organic compounds

Octane-1,8-diammonium dichloride monohydrate

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The crystal structure of the title compound, $C_8H_{22}N_2{}^{2+} \cdot 2Cl^- \cdot H_2O$, exhibits layered stacking in which the organic cations are separated by inorganic layers containing the chloride anions and the water molecules. The diammonium octane chain straddles a centre of inversion and the single water of crystallization sits on a twofold rotation axis. The diammonium octane chains pack in parallel layers with every second hydrocarbon layer alternating in a staggered configuration with respect to the previous layer. The three-dimensional hydrogen-bonding network links the organic and inorganic layers together in a highly intricate and complex manner. The torsion angles of the hydrocarbon chain deviate from 180° as a result of hydrogen-bonding interactions to the water molecule and the surrounding chloride anions.

Related literature

For related structural studies of octane-1,8-diammonium salts see: Brisson & Brisse (1984); Baur & Tillmanns (1986). For related literature see: Allen (2002).
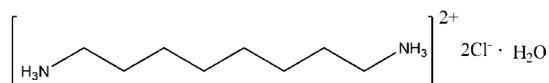
Experimental

Crystal data

$C_8H_{22}N_2{}^{2+} \cdot 2Cl^- \cdot H_2O$
$M_r = 235.19$
Monoclinic, $C2/c$
$a = 24.719\,(3)$ Å
$b = 5.0827\,(6)$ Å
$c = 10.8593\,(14)$ Å
$\beta = 103.590\,(3)°$

$V = 1326.2\,(3)$ Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.46$ mm⁻¹
$T = 293\,(2)$ K
$0.40 \times 0.22 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.837$, $T_{max} = 0.947$

3965 measured reflections
1647 independent reflections
1209 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.04$
1647 reflections
65 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.18$ e Å⁻³
$\Delta\rho_{min} = -0.12$ e Å⁻³

Table 1
Selected torsion angles (°).

N1—C1—C2—C3	−164.65 (14)	C2—C3—C4—C4^i	−173.09 (17)
C1—C2—C3—C4	−179.66 (14)		

Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$C\cdots$Cl1^{ii}	0.89	2.29	3.1777 (15)	175
N1—H1$D\cdots$Cl1^{iii}	0.89	2.40	3.2215 (14)	153
N1—H1$E\cdots$O1	0.89	2.19	2.9660 (17)	145
O1—H1$\cdots$Cl1^{iv}	0.87 (2)	2.34 (2)	3.2036 (13)	173 (2)

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2003) and *publCIF* (Westrip, 2007).

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supplementary materials

Octane-1,8-diammonium dichloride monohydrate

C. van Blerk and **G. J. Kruger**

Comment

In an ongoing study of the structural characteristics of layered diammonium salts, we are determining the crystal structures of long-chained diammonium salts. Colourless crystals of octane-1,8-diammonium dichloride hydrate formed when we attempted to synthesize the unhydrated chloride salt. A search of the Cambridge Structural Database (Version 5.28, May 2007 release; Allen, 2002) revealed that only the octane-1,8-diammonium dibromide salt has previously been studied (Brisson & Brisse, 1984; Baur & Tillmanns, 1986) and the crystal structure of the title compound (I) had not previously been determined.

The diammonium octane chain straddles a centre of inversion and the single water of crystallization sits on a twofold rotation axis. Therefore the asymmetric unit contains one chloride anion, one half of the diammonium cation and one half of the water molecule (Figure 1).

Figure 2 illustrates the layered packing arrangement of the title compound (I). Single layers of the extended cations pack end on between two layers of chloride ions. Sandwiched in-between the chloride ions is a single layer of water molecules that hydrogen bonds to the chloride anions and the diammonium cations. The hydrocarbon chains pack in parallel layers with every second hydrocarbon chain layer alternating in a staggered, alternating configuration with respect to the previous layer. Since the packing configuration is a complex, staggered, alternating pattern, the hydrogen bonding network that is formed is an intricately complex bridge between the layers through the water molecules and chloride anions.

Figure 3 shows the hydrogen bonding contacts for the title compound (I). The hydrogen atoms around the ammonium group are involved in hydrogen bonds with two chloride anions and the oxygen of the water molecule. The hydrogen atoms of the water molecule hydrogen bond to a further two chloride anions resulting in four tetrahedrally oriented hydrogen bonds around the water molecule. The hydrogen bond distances and angles for (I) can be found in Table 1. Figure 3 also shows that the hydrocarbon chain is slightly twisted out of its fully extended configuration by up to 15° (where the torsion angles for a standard configuration hydrocarbon chain should be 180°). When examining the torsion angles (Table 2) along the hydrocarbon chain of (I) it is evident that the hydrogen bonding interactions to H1 attached to the water and the chloride anion affect the chain configuration.

Experimental

Compound (I) was prepared by adding 1,8-diamino-octane (0.50 g, 3.47 mmol) to 32% hydrochloric acid (2 ml, 69.1 mmol) in a sample vial. The mixture was then refluxed at 363 K for 2 h. The solution was cooled at 2 K h^{-1} to room temperature. Colourless crystals of octane-1,8-diammonium dichloride hydrate were collected and a suitable single-crystal was taken for the X-ray diffraction study.

supplementary materials

Refinement

H atoms were geometrically positioned and refined in the riding-model approximation, with C—H = 0.97 Å, N—H = 0.89 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. For (I), the highest peak in the final difference map is 0.87 Å from Cl1 and the deepest hole is 1.03 Å from H1.
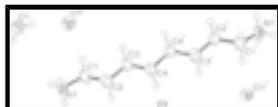
Figures

Fig. 1. Molecular structure of (I), with the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. Atoms labelled with ' are at the symmetry position $(1/2 − x, 1/2 − y, −z)$.

Fig. 2. Packing arrangement of (I) viewed down the b axis (on the left) and the c axis (on the right). Hydrogen bonds are indicated by dashed lines.
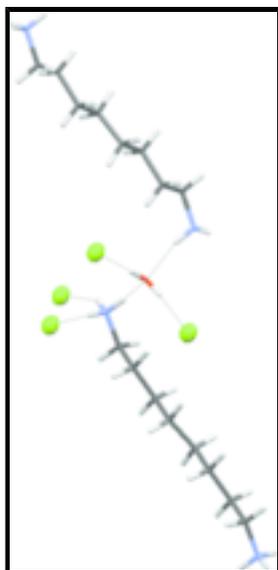

Fig. 3. Close-up view of (I) showing the hydrogen bonding contacts. Hydrogen bonds are indicated by dashed lines.

Octane-1,8-diammonium dichloride monohydrate

Crystal data

$C_8H_{22}N_2{}^{2+}·2Cl^-·H_2O$	$F_{000} = 512$
$M_r = 235.19$	$D_x = 1.178$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1647 reflections
$a = 24.719$ (3) Å	$\theta = 1.7–28.3°$
$b = 5.0827$ (6) Å	$\mu = 0.46$ mm^{-1}
$c = 10.8593$ (14) Å	$T = 293$ (2) K
$\beta = 103.590$ (3)°	Block, colourless

$V = 1326.2$ (3) Å^3

$Z = 4$

$0.40 \times 0.22 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1647 independent reflections
Radiation source: fine-focus sealed tube	1209 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
$T = 293(2)$ K	$\theta_{max} = 28.3°$
φ and ω scans	$\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -32 \rightarrow 29$
$T_{min} = 0.837$, $T_{max} = 0.947$	$k = -6 \rightarrow 5$
3965 measured reflections	$l = -14 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	All H-atom parameters refined
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.1994P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
1647 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
65 parameters	$\Delta\rho_{min} = -0.12$ 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 > 2sigma(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	0.62661 (7)	0.6672 (3)	0.20031 (15)	0.0486 (4)
H1A	0.6280	0.8093	0.2606	0.058*
H1B	0.6498	0.7160	0.1433	0.058*

C2	0.64942 (7)	0.4197 (3)	0.27064 (15)	0.0493 (4)
H2A	0.6574	0.2924	0.2108	0.059*
H2B	0.6214	0.3445	0.3094	0.059*
C3	0.70194 (6)	0.4707 (3)	0.37245 (14)	0.0497 (4)
H3A	0.6938	0.5977	0.4322	0.060*
H3B	0.7298	0.5474	0.3335	0.060*
C4	0.72584 (6)	0.2236 (3)	0.44406 (14)	0.0461 (4)
H4A	0.6966	0.1353	0.4740	0.055*
H4B	0.7382	0.1054	0.3860	0.055*
N1	0.56868 (5)	0.6322 (3)	0.12689 (13)	0.0519 (3)
H1C	0.5672	0.5002	0.0724	0.078*
H1D	0.5570	0.7795	0.0846	0.078*
H1E	0.5470	0.5960	0.1794	0.078*
Cl1	0.566023 (17)	0.86236 (8)	0.44656 (4)	0.05515 (17)
O1	0.5000	0.2880 (4)	0.2500	0.0574 (4)
H1	0.4814 (10)	0.184 (5)	0.192 (2)	0.098 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0510 (8)	0.0405 (8)	0.0498 (8)	−0.0002 (7)	0.0030 (6)	0.0041 (7)
C2	0.0507 (9)	0.0385 (8)	0.0519 (9)	0.0024 (6)	−0.0013 (7)	0.0033 (7)
C3	0.0501 (8)	0.0419 (8)	0.0517 (8)	0.0004 (7)	0.0010 (7)	0.0043 (7)
C4	0.0471 (8)	0.0414 (8)	0.0458 (8)	0.0024 (7)	0.0032 (6)	0.0019 (7)
N1	0.0520 (7)	0.0473 (8)	0.0524 (8)	0.0094 (6)	0.0042 (6)	0.0102 (6)
Cl1	0.0640 (3)	0.0467 (3)	0.0507 (2)	0.00232 (18)	0.00525 (17)	−0.00322 (17)
O1	0.0654 (11)	0.0490 (10)	0.0520 (10)	0.000	0.0021 (8)	0.000

Geometric parameters (Å, °)

C1—N1	1.477 (2)	C3—H3B	0.9700
C1—C2	1.510 (2)	C4—C4^i	1.514 (3)
C1—H1A	0.9700	C4—H4A	0.9700
C1—H1B	0.9700	C4—H4B	0.9700
C2—C3	1.517 (2)	N1—H1C	0.8900
C2—H2A	0.9700	N1—H1D	0.8900
C2—H2B	0.9700	N1—H1E	0.8900
C3—C4	1.522 (2)	O1—H1	0.87 (2)
C3—H3A	0.9700		
N1—C1—C2	111.86 (12)	C2—C3—H3B	108.9
N1—C1—H1A	109.2	C4—C3—H3B	108.9
C2—C1—H1A	109.2	H3A—C3—H3B	107.7
N1—C1—H1B	109.2	C4^i—C4—C3	113.70 (16)
C2—C1—H1B	109.2	C4^i—C4—H4A	108.8
H1A—C1—H1B	107.9	C3—C4—H4A	108.8
C1—C2—C3	112.36 (13)	C4^i—C4—H4B	108.8
C1—C2—H2A	109.1	C3—C4—H4B	108.8
C3—C2—H2A	109.1	H4A—C4—H4B	107.7

C1—C2—H2B	109.1	C1—N1—H1C	109.5
C3—C2—H2B	109.1	C1—N1—H1D	109.5
H2A—C2—H2B	107.9	H1C—N1—H1D	109.5
C2—C3—C4	113.25 (13)	C1—N1—H1E	109.5
C2—C3—H3A	108.9	H1C—N1—H1E	109.5
C4—C3—H3A	108.9	H1D—N1—H1E	109.5
N1—C1—C2—C3	−164.65 (14)	C2—C3—C4—C4^i	−173.09 (17)
C1—C2—C3—C4	−179.66 (14)		

Symmetry codes: (i) −x+3/2, −y+1/2, −z+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···Cl1^{ii}	0.89	2.29	3.1777 (15)	175
N1—H1D···Cl1^{iii}	0.89	2.40	3.2215 (14)	153
N1—H1E···O1	0.89	2.19	2.9660 (17)	145
O1—H1···Cl1^{iv}	0.87 (2)	2.34 (2)	3.2036 (13)	173 (2)

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

Fig. 1

(I)

Fig. 2

Fig. 3