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Poly[(*R*)-2-methylpiperazinediium [μ_3-chlorido-μ_2-chlorido-dichloridodicopper(I)]]

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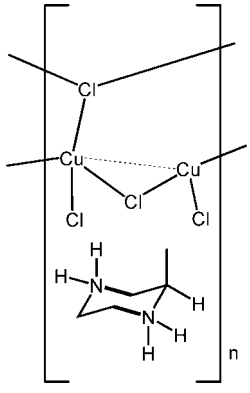
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.040; wR factor = 0.091; data-to-parameter ratio = 23.2.

The title compound, $\{(C_5H_{14}N_2)[Cu_2Cl_4]\}_n$, was synthesized by the hydrothermal reaction of $CuCl_2$ with homochiral (*R*)-2-methylpiperazine. One Cu atom has a slightly distorted tetrahedral geometry defined by one terminal and three bridging Cl^- anions, while the other displays a trigonal planar geometry composed of one terminal and two bridging Cl^- anions. The crystal structure contains a polymeric anion forming a chain running along the *a* axis and (*R*)-2-methylpiperazinediium cations filling the space between these chains. Cations and anions are connected by hydrogen bonds.

Related literature

For macrophysical properties of non-centrosymmetric bulk materials, see: Newnham (1975); Qu *et al.* (2004).



Experimental

Crystal data

$(C_5H_{14}N_2)[Cu_2Cl_4]$
M_r = 371.06
Orthorhombic, $P2_12_12_1$
a = 6.1943 (16) Å
b = 12.544 (4) Å
c = 15.561 (5) Å
V = 1209.1 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.36 mm^{-1}
T = 293 (2) K
0.25 × 0.06 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.721, T_{max} = 1.000
(expected range = 0.580–0.804)
12245 measured reflections
2756 independent reflections
2439 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.091
S = 1.06
2756 reflections
119 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), with 1149 Friedel pairs
Flack parameter: −0.04 (2)

Table 1
Selected bond lengths (Å).

Cu1—Cl4	2.3068 (15)	Cu2—Cl3^{ii}	2.2278 (14)
Cu1—Cl1	2.3453 (16)	Cu2—Cl1	2.2308 (15)
Cu1—Cl3^{i}	2.4099 (14)	Cu2—Cl2	2.3057 (15)
Cu1—Cl3	2.4317 (15)	Cl3—Cu2^{i}	2.2277 (14)
Cu1···Cu2	2.8893 (12)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl4	0.90	2.45	3.203 (4)	142
N1—H1A···Cl2	0.90	2.90	3.442 (4)	120
N1—H1B···Cl4^{iii}	0.90	2.36	3.236 (4)	163
N2—H2A···Cl2^{iv}	0.90	2.39	3.260 (4)	162
N2—H2B···Cl2^{v}	0.90	2.42	3.187 (4)	143

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2555).

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  doi:10.1107/S1600536807052774

supplementary materials

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Poly[(*R*)-2-methylpiperazinediium [μ_3-chlorido-μ_2-chlorido-dichloridodicopper(I)]]

H.-Z. Luo and H.-Y. Ye

Comment

Macro-physical properties, such as ferroelectricity and second harmonic generation, are only found in noncentrosymmetric bulk material (Newnham, 1975). We have focused on the synthesis and design of noncentrosymmetric coordination compounds constructed by chiral organic ligand as building block with inorganic metal ions through hydrothermal synthesis (Qu *et al.*, 2004). We report here the crystal structure of the title compound, cantena Poly [(*R*)-2-methylpiperazine-dium (μ_2-chloro)-(μ_3-chloro)-dichloro-di-copper(I)].

In I, there are two chemically and crystallographically independent Cu atoms with a distance of Cu1—Cu2 2.8893 (12) Å. As shown in Fig.1, Cu1 has a slightly distorted tetrahedral geometry defined by one terminal and three bridging Cl anions; Cu2 displays a trigonal geometry composed of one terminal and two bridging Cl anions. The distance from Cu2 to the plane of Cl1 Cl2 Cl3B is of 0.0426 (10) Å. The six atoms Cu1 Cl1 Cu2 Cl3B Cu1B Cl3 form a six-membered ring. Besides the terminal Cl atoms, the adjacent six-membered rings share edges to form the Cl-bridged Cu chain. The diprotonated piperidine molecules and the chains are connected by hydrogen bonds.

Experimental

A mixture of (*R*)-2-methylpiperazine (20 mg, 0.2 mmol), $CuCl_2$ (27 mg, 0.2 mmol), water (1 ml) and methanol (1 ml) sealed in a glass tube were maintained at 110–115 °C. Crystals suitable for X-ray analysis were obtained after 5 days.

Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C and N atoms to which they are bonded, with U_{iso}(H) = 1.2Ueq(C or N).

Figures

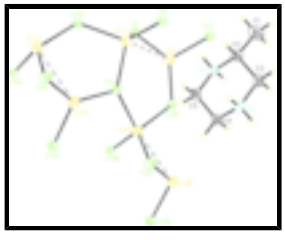


Fig. 1. A view of the title compoud with atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. Atoms with suffix A and B are generated by the symmetry operator 1/2 + *x*, −1/2 − *y*, −1 − *z* and −1/2 + *x*, −1/2 − *y*, −1 − *z*, respectively. The dashed open lines show the Cu—Cu interaction.

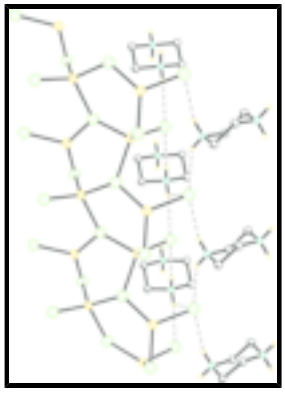


Fig. 2. The chain structure of the title compound. Methyl C atoms and H atoms bonded to C atoms were omitted for clarity. The dashed lines show the N—H···Cl hydrogen bonds presented in Table 2.

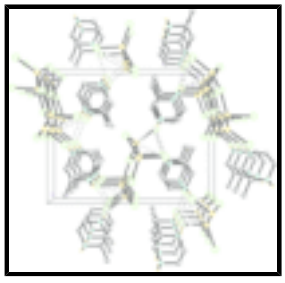


Fig. 3. The crystal packing of the title compound viewed along the *a* axis. H atoms bonded to C atoms were omitted for clarity. The dashed lines show hydrogen bonds.

Poly[(*R*)-2-methylpiperazinediium [μ$_3$-chlorido-μ$_2$-chlorido-dichloridodicopper(I)]]

Crystal data

$(C_5H_{14}N_2)[Cu_2Cl_4]$	F_{000} = 736
M_r = 371.06	D_x = 2.038 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 3251 reflections
a = 6.1943 (16) Å	θ = 3.1–27.5º
b = 12.544 (4) Å	μ = 4.36 mm^{-1}
c = 15.561 (5) Å	T = 293 (2) K
V = 1209.1 (6) Å^3	Block, colourless
Z = 4	0.25 × 0.06 × 0.05 mm

Data collection

Rigaku Mercury2 (2x2 bin mode) diffractometer	2756 independent reflections
Radiation source: fine-focus sealed tube	2439 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.058
Detector resolution: 13.6612 pixels mm^{-1}	θ_{max} = 27.5º
T = 293(2) K	θ_{min} = 3.1º
ω scans	h = −8→8
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	k = −16→16
T_{min} = 0.721, T_{max} = 1.000	l = −20→20

12245 measured reflections

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.091$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.75$ e Å^{-3}
2756 reflections	$\Delta\rho_{min} = -0.52$ e Å^{-3}
119 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 1149 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.04 (2)

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 $F^2 > \sigma(F^2)$ 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	0.34591 (11)	−0.14923 (6)	−0.54943 (4)	0.0524 (2)
Cu2	−0.07136 (10)	−0.04816 (6)	−0.53360 (4)	0.04967 (19)
Cl1	0.2405 (2)	0.00613 (11)	−0.47681 (8)	0.0450 (3)
Cl2	−0.18532 (19)	0.05572 (11)	−0.64711 (9)	0.0495 (3)
Cl3	0.20460 (19)	−0.32180 (10)	−0.50581 (8)	0.0427 (3)
Cl4	0.30984 (18)	−0.14203 (9)	−0.69686 (7)	0.0361 (2)
N1	−0.1874 (6)	−0.1985 (3)	−0.7303 (2)	0.0357 (8)
H1A	−0.0828	−0.1566	−0.7087	0.043*
H1B	−0.3155	−0.1712	−0.7142	0.043*
N2	−0.3208 (6)	−0.3814 (3)	−0.8259 (2)	0.0377 (9)
H2A	−0.1932	−0.4097	−0.8415	0.045*
H2B	−0.4262	−0.4232	−0.8470	0.045*
C1	−0.2082 (11)	−0.0895 (5)	−0.8625 (4)	0.0707 (18)
H8A	−0.2054	−0.0927	−0.9242	0.106*
H8B	−0.0961	−0.0427	−0.8427	0.106*
H8C	−0.3458	−0.0630	−0.8439	0.106*

C2	−0.1730 (8)	−0.1982 (4)	−0.8266 (3)	0.0387 (11)
H4A	−0.0294	−0.2233	−0.8437	0.046*
C3	−0.3411 (8)	−0.2726 (4)	−0.8632 (3)	0.0430 (11)
H5A	−0.4839	−0.2447	−0.8511	0.052*
H5B	−0.3243	−0.2766	−0.9251	0.052*
C4	−0.3356 (8)	−0.3795 (4)	−0.7302 (3)	0.0383 (10)
H6A	−0.3169	−0.4511	−0.7077	0.046*
H6B	−0.4769	−0.3541	−0.7129	0.046*
C5	−0.1646 (8)	−0.3078 (4)	−0.6943 (3)	0.0384 (10)
H3A	−0.1772	−0.3051	−0.6322	0.046*
H3B	−0.0231	−0.3359	−0.7084	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0531 (4)	0.0554 (4)	0.0486 (4)	0.0069 (3)	−0.0020 (3)	0.0041 (3)
Cu2	0.0480 (4)	0.0455 (4)	0.0555 (4)	−0.0046 (3)	0.0058 (3)	−0.0045 (3)
Cl1	0.0429 (6)	0.0455 (6)	0.0467 (7)	0.0023 (5)	−0.0051 (5)	−0.0029 (5)
Cl2	0.0329 (6)	0.0514 (7)	0.0642 (8)	−0.0014 (6)	−0.0048 (6)	0.0195 (7)
Cl3	0.0311 (5)	0.0369 (6)	0.0600 (7)	−0.0024 (5)	0.0010 (5)	0.0114 (5)
Cl4	0.0311 (5)	0.0378 (5)	0.0395 (6)	0.0010 (5)	−0.0001 (4)	0.0033 (5)
N1	0.0295 (19)	0.0309 (18)	0.047 (2)	−0.0047 (17)	−0.0019 (18)	−0.0051 (17)
N2	0.034 (2)	0.040 (2)	0.039 (2)	−0.0001 (18)	−0.0053 (18)	−0.0113 (17)
C1	0.076 (4)	0.058 (4)	0.078 (4)	0.008 (3)	0.013 (4)	0.016 (3)
C2	0.033 (2)	0.041 (3)	0.042 (3)	0.003 (2)	0.007 (2)	0.003 (2)
C3	0.037 (3)	0.057 (3)	0.035 (2)	0.003 (2)	−0.002 (2)	−0.002 (2)
C4	0.042 (3)	0.033 (2)	0.040 (2)	0.000 (2)	−0.002 (2)	0.003 (2)
C5	0.046 (3)	0.036 (2)	0.034 (2)	0.002 (2)	−0.005 (2)	−0.0025 (19)

Geometric parameters (Å, °)

Cu1—Cl4	2.3068 (15)	N2—H2A	0.9000
Cu1—Cl1	2.3453 (16)	N2—H2B	0.9000
Cu1—Cl3^{i}	2.4099 (14)	C1—C2	1.490 (7)
Cu1—Cl3	2.4317 (15)	C1—H8A	0.9600
Cu1—Cu2	2.8893 (12)	C1—H8B	0.9600
Cu2—Cl3^{ii}	2.2278 (14)	C1—H8C	0.9600
Cu2—Cl1	2.2308 (15)	C2—C3	1.510 (7)
Cu2—Cl2	2.3057 (15)	C2—H4A	0.9800
Cl3—Cu2^{i}	2.2277 (14)	C3—H5A	0.9700
Cl3—Cu1^{ii}	2.4099 (14)	C3—H5B	0.9700
N1—C5	1.488 (6)	C4—C5	1.498 (6)
N1—C2	1.501 (6)	C4—H6A	0.9700
N1—H1A	0.9000	C4—H6B	0.9700
N1—H1B	0.9000	C5—H3A	0.9700
N2—C3	1.488 (6)	C5—H3B	0.9700
N2—C4	1.492 (6)		
Cl4—Cu1—Cl1	114.81 (5)	H2A—N2—H2B	107.9

Cl4—Cu1—Cl3^{i}	116.74 (5)	C2—C1—H8A	109.5
Cl1—Cu1—Cl3^{i}	102.13 (5)	C2—C1—H8B	109.5
Cl4—Cu1—Cl3	106.12 (5)	H8A—C1—H8B	109.5
Cl1—Cu1—Cl3	120.33 (5)	C2—C1—H8C	109.5
Cl3^{i}—Cu1—Cl3	95.63 (4)	H8A—C1—H8C	109.5
Cl4—Cu1—Cu2	88.91 (4)	H8B—C1—H8C	109.5
Cl1—Cu1—Cu2	49.11 (4)	C1—C2—N1	111.6 (4)
Cl3^{i}—Cu1—Cu2	149.37 (5)	C1—C2—C3	108.9 (4)
Cl3—Cu1—Cu2	92.57 (4)	N1—C2—C3	109.5 (4)
Cl3^{ii}—Cu2—Cl1	130.84 (6)	C1—C2—H4A	108.9
Cl3^{ii}—Cu2—Cl2	115.72 (6)	N1—C2—H4A	108.9
Cl1—Cu2—Cl2	113.33 (6)	C3—C2—H4A	108.9
Cl3^{ii}—Cu2—Cu1	105.04 (5)	N2—C3—C2	111.2 (4)
Cl1—Cu2—Cu1	52.63 (4)	N2—C3—H5A	109.4
Cl2—Cu2—Cu1	117.17 (4)	C2—C3—H5A	109.4
Cu2—Cl1—Cu1	78.26 (5)	N2—C3—H5B	109.4
Cu2^{i}—Cl3—Cu1^{ii}	111.45 (5)	C2—C3—H5B	109.4
Cu2^{i}—Cl3—Cu1	120.29 (6)	H5A—C3—H5B	108.0
Cu1^{ii}—Cl3—Cu1	124.45 (5)	N2—C4—C5	109.8 (4)
C5—N1—C2	111.9 (4)	N2—C4—H6A	109.7
C5—N1—H1A	109.2	C5—C4—H6A	109.7
C2—N1—H1A	109.2	N2—C4—H6B	109.7
C5—N1—H1B	109.2	C5—C4—H6B	109.7
C2—N1—H1B	109.2	H6A—C4—H6B	108.2
H1A—N1—H1B	107.9	N1—C5—C4	110.2 (4)
C3—N2—C4	111.7 (3)	N1—C5—H3A	109.6
C3—N2—H2A	109.3	C4—C5—H3A	109.6
C4—N2—H2A	109.3	N1—C5—H3B	109.6
C3—N2—H2B	109.3	C4—C5—H3B	109.6
C4—N2—H2B	109.3	H3A—C5—H3B	108.1

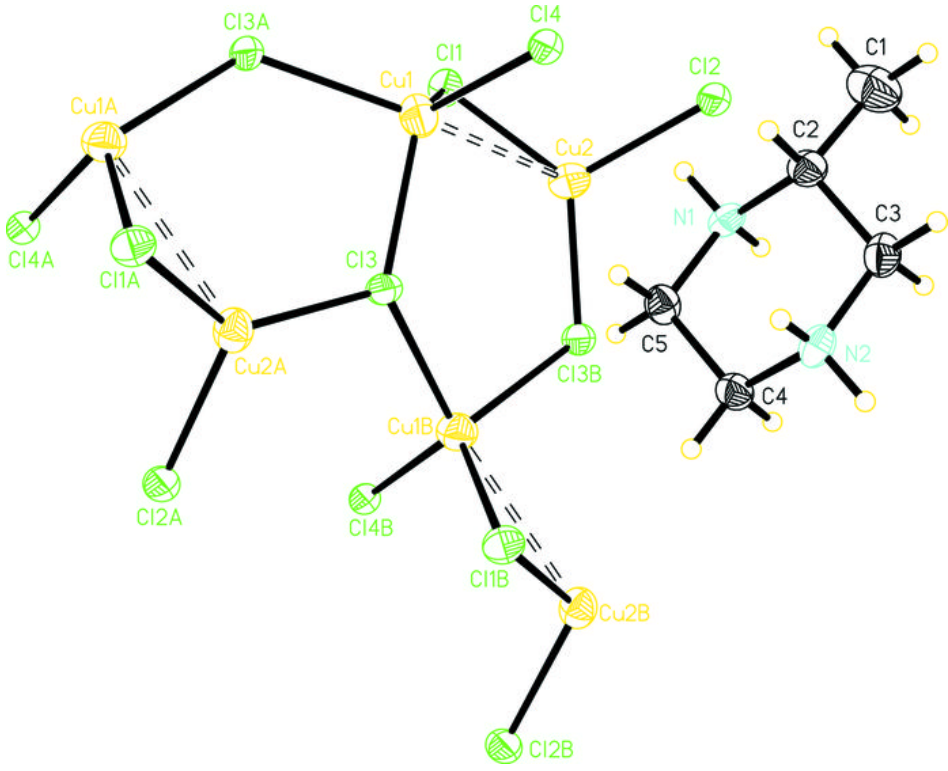
Symmetry codes: (i) *x*+1/2, −*y*−1/2, −*z*−1; (ii) *x*−1/2, −*y*−1/2, −*z*−1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···Cl4	0.90	2.45	3.203 (4)	142
N1—H1A···Cl2	0.90	2.90	3.442 (4)	120
N1—H1B···Cl4^{iii}	0.90	2.36	3.236 (4)	163
N2—H2A···Cl2^{iv}	0.90	2.39	3.260 (4)	162
N2—H2B···Cl2^{v}	0.90	2.42	3.187 (4)	143

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

Fig. 1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C3
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Cl1B
Cu2B
Cl2B

Fig. 2

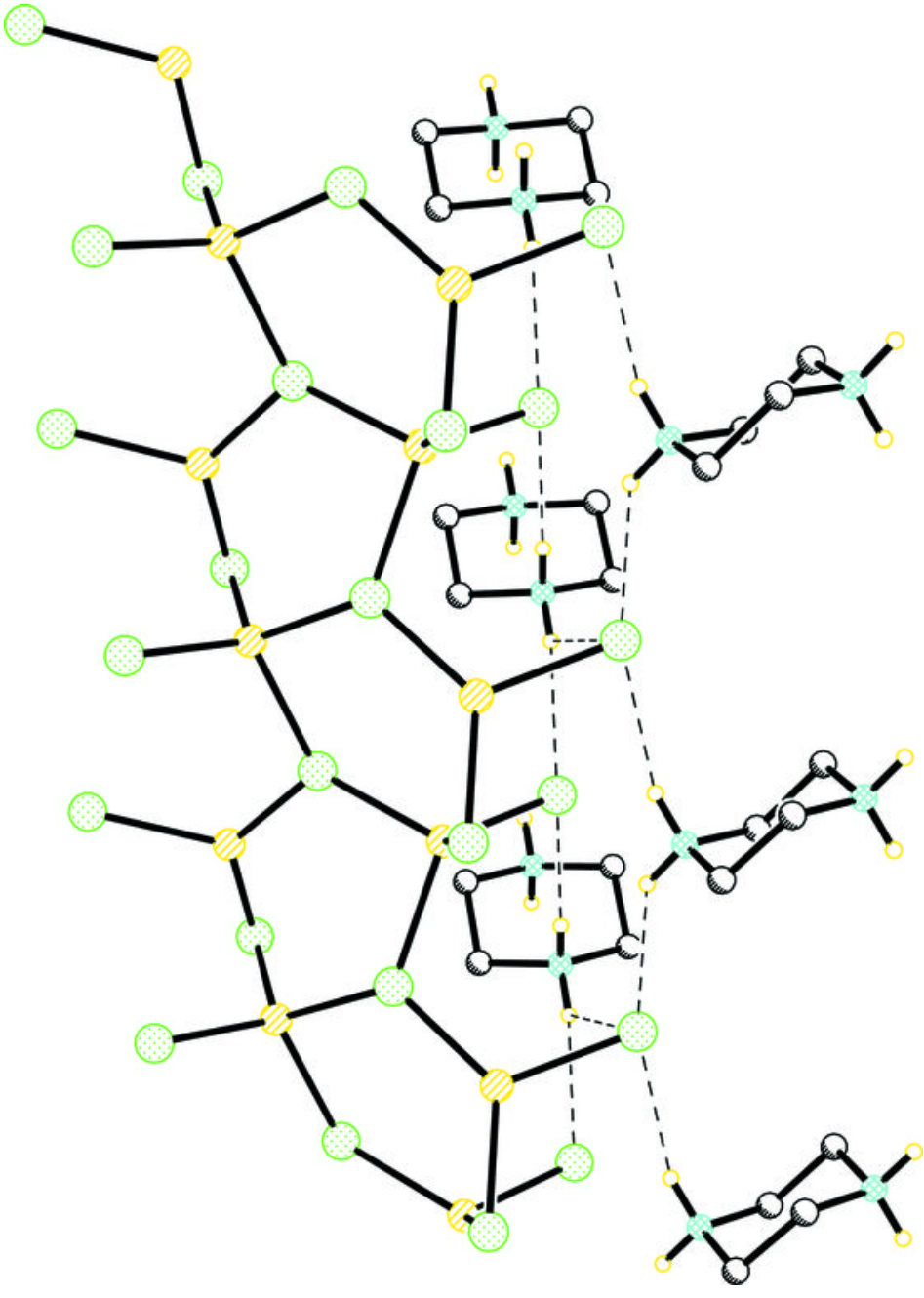

Fig. 3