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A low-temperature determination of triethylene-diaminium dichloride dihydrate

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The structure determination at 150 K of triethylenediaminium dichloride dihydrate (also know as 1,4-diazaoniabicyclo[2.2.2]-octane dichloride dihydrate), $C_6H_{14}N_2{}^{2+} \cdot 2Cl^- \cdot 2H_2O$, obtained as part of an experimental polymorph screen on guanine, is reported here. The packing consists of a hydrogen-bonded chain structure, with one of the water molecules of crystallization involved in weak $O-H \cdots Cl$ contacts.

Comment

Triethylenediamine, also known as 1,4-diazabicyclo[2.2.2]-octane, is a strong base allowing protons to be removed from other compounds to give anionic intermediates. Triethylenediamine has two reported anhydrous polymorphs, a room-temperature phase (Nimmo & Lucas, 1976a) and a high-temperature phase (Nimmo & Lucas, 1976b). This high-temperature structure assumes a 'plastic' phase, and is of interest as triethylenediamine is a one of a select group of globular molecules which undergo thermal transitions to plastic crystals because of the high degree of molecular mobility which can be achieved in the solid state (Weiss et al., 1964). There are also a number of co-crystals of triethylenediamine, including with hydroquinone (Mak et al., 1984), sulfate hemihydrate (Jayaraman et al., 2002), and bis-(hydrogen oxalate) (Vaidhyanathan et al., 2001). In addition, there are also triethylenediamine salts, including the dihydrochloride (Kennedy et al., 1987) and hydrobromide (Katrusiak et al., 1999). In this paper, we report the dihydrochloride dihydrate salt, (I), of triethylenediamine.

(I)
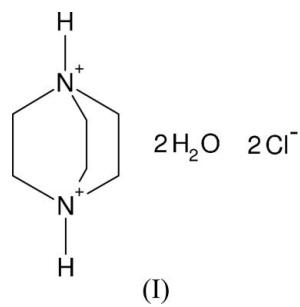
In (I), atoms N1 and N2 are both protonated, with the molecule in a slightly twisted conformation, different from the symmetric cage-like structure present in the room-temperature anhydrous crystal structure of unprotonated triethylenediamine (Nimmo & Lucas, 1976a). The bond lengths and angles are within expected values (Allen et al., 1987), with the C–N bond lengths in the range 1.4942 (15)–1.5009 (15) Å, and the C—C bond lengths in the range 1.5227 (17)–1.5368 (16) Å.
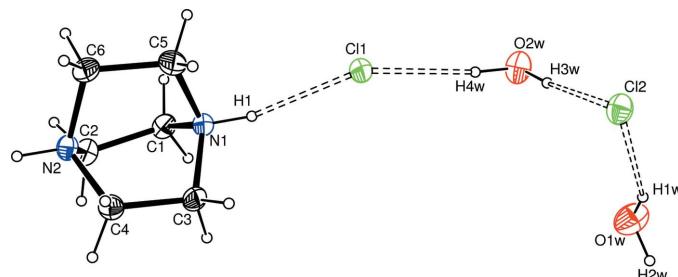
Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The packing consists of a hydrogen-bonded chain structure (Fig. 2), with atom N2 hydrogen bonded to O2*W*, through an N—H⋯O hydrogen bond (Table 1). Water atom O2*W* acts as a hydrogen-bond donor to both Cl1 and Cl2, through O—H⋯Cl hydrogen bonds (Table 1). The ion Cl1 is also hydrogen bonded through an N—H⋯Cl interaction to the N1 amine group, forming the chain motif. The O1*W* water of crystallization forms weak hydrogen bonds to Cl2, as shown in Table 1.

Experimental

As part of an experimental polymorph screen on guanine, (I) was obtained from a saturated solution of triethylenediamine in dilute hydrochloric acid, in which approximately 0.03 g of guanine was added in an attempt to crystallize this purine base. The solution was stirred, filtered, then evaporated at room temperature (10 ml solution, in 75 × 25 mm vessels). Colourless block-shaped crystals of (I) were formed over a number of weeks. It should also be noted that large block-shaped crystals of triethylenediamine dihydrochloride were also obtained (Kennedy *et al.*, 1987).

Crystal data

$C_6H_{14}N_2^{2+}$·2Cl$^-$·2H$_2$O
$M_r = 221.12$
Orthorhombic, $P2_12_12_1$
$a = 7.1407 (8)$ Å
$b = 8.7188 (10)$ Å
$c = 16.8945 (19)$ Å
$V = 1051.8 (2)$ Å^3
$Z = 4$
$D_x = 1.396$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7311 reflections
$\theta = 2.3–28.2°$
$\mu = 0.59$ mm^{-1}
$T = 150 (2)$ K
Block, colourless
$0.98 \times 0.24 \times 0.21$ mm

Data collection

Bruker SMART APEX diffractometer
Narrow-frame ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.598$, $T_{max} = 0.887$
9177 measured reflections

2508 independent reflections
2473 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 28.2°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.053$
$S = 1.06$
2508 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 0.1405P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.01 (4)
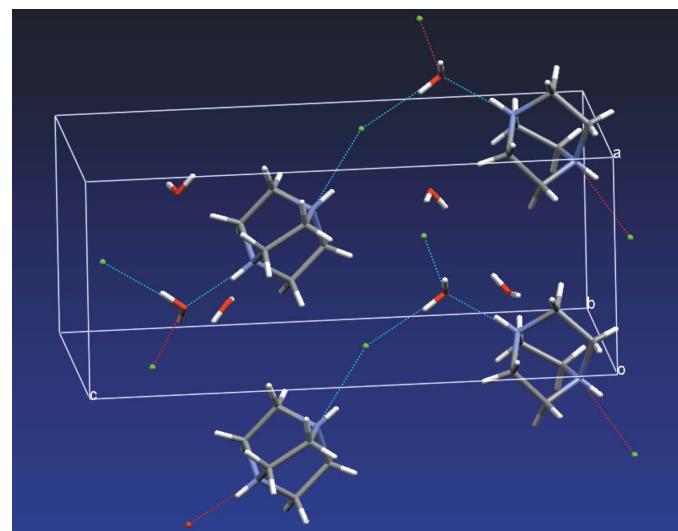
Figure 2
The packing in (I), showing the hydrogen-bonded chain structure. The hydrogen bonds with $D\cdots A > 3.2$ Å have been omitted for clarity.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1W⋯Cl2	0.84 (2)	2.50 (2)	3.2848 (12)	156 (2)
O1W—H2W⋯Cl2^i	0.83 (2)	2.54 (2)	3.3537 (11)	169 (2)
O2W—H3W⋯Cl2	0.83 (1)	2.30 (1)	3.1109 (10)	167 (2)
O2W—H4W⋯Cl1	0.84 (1)	2.22 (1)	3.0585 (10)	173 (2)
N1—H1⋯Cl1	0.91	2.16	3.0110 (11)	156
N2—H2⋯O2W^{ii}	0.91	1.77	2.6634 (13)	168

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

The triethylenediaminium H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, whilst the water H atoms were refined, with O—H and H⋯H distance restraints of 0.84 Å and 1.33 (2) Å, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); 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* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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1,4-diazaoniabicyclo[2.2.2]octane dichloride dihydrate

Crystal data

$C_6H_{14}N_2^{2+}\cdot2Cl^-\cdot2H_2O$	$F(000) = 472$
$M_r = 221.12$	$D_x = 1.396$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 7311 reflections
$a = 7.1407$ (8) Å	$\theta = 2.3$–28.2°
$b = 8.7188$ (10) Å	$\mu = 0.59$ mm^{-1}
$c = 16.8945$ (19) Å	$T = 150$ K
$V = 1051.8$ (2) Å^3	Block, colourless
$Z = 4$	$0.98 \times 0.24 \times 0.21$ mm

Data collection

Bruker SMART APEX diffractometer	9177 measured reflections
Radiation source: fine-focus sealed tube	2508 independent reflections
Graphite monochromator	2473 reflections with $I > 2\sigma(I)$
ω rotation with narrow frames scans	$R_{int} = 0.027$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 28.2°$, $\theta_{min} = 2.4°$
	$h = -9\rightarrow9$
	$k = -11\rightarrow11$
$T_{min} = 0.598$, $T_{max} = 0.887$	$l = -22\rightarrow22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.021$	
$wR(F^2) = 0.053$	
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 0.1405P]$ where $P = (F_o^2 + 2F_c^2)/3$
2508 reflections	
121 parameters	$(\Delta/\sigma)_{max} = 0.001$
6 restraints	$\Delta\rho_{max} = 0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.16$ e Å^{-3}
	Absolute structure: Flack 1983)
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.01 (4)

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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Cl1	0.51446 (4)	−0.04577 (3)	0.554391 (16)	0.02113 (7)
Cl2	1.07647 (4)	0.17252 (4)	0.656610 (17)	0.02424 (8)
O1W	0.83585 (16)	0.30071 (12)	0.80854 (6)	0.0352 (2)
H1W	0.924 (3)	0.283 (2)	0.7773 (11)	0.053*
H2W	0.845 (3)	0.3922 (18)	0.8215 (12)	0.053*
O2W	0.74444 (14)	−0.03678 (11)	0.70705 (5)	0.0254 (2)
H3W	0.829 (2)	0.0263 (19)	0.7005 (10)	0.038*
H4W	0.674 (2)	−0.034 (2)	0.6671 (9)	0.038*
N1	0.16941 (14)	0.00540 (11)	0.45541 (6)	0.0185 (2)
H1	0.2499	−0.0034	0.4969	0.022*
N2	−0.05023 (13)	0.02830 (11)	0.34157 (5)	0.01770 (19)
H2	−0.1300	0.0367	0.2998	0.021*
C1	−0.01906 (17)	−0.05314 (13)	0.47979 (6)	0.0202 (2)
H1A	−0.0572	−0.0054	0.5291	0.024*
H1B	−0.0141	−0.1632	0.4878	0.024*
C2	−0.15987 (18)	−0.01430 (14)	0.41399 (7)	0.0198 (2)
H2A	−0.2391	−0.1022	0.4031	0.024*
H2B	−0.2389	0.0706	0.4302	0.024*
C3	0.15394 (18)	0.17045 (14)	0.43252 (7)	0.0206 (2)
H3A	0.2777	0.2146	0.4261	0.025*
H3B	0.0885	0.2273	0.4734	0.025*
C4	0.04533 (17)	0.17919 (13)	0.35432 (7)	0.0203 (2)
H4A	−0.0466	0.2610	0.3567	0.024*
H4B	0.1305	0.2003	0.3109	0.024*
C5	0.24379 (18)	−0.08551 (15)	0.38683 (8)	0.0253 (3)
H5A	0.2782	−0.1878	0.4041	0.030*
H5B	0.3542	−0.0361	0.3652	0.030*
C6	0.09099 (18)	−0.09438 (15)	0.32414 (7)	0.0224 (2)
H6A	0.1444	−0.0789	0.2719	0.027*
H6B	0.0317	−0.1944	0.3254	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02161 (13)	0.01921 (12)	0.02256 (13)	0.00056 (11)	−0.00470 (10)	−0.00008 (10)
Cl2	0.02123 (13)	0.02818 (14)	0.02332 (13)	−0.00414 (11)	0.00041 (11)	−0.00136 (11)
O1W	0.0358 (5)	0.0323 (6)	0.0376 (5)	−0.0077 (5)	0.0103 (5)	−0.0058 (4)
O2W	0.0263 (5)	0.0338 (5)	0.0159 (4)	−0.0065 (4)	0.0015 (3)	0.0022 (4)
N1	0.0194 (5)	0.0169 (4)	0.0191 (5)	0.0006 (4)	−0.0043 (4)	−0.0007 (4)
N2	0.0178 (4)	0.0209 (4)	0.0144 (4)	−0.0013 (4)	−0.0006 (3)	−0.0001 (3)

C1	0.0250 (6)	0.0190 (5)	0.0166 (5)	−0.0037 (5)	0.0006 (4)	0.0008 (4)
C2	0.0177 (5)	0.0242 (6)	0.0175 (5)	−0.0042 (5)	0.0031 (4)	−0.0004 (4)
C3	0.0227 (5)	0.0153 (5)	0.0237 (5)	−0.0044 (5)	−0.0036 (5)	0.0006 (4)
C4	0.0218 (5)	0.0178 (5)	0.0212 (5)	−0.0018 (4)	−0.0008 (4)	0.0032 (4)
C5	0.0215 (6)	0.0267 (6)	0.0277 (6)	0.0073 (5)	−0.0001 (5)	−0.0053 (5)
C6	0.0248 (6)	0.0230 (6)	0.0195 (5)	0.0027 (5)	0.0021 (5)	−0.0056 (4)

Geometric parameters (Å, º)

O1W—H1W	0.836 (15)	C1—H1B	0.9700
O1W—H2W	0.829 (15)	C2—H2A	0.9700
O2W—H3W	0.827 (13)	C2—H2B	0.9700
O2W—H4W	0.841 (13)	C3—C4	1.5339 (16)
N1—C3	1.4942 (15)	C3—H3A	0.9700
N1—C1	1.4971 (15)	C3—H3B	0.9700
N1—C5	1.5009 (15)	C4—H4A	0.9700
N1—H1	0.9100	C4—H4B	0.9700
N2—C4	1.4976 (15)	C5—C6	1.5227 (17)
N2—C6	1.4992 (16)	C5—H5A	0.9700
N2—C2	1.4993 (14)	C5—H5B	0.9700
N2—H2	0.9100	C6—H6A	0.9700
C1—C2	1.5368 (16)	C6—H6B	0.9700
C1—H1A	0.9700		
H1W—O1W—H2W	106.7 (17)	H2A—C2—H2B	108.5
H3W—O2W—H4W	108.0 (15)	N1—C3—C4	107.95 (9)
C3—N1—C1	109.46 (9)	N1—C3—H3A	110.1
C3—N1—C5	109.58 (9)	C4—C3—H3A	110.1
C1—N1—C5	110.52 (9)	N1—C3—H3B	110.1
C3—N1—H1	109.1	C4—C3—H3B	110.1
C1—N1—H1	109.1	H3A—C3—H3B	108.4
C5—N1—H1	109.1	N2—C4—C3	108.10 (9)
C4—N2—C6	110.40 (9)	N2—C4—H4A	110.1
C4—N2—C2	109.77 (9)	C3—C4—H4A	110.1
C6—N2—C2	109.56 (9)	N2—C4—H4B	110.1
C4—N2—H2	109.0	C3—C4—H4B	110.1
C6—N2—H2	109.0	H4A—C4—H4B	108.4
C2—N2—H2	109.0	N1—C5—C6	108.07 (9)
N1—C1—C2	108.30 (9)	N1—C5—H5A	110.1
N1—C1—H1A	110.0	C6—C5—H5A	110.1
C2—C1—H1A	110.0	N1—C5—H5B	110.1
N1—C1—H1B	110.0	C6—C5—H5B	110.1
C2—C1—H1B	110.0	H5A—C5—H5B	108.4
H1A—C1—H1B	108.4	N2—C6—C5	108.01 (9)
N2—C2—C1	107.65 (10)	N2—C6—H6A	110.1
N2—C2—H2A	110.2	C5—C6—H6A	110.1
C1—C2—H2A	110.2	N2—C6—H6B	110.1
N2—C2—H2B	110.2	C5—C6—H6B	110.1

C1—C2—H2B	110.2	H6A—C6—H6B	108.4

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*W*⋯Cl2	0.84 (2)	2.50 (2)	3.2848 (12)	156 (2)
O1*W*—H2*W*⋯Cl2ⁱ	0.83 (2)	2.54 (2)	3.3537 (11)	169 (2)
O2*W*—H3*W*⋯Cl2	0.83 (1)	2.30 (1)	3.1109 (10)	167 (2)
O2*W*—H4*W*⋯Cl1	0.84 (1)	2.22 (1)	3.0585 (10)	173 (2)
N1—H1⋯Cl1	0.91	2.16	3.0110 (11)	156
N2—H2⋯O2*W*ⁱⁱ	0.91	1.77	2.6634 (13)	168

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