

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(S)-2-Methylpiperazinediium dichloride 0.42-hydrate

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen
AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

Received 27 February 2008; accepted 16 April 2008

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; H-atom completeness 95%; disorder in solvent or counterion; R factor = 0.043; wR factor = 0.110; data-to-parameter ratio = 21.5.

The cations and anions of the chiral title compound, $\text{C}_5\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{Cl}^- \cdot 0.42\text{H}_2\text{O}$, are linked by $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonds into chains propagating in $[100]$, which contain $R_4^2(14)$ loops.

Related literature

For crystal structures containing the same chiral cation, see: Muller *et al.* (2005); Tuel *et al.* (2002). For background on graph theory, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_5\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{Cl}^- \cdot 0.42\text{H}_2\text{O}$ $V = 445.57(3) \text{ \AA}^3$
 $M_r = 180.65$ $Z = 2$
 Monoclinic, $P2_1$ $\text{Mo K}\alpha$ radiation
 $a = 5.7548(2) \text{ \AA}$ $\mu = 0.66 \text{ mm}^{-1}$
 $b = 11.6176(4) \text{ \AA}$ $T = 120(2) \text{ K}$
 $c = 6.9248(2) \text{ \AA}$ $0.10 \times 0.08 \times 0.02 \text{ mm}$
 $\beta = 105.7599(16)^\circ$

Data collection

Nonius KappaCCD diffractometer 1999 independent reflections
 Absorption correction: none 1952 reflections with $I > 2\sigma(I)$
 5193 measured reflections $R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.110$
 $S = 1.05$
 1999 reflections
 93 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.93 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 929 Friedel pairs
 Flack parameter: 0.04 (9)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H2} \cdots \text{Cl2}$	0.92	2.25	3.096 (2)	153
$\text{N1}-\text{H1} \cdots \text{Cl2}^i$	0.92	2.24	3.136 (2)	166
$\text{N2}-\text{H3} \cdots \text{Cl1}$	0.92	2.26	3.149 (2)	163
$\text{N2}-\text{H4} \cdots \text{Cl1}^i$	0.92	2.30	3.137 (2)	152

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

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997), SCALEPACK and SORTAV (Blessing, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

I thank the EPSRC National Crystallography Service (University of Southampton) for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2428).

References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Muller, E. A., Cannon, R. J., Sarjeant, A. N., Ok, K. M., Halasyamani, P. S. & Norquist, A. J. (2005). *Cryst. Growth Des.* **5**, 1913–1917.
 Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter, Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Tuel, A., Gramlich, V. & Ch. Baerlocher, Ch. (2002). *Micropor. Mesopor. Mater.* **56**, 119–130.

supplementary materials

Acta Cryst. (2008). E64, o878 [doi:10.1107/S1600536808010519]

(S)-2-Methylpiperazinediium dichloride 0.42-hydrate

W. T. A. Harrison

Comment

The title compound, (I), is a chiral molecular salt, in which the organic species has accepted two protons from the hydrochloric acid. The geometrical parameters of the $C_5H_{14}N_2^{2+}$ dication (Fig. 1) are similar to those of the same species in other structures (Muller *et al.*, 2005; Tuel *et al.*, 2002) and its six-membered ring is a typical chair. The C4 stereogenic centre has S configuration and the pendant C5 methyl group occupies an equatorial position with respect to the ring.

In the crystal of (I), the cations and anions are linked by N—H \cdots Cl hydrogen bonds (Table 1) into chains propagating in [100], with two chloride ions bridging each dication, as shown in Fig 2. In terms of graph theory (Bernstein *et al.*, 1995), $R_4^2(14)$ loops arise from this connectivity.

The O1 water molecule is partially occupied in the crystal of (I), although there is no obvious crystallographic reason (*e.g.* symmetry generated close contacts) as to why this should be the case. Based on short O \cdots Cl contacts of less than 3.5 Å, the water molecule probably participates in O—H \cdots Cl hydrogen bonds thereby helping to crosslink the [100] chains, but the water H atoms could not be found or placed unambiguously in the present study.

Experimental

Equimolar quantities of 0.1 M aqueous (S)-2-methylpiperazine and 0.1 M aqueous hydrochloric acid were mixed, leading to a clear solution. Colourless plates of (I) grew as the water slowly evaporated.

Refinement

When refined with full occupancy, atom O1 showed an excessively large U_{iso} value of 0.15 Å². Its fractional site occupancy was refined and rapidly converged to 0.420 (11) with a more reasonable U_{iso} value and improvement in fit. Its U^{ij} values were subsequently refined and converged without difficulty. Its presumed attached H atoms could not be located from difference maps in the present study. Attempts at geometrical placement were ambiguous, as there are several possible O \cdots Cl contacts that might correspond to O—H \cdots Cl hydrogen bonds.

The other hydrogen atoms were geometrically placed (C—H = 0.95–0.99 Å, N—H = 0.92 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(\text{methyl C})$. The methyl group was allowed to rotate, but not tip, to best fit the electron density.

The highest difference peak is 0.73 Å from H1.

Figures

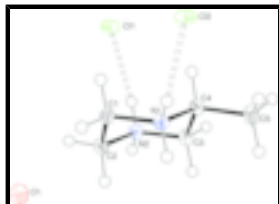


Fig. 1. View of the molecular structure of (I) showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Hydrogen bonds are indicated by double-dashed lines.

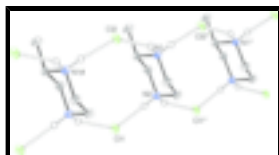
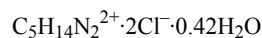


Fig. 2. Fragment of a [100] hydrogen bonded chain of cations and anions in the crystal of (I). The carbon-bound H atoms are omitted for clarity. Symmetry code suffixes: (*) $x - 1, y, z$; (#) $x + 1, y, z$.

(S)-2-Methylpiperazinediium dichloride 0.42-hydrate

Crystal data



$M_r = 180.65$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 5.7548$ (2) Å

$b = 11.6176$ (4) Å

$c = 6.9248$ (2) Å

$\beta = 105.7599$ (16)°

$V = 445.57$ (3) Å³

$Z = 2$

$F_{000} = 192$

$D_x = 1.346$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2691 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 0.66$ mm⁻¹

$T = 120$ (2) K

Plate, colourless

$0.10 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 120$ (2) K

ω and ϕ scans

Absorption correction: none

5193 measured reflections

1999 independent reflections

1952 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -7 \rightarrow 7$

$k = -14 \rightarrow 15$

$l = -8 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.1729P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\max} < 0.001$
1999 reflections	$\Delta\rho_{\max} = 0.93 \text{ e } \text{\AA}^{-3}$
93 parameters	$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 929 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.04 (9)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.7382 (4)	-0.00043 (19)	0.4593 (3)	0.0150 (4)	
H1	0.6241	-0.0130	0.5278	0.018*	
H2	0.8880	-0.0125	0.5468	0.018*	
N2	0.4376 (4)	0.06003 (19)	0.0680 (3)	0.0171 (5)	
H3	0.5504	0.0729	-0.0016	0.020*	
H4	0.2869	0.0723	-0.0181	0.020*	
C1	0.7209 (4)	0.1215 (3)	0.3871 (4)	0.0181 (5)	
H5	0.8509	0.1372	0.3220	0.022*	
H6	0.7418	0.1745	0.5025	0.022*	
C2	0.4781 (5)	0.1420 (2)	0.2391 (4)	0.0190 (5)	
H7	0.3490	0.1324	0.3076	0.023*	
H8	0.4703	0.2219	0.1881	0.023*	
C3	0.4563 (5)	-0.0617 (2)	0.1406 (4)	0.0176 (5)	
H9	0.4345	-0.1146	0.0249	0.021*	
H10	0.3263	-0.0774	0.2058	0.021*	
C4	0.7000 (5)	-0.0841 (2)	0.2891 (4)	0.0164 (5)	
H11	0.8297	-0.0729	0.2197	0.020*	
C5	0.7142 (6)	-0.2064 (3)	0.3697 (5)	0.0228 (6)	
H12	0.8577	-0.2143	0.4839	0.034*	
H13	0.7248	-0.2605	0.2639	0.034*	
H14	0.5694	-0.2232	0.4133	0.034*	
Cl1	0.88946 (10)	0.12630 (6)	-0.08251 (9)	0.02299 (18)	

supplementary materials

C12	1.28588 (11)	-0.04977 (5)	0.61677 (10)	0.02002 (17)	
O1	0.1426 (11)	0.3549 (5)	0.1162 (10)	0.039 (2)	0.420 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0128 (10)	0.0182 (10)	0.0123 (11)	0.0011 (7)	0.0003 (8)	0.0017 (8)
N2	0.0175 (10)	0.0190 (11)	0.0128 (11)	0.0002 (8)	0.0010 (9)	0.0012 (8)
C1	0.0173 (12)	0.0148 (12)	0.0210 (13)	-0.0016 (11)	0.0033 (10)	-0.0015 (13)
C2	0.0188 (11)	0.0174 (12)	0.0204 (12)	0.0027 (9)	0.0048 (9)	0.0000 (10)
C3	0.0206 (12)	0.0166 (12)	0.0139 (12)	0.0009 (10)	0.0017 (10)	-0.0010 (10)
C4	0.0180 (11)	0.0165 (11)	0.0146 (12)	0.0031 (9)	0.0042 (9)	-0.0003 (9)
C5	0.0228 (15)	0.0182 (14)	0.0241 (17)	0.0033 (10)	0.0008 (13)	0.0022 (11)
H1	0.0175 (3)	0.0339 (4)	0.0176 (3)	0.0027 (3)	0.0048 (2)	0.0015 (3)
H2	0.0129 (3)	0.0300 (3)	0.0166 (3)	-0.0009 (2)	0.0031 (2)	-0.0016 (3)
O1	0.042 (4)	0.027 (4)	0.050 (4)	0.004 (2)	0.017 (3)	0.003 (3)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.497 (4)	C2—H7	0.9900
N1—C4	1.497 (3)	C2—H8	0.9900
N1—H1	0.9200	C3—C4	1.519 (4)
N1—H2	0.9200	C3—H9	0.9900
N2—C2	1.488 (3)	C3—H10	0.9900
N2—C3	1.495 (3)	C4—C5	1.521 (4)
N2—H3	0.9200	C4—H11	1.0000
N2—H4	0.9200	C5—H12	0.9800
C1—C2	1.510 (3)	C5—H13	0.9800
C1—H5	0.9900	C5—H14	0.9800
C1—H6	0.9900		
C1—N1—C4	111.7 (2)	N2—C2—H8	109.5
C1—N1—H1	109.3	C1—C2—H8	109.5
C4—N1—H1	109.3	H7—C2—H8	108.1
C1—N1—H2	109.3	N2—C3—C4	111.0 (2)
C4—N1—H2	109.3	N2—C3—H9	109.4
H1—N1—H2	107.9	C4—C3—H9	109.4
C2—N2—C3	110.9 (2)	N2—C3—H10	109.4
C2—N2—H3	109.5	C4—C3—H10	109.4
C3—N2—H3	109.5	H9—C3—H10	108.0
C2—N2—H4	109.5	N1—C4—C3	109.5 (2)
C3—N2—H4	109.5	N1—C4—C5	109.6 (2)
H3—N2—H4	108.1	C3—C4—C5	110.8 (2)
N1—C1—C2	110.0 (2)	N1—C4—H11	109.0
N1—C1—H5	109.7	C3—C4—H11	109.0
C2—C1—H5	109.7	C5—C4—H11	109.0
N1—C1—H6	109.7	C4—C5—H12	109.5
C2—C1—H6	109.7	C4—C5—H13	109.5
H5—C1—H6	108.2	H12—C5—H13	109.5

N2—C2—C1	110.8 (2)	C4—C5—H14	109.5
N2—C2—H7	109.5	H12—C5—H14	109.5
C1—C2—H7	109.5	H13—C5—H14	109.5

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H2 \cdots C12	0.92	2.25	3.096 (2)	153
N1—H1 \cdots C12 ⁱ	0.92	2.24	3.136 (2)	166
N2—H3 \cdots C11	0.92	2.26	3.149 (2)	163
N2—H4 \cdots C11 ⁱ	0.92	2.30	3.137 (2)	152

Symmetry codes: (i) $x-1, y, z$.

Fig. 1

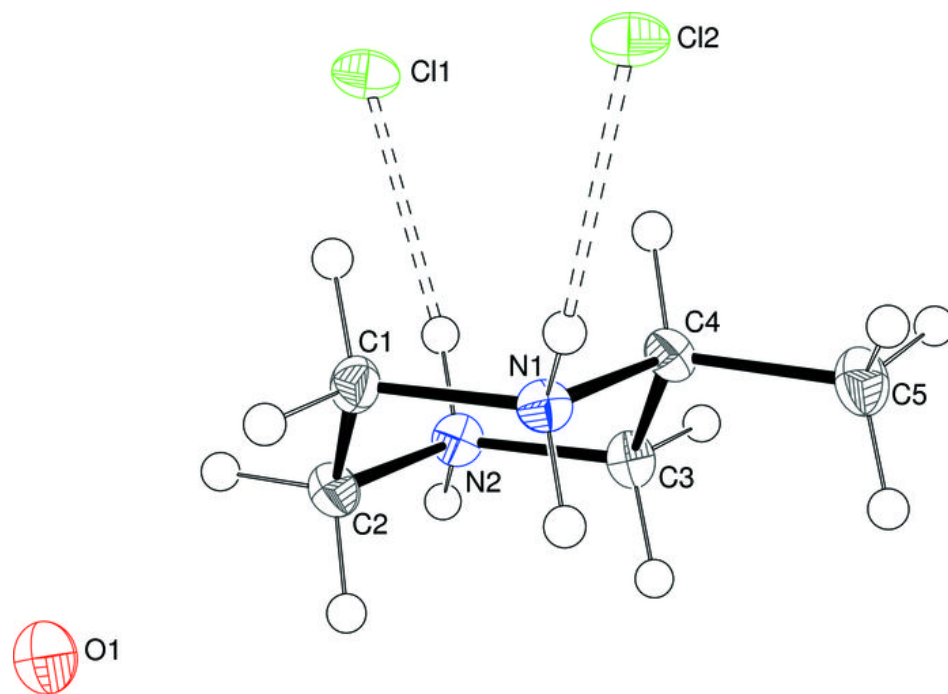


Fig. 2

