0005 (6)
N28	0.0143 (8)	0.0132 (8)	0.0128 (8)	−0.0003 (6)	0.0000 (7)	−0.0003 (6)

Geometric parameters (Å, °)

C1—C2	1.509 (3)	C20—H20B	0.9800
C1—H1A	0.9800	C20—H20C	0.9800
C1—H1B	0.9800	C21—C22	1.504 (3)
C1—H1C	0.9800	C21—H21A	0.9800
C2—N3	1.491 (3)	C21—H21B	0.9800
C2—H2A	0.9900	C21—H21C	0.9800
C2—H2B	0.9900	C22—N23	1.489 (3)
C4—N3	1.496 (3)	C22—H22A	0.9900
C4—C5	1.510 (3)	C22—H22B	0.9900
C4—H4A	0.9900	C24—N23	1.495 (3)
C4—H4B	0.9900	C24—C25	1.511 (3)
C5—H5A	0.9800	C24—H24A	0.9900
C5—H5B	0.9800	C24—H24B	0.9900
C5—H5C	0.9800	C25—H25A	0.9800
C6—C7	1.512 (3)	C25—H25B	0.9800
C6—H6A	0.9800	C25—H25C	0.9800
C6—H6B	0.9800	C26—C27	1.510 (3)
C6—H6C	0.9800	C26—H26A	0.9800
C7—N8	1.494 (3)	C26—H26B	0.9800
C7—H7A	0.9900	C26—H26C	0.9800
C7—H7B	0.9900	C27—N28	1.489 (3)
C9—N8	1.496 (3)	C27—H27A	0.9900
C9—C10	1.507 (3)	C27—H27B	0.9900
C9—H9A	0.9900	C29—N28	1.490 (2)
C9—H9B	0.9900	C29—C30	1.515 (3)
C10—H10A	0.9800	C29—H29A	0.9900
C10—H10B	0.9800	C29—H29B	0.9900
C10—H10C	0.9800	C30—H30A	0.9800
C11—C12	1.509 (3)	C30—H30B	0.9800
C11—H11A	0.9800	C30—H30C	0.9800
C11—H11B	0.9800	Cl1—Cu1	2.2754 (7)
C11—H11C	0.9800	Cl2—Cu1	2.2617 (7)
C12—N13	1.496 (2)	Cl3—Cu1	2.2490 (7)
C12—H12A	0.9900	Cl4—Cu1	2.2629 (8)
C12—H12B	0.9900	Cl5—Cu2	2.2692 (6)
C14—N13	1.494 (3)	Cl6—Cu2	2.2659 (6)
C14—C15	1.515 (3)	Cl7—Cu2	2.2684 (7)
C14—H14A	0.9900	Cl8—Cu2	2.2689 (7)
C14—H14B	0.9900	Cl9—Cu3	2.2475 (7)
C15—H15A	0.9800	Cl10—Cu3	2.2486 (7)
C15—H15B	0.9800	Cl11—Cu3	2.2495 (7)
C15—H15C	0.9800	Cl12—Cu3	2.2509 (7)

C16—C17	1.512 (3)	N3—H3A	0.9200
C16—H16A	0.9800	N3—H3B	0.9200
C16—H16B	0.9800	N8—H8A	0.9200
C16—H16C	0.9800	N8—H8B	0.9200
C17—N18	1.495 (3)	N13—H13A	0.9200
C17—H17A	0.9900	N13—H13B	0.9200
C17—H17B	0.9900	N18—H18A	0.9200
C19—N18	1.495 (3)	N18—H18B	0.9200
C19—C20	1.508 (3)	N23—H23A	0.9200
C19—H19A	0.9900	N23—H23B	0.9200
C19—H19B	0.9900	N28—H28A	0.9200
C20—H20A	0.9800	N28—H28B	0.9200
C2—C1—H1A	109.5	C22—C21—H21C	109.5
C2—C1—H1B	109.5	H21A—C21—H21C	109.5
H1A—C1—H1B	109.5	H21B—C21—H21C	109.5
C2—C1—H1C	109.5	N23—C22—C21	110.78 (18)
H1A—C1—H1C	109.5	N23—C22—H22A	109.5
H1B—C1—H1C	109.5	C21—C22—H22A	109.5
N3—C2—C1	110.71 (18)	N23—C22—H22B	109.5
N3—C2—H2A	109.5	C21—C22—H22B	109.5
C1—C2—H2A	109.5	H22A—C22—H22B	108.1
N3—C2—H2B	109.5	N23—C24—C25	110.54 (17)
C1—C2—H2B	109.5	N23—C24—H24A	109.5
H2A—C2—H2B	108.1	C25—C24—H24A	109.5
N3—C4—C5	110.52 (17)	N23—C24—H24B	109.5
N3—C4—H4A	109.5	C25—C24—H24B	109.5
C5—C4—H4A	109.5	H24A—C24—H24B	108.1
N3—C4—H4B	109.5	C24—C25—H25A	109.5
C5—C4—H4B	109.5	C24—C25—H25B	109.5
H4A—C4—H4B	108.1	H25A—C25—H25B	109.5
C4—C5—H5A	109.5	C24—C25—H25C	109.5
C4—C5—H5B	109.5	H25A—C25—H25C	109.5
H5A—C5—H5B	109.5	H25B—C25—H25C	109.5
C4—C5—H5C	109.5	C27—C26—H26A	109.5
H5A—C5—H5C	109.5	C27—C26—H26B	109.5
H5B—C5—H5C	109.5	H26A—C26—H26B	109.5
C7—C6—H6A	109.5	C27—C26—H26C	109.5
C7—C6—H6B	109.5	H26A—C26—H26C	109.5
H6A—C6—H6B	109.5	H26B—C26—H26C	109.5
C7—C6—H6C	109.5	N28—C27—C26	110.65 (17)
H6A—C6—H6C	109.5	N28—C27—H27A	109.5
H6B—C6—H6C	109.5	C26—C27—H27A	109.5
N8—C7—C6	110.77 (17)	N28—C27—H27B	109.5
N8—C7—H7A	109.5	C26—C27—H27B	109.5
C6—C7—H7A	109.5	H27A—C27—H27B	108.1
N8—C7—H7B	109.5	N28—C29—C30	110.66 (16)
C6—C7—H7B	109.5	N28—C29—H29A	109.5
H7A—C7—H7B	108.1	C30—C29—H29A	109.5
N8—C9—C10	110.77 (18)	N28—C29—H29B	109.5

N8—C9—H9A	109.5	C30—C29—H29B	109.5
C10—C9—H9A	109.5	H29A—C29—H29B	108.1
N8—C9—H9B	109.5	C29—C30—H30A	109.5
C10—C9—H9B	109.5	C29—C30—H30B	109.5
H9A—C9—H9B	108.1	H30A—C30—H30B	109.5
C9—C10—H10A	109.5	C29—C30—H30C	109.5
C9—C10—H10B	109.5	H30A—C30—H30C	109.5
H10A—C10—H10B	109.5	H30B—C30—H30C	109.5
C9—C10—H10C	109.5	Cl3—Cu1—Cl2	92.05 (2)
H10A—C10—H10C	109.5	Cl3—Cu1—Cl4	93.11 (2)
H10B—C10—H10C	109.5	Cl2—Cu1—Cl4	161.53 (2)
C12—C11—H11A	109.5	Cl3—Cu1—Cl1	160.34 (2)
C12—C11—H11B	109.5	Cl2—Cu1—Cl1	90.72 (2)
H11A—C11—H11B	109.5	Cl4—Cu1—Cl1	90.36 (2)
C12—C11—H11C	109.5	Cl6—Cu2—Cl7	90.17 (2)
H11A—C11—H11C	109.5	Cl6—Cu2—Cl8	177.81 (2)
H11B—C11—H11C	109.5	Cl7—Cu2—Cl8	89.83 (2)
N13—C12—C11	109.63 (17)	Cl6—Cu2—Cl5	89.83 (2)
N13—C12—H12A	109.7	Cl7—Cu2—Cl5	179.39 (2)
C11—C12—H12A	109.7	Cl8—Cu2—Cl5	90.15 (2)
N13—C12—H12B	109.7	Cl9—Cu3—Cl10	94.63 (2)
C11—C12—H12B	109.7	Cl9—Cu3—Cl11	146.36 (2)
H12A—C12—H12B	108.2	Cl10—Cu3—Cl11	94.95 (3)
N13—C14—C15	110.14 (17)	Cl9—Cu3—Cl12	95.01 (3)
N13—C14—H14A	109.6	Cl10—Cu3—Cl12	146.12 (2)
C15—C14—H14A	109.6	Cl11—Cu3—Cl12	94.75 (2)
N13—C14—H14B	109.6	C2—N3—C4	113.96 (16)
C15—C14—H14B	109.6	C2—N3—H3A	108.8
H14A—C14—H14B	108.1	C4—N3—H3A	108.8
C14—C15—H15A	109.5	C2—N3—H3B	108.8
C14—C15—H15B	109.5	C4—N3—H3B	108.8
H15A—C15—H15B	109.5	H3A—N3—H3B	107.7
C14—C15—H15C	109.5	C7—N8—C9	114.01 (16)
H15A—C15—H15C	109.5	C7—N8—H8A	108.8
H15B—C15—H15C	109.5	C9—N8—H8A	108.8
C17—C16—H16A	109.5	C7—N8—H8B	108.8
C17—C16—H16B	109.5	C9—N8—H8B	108.8
H16A—C16—H16B	109.5	H8A—N8—H8B	107.6
C17—C16—H16C	109.5	C14—N13—C12	114.38 (16)
H16A—C16—H16C	109.5	C14—N13—H13A	108.7
H16B—C16—H16C	109.5	C12—N13—H13A	108.7
N18—C17—C16	110.17 (17)	C14—N13—H13B	108.7
N18—C17—H17A	109.6	C12—N13—H13B	108.7
C16—C17—H17A	109.6	H13A—N13—H13B	107.6
N18—C17—H17B	109.6	C19—N18—C17	114.64 (16)
C16—C17—H17B	109.6	C19—N18—H18A	108.6
H17A—C17—H17B	108.1	C17—N18—H18A	108.6
N18—C19—C20	110.09 (17)	C19—N18—H18B	108.6
N18—C19—H19A	109.6	C17—N18—H18B	108.6

C20—C19—H19A	109.6	H18A—N18—H18B	107.6
N18—C19—H19B	109.6	C22—N23—C24	114.25 (16)
C20—C19—H19B	109.6	C22—N23—H23A	108.7
H19A—C19—H19B	108.2	C24—N23—H23A	108.7
C19—C20—H20A	109.5	C22—N23—H23B	108.7
C19—C20—H20B	109.5	C24—N23—H23B	108.7
H20A—C20—H20B	109.5	H23A—N23—H23B	107.6
C19—C20—H20C	109.5	C27—N28—C29	114.35 (15)
H20A—C20—H20C	109.5	C27—N28—H28A	108.7
H20B—C20—H20C	109.5	C29—N28—H28A	108.7
C22—C21—H21A	109.5	C27—N28—H28B	108.7
C22—C21—H21B	109.5	C29—N28—H28B	108.7
H21A—C21—H21B	109.5	H28A—N28—H28B	107.6

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···Cl2	0.92	2.53	3.3754 (19)	153
N3—H3A···Cl1	0.92	2.55	3.192 (2)	127
N3—H3B···Cl10^{i}	0.92	2.30	3.1986 (18)	167
N3—H3B···Cl9^{i}	0.92	2.92	3.421 (2)	116
N8—H8A···Cl1	0.92	2.27	3.1835 (18)	172
N8—H8B···Cl3^{ii}	0.92	2.47	3.3076 (19)	151
N8—H8B···Cl2^{ii}	0.92	2.64	3.3148 (18)	130
N13—H13A···Cl5	0.92	2.45	3.3116 (18)	155
N13—H13A···Cl6	0.92	2.67	3.312 (2)	127
N13—H13B···Cl4	0.92	2.28	3.1948 (18)	176
N18—H18A···Cl11	0.92	2.31	3.2095 (18)	166
N18—H18A···Cl10	0.92	2.88	3.3683 (18)	115
N18—H18B···Cl8	0.92	2.41	3.2833 (19)	158
N18—H18B···Cl5	0.92	2.70	3.3128 (18)	124
N23—H23A···Cl7^{iii}	0.92	2.44	3.3079 (18)	157
N23—H23A···Cl8^{iii}	0.92	2.69	3.3229 (19)	126
N23—H23B···Cl12	0.92	2.31	3.2135 (18)	168
N23—H23B···Cl11	0.92	2.93	3.413 (2)	114
N28—H28A···Cl9^{iv}	0.92	2.30	3.2012 (18)	167
N28—H28A···Cl12^{iv}	0.92	2.90	3.3997 (18)	115
N28—H28B···Cl6	0.92	2.43	3.2874 (18)	155
N28—H28B···Cl7	0.92	2.67	3.3101 (18)	127

Symmetry codes: (i) −*x*+3/2, *y*+1/2, −*z*+1/2; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*+1, *z*.

Fig. 1

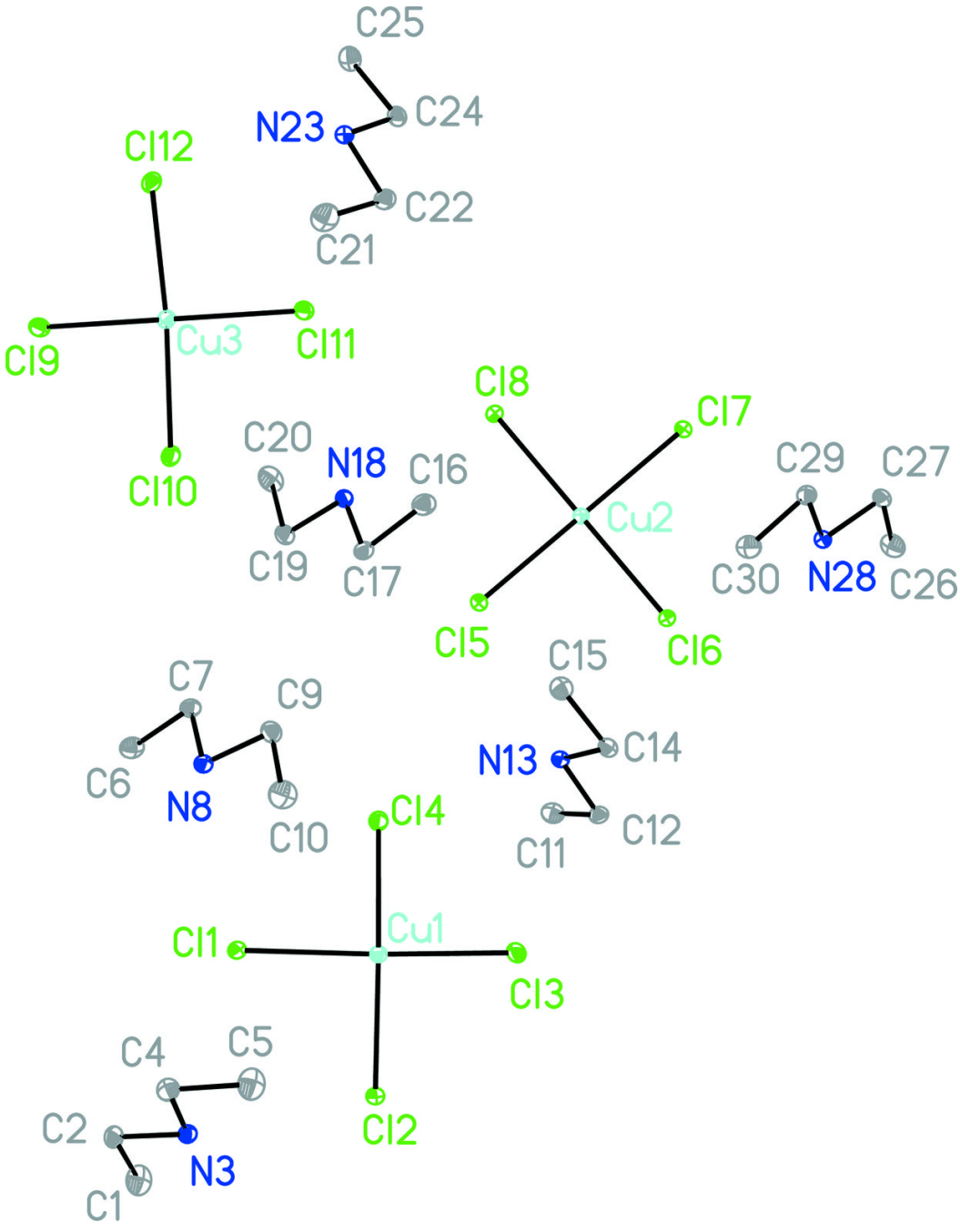
C25
C24
N23
Cl12
C22
C21
Cl9
Cu3
Cl11
Cl10
C20
N18
C16
C19
C17
Cl8
Cl7
Cu2
Cl5
Cl6
C29
C27
C30
N28
C26
C7
C9
C6
N8
C10
C15
N13
C14
C11
C12
Cl4
Cl1
Cu1
Cl3
C4
C5
C2
N3
C1
Cl2

Fig. 2