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A low-temperature determination of triethylenediaminium dichloride dihydrate

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The structure determination at 150 K of triethylenediaminium dichloride dihydrate (also know as 1,4-diazoniabicyclo[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···Cl contacts.

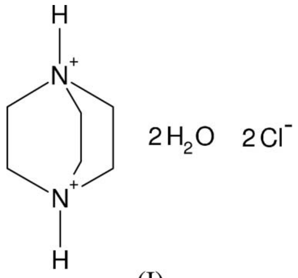
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.0017 Å
R factor = 0.021
wR factor = 0.052
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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, 1976*a*) and a high-temperature phase (Nimmo & Lucas, 1976*b*). 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, 1976*a*). 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.

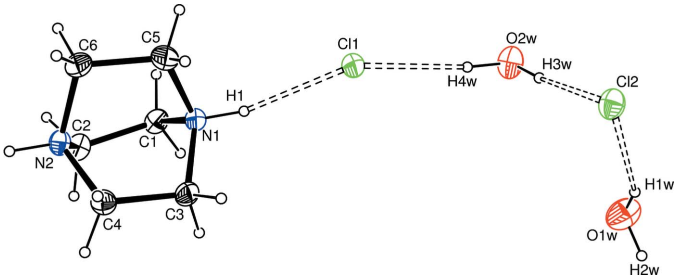


Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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

$C_6H_{14}N_2^{2+}\cdot 2Cl^-\cdot 2H_2O$
$M_r = 221.12$
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 × 0.24 × 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 28.2°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -22 \rightarrow 22$

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)

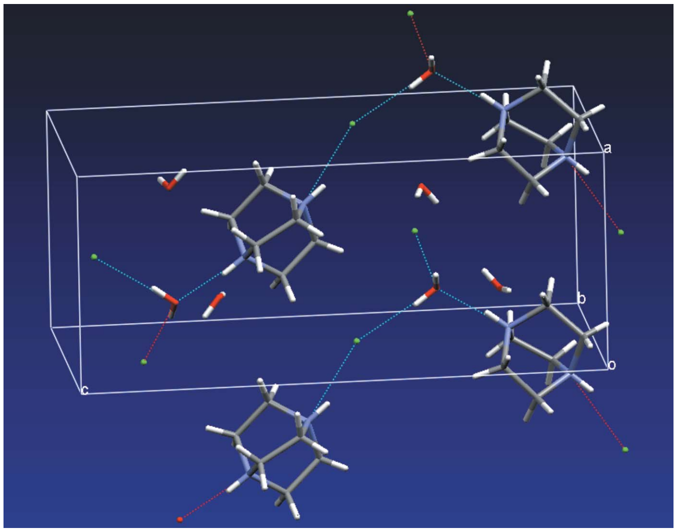


Figure 2
The packing in (I), showing the hydrogen-bonded chain structure. The hydrogen bonds with *D*···A > 3.2 Å have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···Cl2	0.84 (2)	2.50 (2)	3.2848 (12)	156 (2)
O1*W*—H2*W*···Cl2$^{\rm i}$	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*$^{\rm ii}$	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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