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1,4-Bis(2-ammonioethyl)piperazin-1,4-ium tetraperchlorate tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.146
Data-to-parameter ratio = 14.8

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

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The tetracation of bis(2-ammonioethyl)piperazin-1,4-ium tetraperchlorate tetrahydrate, $C_8H_{24}N_4^{4+}\cdot 4ClO_4^-\cdot 4H_2O$, lies over a center of symmetry and the piperazinyl ring adopts a chair conformation. Four ammonium N atoms, perchlorate anions and lattice water molecules are linked by hydrogen bonds into an infinite three-dimensional framework.

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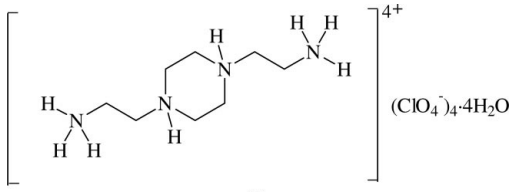
Comment

The red title tetraammonium perchorate, (I), was a suprise product from the reaction between triethylenetetramine and perchloric acid; the reaction is probably catalysed by ferrous ions. A search of the Cambridge Structural Database (Allen *et al.*, 1983) for the neutral bis(2-ethylamino)-1,4-piperazine residue found only one example where this ligand forms a complex with silver nitrate in which the amino group and one of the tertiary N atoms of the piperazinyl ring chelate to the metal atom (Zhang *et al.*, 2001; Cai & Ng, 2002).



(I)

The piperazinium portion of the cation adopts a chair conformation, and both ammonioethyl groups occupy equatorial positions (Fig. 1). A pair of ammonio and piperazinium groups form two hydrogen bonds to a water molecule [$N_{ammonio}\cdots O$ = 2.695 (2) Å and $N_{piperazinium}\cdots O$ = 2.905 (3) Å]; this water molecule then uses one of its H atoms to interact with a perchlorate anion and the other with a second lattice water molecule. The second water molecule interacts with two other perchlorate O atoms to furnish a three-dimensional network structure.

The cationic portion of the structure that has been optimized at the *PM*3 level (Table 2) also adopts a chair conformation, but the calculated bond distances are somewhat longer than the experimental distances. On the other hand, the experimental distances are closer to the values calculated for the neutral ligand itself.

Experimental

Iron(II) chloride (0.13 g, 1 mmol) was dissolved in water (10 ml) and the solution was mixed with an aqueous solution (10 ml) of triethylenetetramine (0.15 g, 1 mmol) to give a green precipitate. Perchloric acid (0.40 g, 4 mmol) was then added to dissolve the precipitate, yielding a red solution. Red crystals separated from the solution after several weeks.

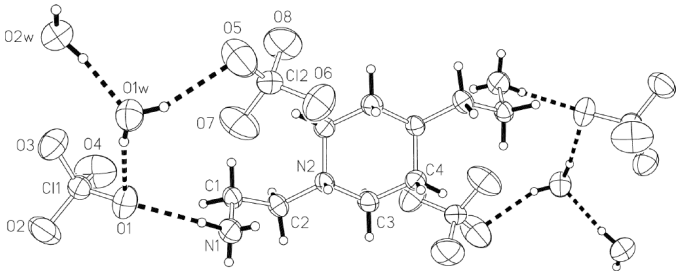


Figure 1
*ORTEP*II (Johnson, 1976) plot of a fragment of the structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Crystal data

$C_8H_{24}N_4^{4+}\cdot 4ClO_4^-\cdot 4H_2O$	D_x = 1.742 Mg m^{-3}
M_r = 646.18	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3500 reflections
a = 7.862 (1) Å	θ = 2.8–28.0°
b = 19.644 (3) Å	μ = 0.58 mm^{-1}
c = 8.204 (1) Å	T = 298 (2) K
β = 103.53 (1)°	Block, red
V = 1231.9 (3) Å^3	0.30 × 0.20 × 0.20 mm
Z = 2	

Data collection

Bruker CCD area-detector diffractometer	2449 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.029
Absorption correction: none	θ_{max} = 28.0°
7255 measured reflections	$h = -9 \rightarrow 10$
2885 independent reflections	$k = -18 \rightarrow 25$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0965P)^2 + 0.3123P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.050	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.146	$\Delta\rho_{max}$ = 0.75 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
2885 reflections	
195 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1w1···O1	0.84 (1)	2.29 (1)	3.113 (3)	167 (3)
O1w—H1w2···O5	0.84 (1)	2.19 (1)	2.990 (3)	160 (3)
O2w—H2w1···O1w	0.84 (1)	1.89 (1)	2.700 (3)	164 (3)
O2w—H2w2···O6^{i}	0.84 (1)	2.31 (2)	3.030 (3)	144 (3)
N1—H1n1···O1	0.86 (1)	2.06 (1)	2.906 (3)	168 (3)
N1—H1n2···O2w^{ii}	0.85 (1)	2.11 (1)	2.905 (3)	155 (2)
N1—H1n3···O1w^{iii}	0.85 (1)	2.15 (2)	2.838 (3)	138 (2)
N2—H2n···O2w^{ii}	0.85 (1)	1.85 (1)	2.695 (2)	175 (2)

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

Table 2
Comparison of the geometry (Å, °) of the 1,4-bis(2-ammonioethyl)-piperazin-1,4-ium cation in the solid-state structure with that of both the *PM*3-optimized tetracationic structure and the *PM*3-optimized 1,4-bis(2-aminoethyl)piperazine molecule.

Bond dimension	X-ray structure	*PM*3-optimized cation	*PM*3-optimized molecule
N1—C1	1.486 (3)	1.529	1.472
N2—C2	1.505 (2)	1.544	1.492
N2—C3	1.503 (3)	1.537	1.492
N2—C4^{i}†	1.493 (3)	1.533	1.492
C1—C2	1.513 (3)	1.542	1.533
C3—C4	1.510 (3)	1.532	1.526
C4^{i}—N2—C3	108.4 (2)	107.0	111.4
C4^{i}—N2—C2	113.0 (2)	112.6	111.8
C3—N2—C2	111.1 (2)	111.0	112.3
N1—C1—C2	113.0 (2)	113.6	111.4
N2—C2—C1	113.5 (2)	113.6	115.6
N2—C3—C4	110.6 (2)	113.0	110.2
N2^{i}—C4—C3	110.9 (2)	113.0	110.7

† Symmetry code for the X-ray structure: (i) $-x, -y, -z$.

For the geometry-optimization calculations, the initial structures of the tetracation and the neutral bis(2-aminoethyl)piperazine were taken from the X-ray structure. They were optimized at their lowest energy state (singlet spin state), using the semi-empirical quantum chemical *PM*3 Hamiltonian in *HYPERCHEM* (Hypercube, 2001). The unrestricted Hartree–Fock method was employed in the optimization.

The nitrogen-bound and water H atoms were located and refined, subject to N—H = 0.85±0.01 Å and O—H = 0.84±0.01 Å, respectively. The H atoms attached to the C atoms were positioned geometrically and were allowed to ride on their parent C atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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