

N,N'-Bis(2-ammonioethyl)propane-1,3-diaminium tris(perchlorate) chloride

Hanna B. Szcześniak, Violetta Patroniak, Wanda Radecka-Paryzek and Maciej Kubicki*

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Correspondence e-mail: mkubicki@amu.edu.pl

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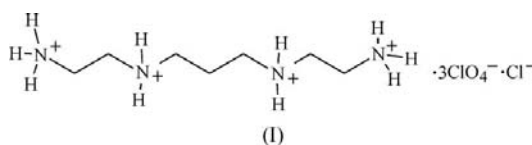
The crystal structure of the title compound, $C_7H_{24}N_4^{4+} \cdot 3ClO_4^- \cdot Cl^-$, is mainly determined by electrostatic interactions between the charged species and a number of relatively weak $N-H \cdots O$ and $N-H \cdots Cl^-$ hydrogen bonds. The rich structure of such hydrogen bonds creates infinite layers of ions extending along the [001] direction. The tetracation has the *gtttttg* conformation, similar to the single previously known example of such a cation. The presence of two different anions can be connected with the undecided competition between them, and some of the packing advantages of such a situation are found in the crystal structure.

Comment

Condensation reactions of carbonyl compounds and primary amines lead to the formation of the azomethine bond (see, for example, Ibrahim & Sharif, 2007), which is a characteristic structural feature of Schiff bases and therefore may be used in analytical determination. The importance of these compounds is mainly due to their resemblance to natural biological substances (de Hoog *et al.*, 2004; Mukherjee *et al.*, 2005), and to their relatively simple preparation procedures and synthetic flexibility, which make the introduction of suitable structural properties relatively easy. Unfortunately, a serious drawback of the majority of Schiff bases is their chemical instability, which concerns equilibrium lability, *i.e.* hydrolysis, tautomeric interconversions or ionized species formation (Galic *et al.*, 1997). In the course of our studies of the synthesis of a macrocyclic Schiff base with the ytterbium ion that has already been reported (Patroniak *et al.*, 2004), we obtained, quite unexpectedly, the title salt, (I), of quadruply protonated *N,N'*-bis(2-aminoethyl)propane-1,3-diamine with one chloride and three perchlorate anions.

In the Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen, 2002) there are only two structures of uncomplexed *N,N'*-bis(2-aminoethyl)propane-1,3-diamine,

one a tetracation (with benzene-1,2,4,5-tetracarboxylate; Su *et al.*, 2002) and one an uncommon trication [with tris(trifluoromethanesulfonate); Patroniak *et al.*, 2008]. Their conformations differ substantially: while the tetracation is *gtttttg* (*g* denotes *gauche* and *t* *trans*), in the trication an intramolecular $N-H \cdots N$ hydrogen bond enforces a more complicated *gttgggt* conformation. The conformation of (I) is similar to that found earlier in the tetracation (Su *et al.*, 2002); the torsion angles along the chain are -72.2 (4), 177.1 (3), 179.9 (3), -161.0 (2), 178.8 (3), -166.6 (2), -166.7 (3) and -94.8 (3)°. The mean length of the Csp^3-Csp^3 bond is 1.519 (8) Å and that of the Nsp^3-Csp^3 bond is 1.491 (5) Å. The perchlorate anions are close to a tetrahedral arrangement, with a mean $Cl-O$ distance of 1.443 (6) Å.



The crystal packing of (I) is determined by the electrostatic interactions between the charged species and by an extensive network of hydrogen bonds. Probably due to the large number of hydrogen-bond donors and acceptors, the resulting interactions are relatively weak (see Table 1). In the crystal structure, these hydrogen bonds create a complicated network of rings and chains.

The presence of both perchlorate and chloride anions in the structure is not particularly rare. There are 160 examples in the CSD (149 of which are organometallics), including the similar structure of diethylenetriammonium chloride diperchlorate (Mazus *et al.*, 1987). Such a situation might be regarded as an example of undecided competition between the anions (see, for example, Warden *et al.*, 2004). In every case one should find the packing advantages of such a composition in the 'supramolecule'. In the case of (I), it might be noted that the terminal hydrogen-bond donor groups (atoms N1 and N11) interact mainly with the perchlorate anions, while the 'internal' donor groups (atoms N4 and N8) interact mainly with the chlorides. This can be connected with the tendency to form centrosymmetric 'face-to-face' dimers by means of $N-H \cdots Cl \cdots H-N$ hydrogen-bond networks, and the small chloride anions, accessible from all directions, are

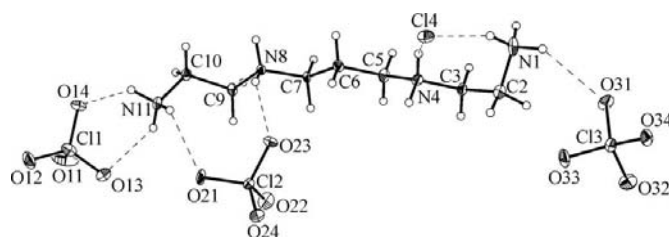
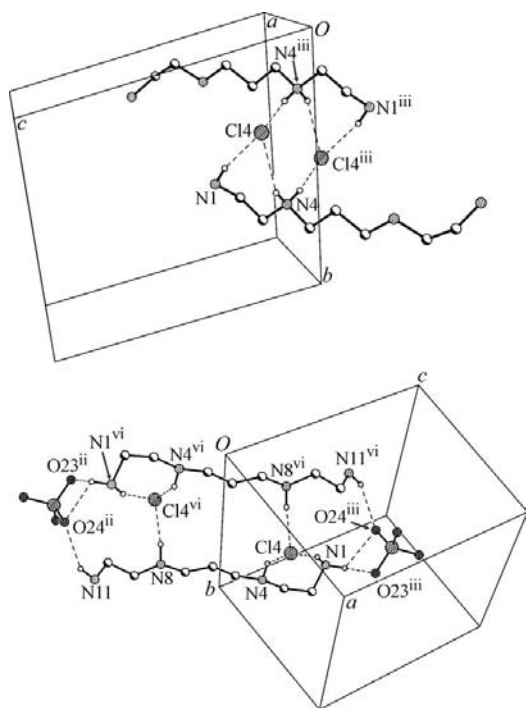


Figure 1

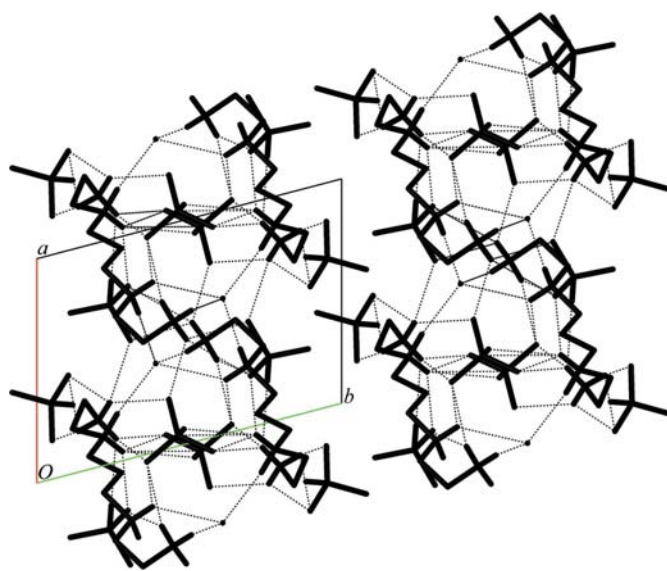
The ionic components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.

**Figure 2**

The two dimeric hydrogen-bonded motifs (see *Comment*). Hydrogen bonds are drawn as dashed lines. The symmetry codes are as in Table 1.

well suited for this. Indeed, such dimers can be seen in the crystal structure of (I). Pairs of cations at (x, y, z) and $(1 - x, 1 - y, -z)$ are connected into a hydrogen-bonded dimer involving both N4—H groups as acceptors, and two Cl4 anions (Fig. 2, top). The graph set (Etter *et al.*, 1990; Bernstein *et al.*, 1995) connected with this dimer is $R_4^2(8)$. Additional N1—H1C...Cl4 hydrogen bonds [$R_2^2(7)$ ring motif] add to the formation of this dimer. Another dimer is created by a pair of cations at (x, y, z) and $(-x, 1 - y, -z)$. While the former dimer displays a kind of shift between the constituent long molecules, the latter dimer is almost exactly in a head-to-tail disposition (Fig. 2, bottom), with the ends closed by hydrogen bonds between terminal amine groups and perchlorate anions. The hydrogen-bond motifs in this dimer can be described by graph-set motifs $R_4^2(16)$ (the 'inner' ring) and $R_4^4(32)$ (the 'outer' ring). Together, these two dimeric structures form a ribbon of cations extending approximately along the $[110]$ direction. N—H...O hydrogen bonds with perchlorate anions connect these ribbons into infinite tapes one unit-cell parameter wide, extending along the $[001]$ direction (Fig. 3). Only weak interactions are observed between these tapes. Some relatively short and directional C—H...O contacts are also present in the structure, but they are probably 'secondary' interactions, a consequence of the geometry of the molecules.

The chloride anion accepts four hydrogen bonds, with the donor N atoms forming a distorted tetrahedral arrangement. Such an arrangement is less common than a three-coordinated one, with the Cl atom on top of a more or less flattened tripodal coordination pyramid (Warden *et al.*, 2004). There are 492 organic structures (N...Cl distances shorter than 3.25 Å)

**Figure 3**

The packing of the ionic species, viewed along the c direction. Hydrogen bonds are depicted as dashed lines.

with three N—H donor groups in the CSD, while only 65 have four such groups.

Experimental

To a mixture of ytterbium chloride hexahydrate (0.096 mg, 0.247 mmol) and 2,6-diacetylpyridine (61.7 mg, 0.38 mmol) in methanol (15 ml), ytterbium perchlorate hexahydrate (72 mg, 0.12 mmol) was added and *N,N'*-bis(2-aminoethyl)propane-1,3-diamine (60.1 mg, 0.38 mmol) was added dropwise with stirring. The reaction mixture was stirred for 24 h at 341 K. Red crystals of (I) were obtained by slow diffusion of toluene into the acetonitrile solution.

Crystal data

$C_7H_{24}N_4^{4+} \cdot 3ClO_4^- \cdot Cl^-$
 $M_r = 498.10$
 Triclinic, $P\bar{1}$
 $a = 7.9755$ (9) Å
 $b = 11.2619$ (15) Å
 $c = 11.4848$ (16) Å
 $\alpha = 77.358$ (11)°
 $\beta = 78.991$ (10)°

$\gamma = 73.488$ (11)°
 $V = 955.9$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.69$ mm⁻¹
 $T = 100$ K
 $0.15 \times 0.1 \times 0.1$ mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrysAlis CCD*; Oxford Diffraction, 2009)
 $T_{min} = 0.901$, $T_{max} = 0.936$

9313 measured reflections
 4148 independent reflections
 2461 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.061$
 $S = 0.90$
 4148 reflections
 302 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.39$ e Å⁻³
 $\Delta\rho_{min} = -0.45$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O21 ⁱ	0.95	2.29	3.147 (3)	149
N1—H1A...O32 ⁱⁱ	0.95	2.52	3.114 (3)	121
N1—H1B...O31	0.95	2.38	3.110 (3)	133
N1—H1B...O23 ⁱⁱⁱ	0.95	2.59	3.310 (3)	133
N1—H1B...O24 ⁱⁱⁱ	0.95	2.53	3.131 (3)	121
N1—H1C...Cl4	0.95	2.24	3.147 (3)	160
C2—H2B...O14 ^{iv}	1.02 (3)	2.43 (3)	3.321 (4)	146 (2)
N4—H4A...O32 ⁱⁱ	0.91 (3)	2.47 (3)	3.026 (3)	120 (2)
N4—H4A...Cl4	0.91 (3)	2.52 (3)	3.187 (3)	130 (2)
N4—H4B...Cl4 ⁱⁱⁱ	0.92 (3)	2.25 (3)	3.156 (3)	168 (2)
C5—H5A...O11 ^v	0.97 (3)	2.54 (3)	3.367 (4)	143 (2)
C6—H6B...O23	0.96 (3)	2.51 (3)	3.238 (4)	133 (2)
C7—H7A...O12 ⁱ	0.97 (3)	2.43 (3)	3.224 (4)	138 (2)
C7—H7B...O13 ^v	1.04 (3)	2.43 (3)	3.370 (4)	150 (2)
N8—H8A...Cl4 ^{vi}	0.96 (3)	2.23 (3)	3.167 (3)	166 (2)
N8—H8B...O23	0.91 (3)	2.12 (3)	2.846 (3)	135 (2)
N8—H8B...O33 ⁱⁱⁱ	0.91 (3)	2.57 (3)	3.252 (3)	132 (2)
N8—H8B...O34 ⁱⁱⁱ	0.91 (3)	2.27 (3)	2.930 (3)	129 (2)
N11—H11A...O13	0.91	2.25	3.026 (3)	143
N11—H11B...O31 ^{vii}	0.91	2.34	3.043 (3)	134
N11—H11B...O24 ⁱⁱ	0.91	2.29	3.037 (3)	139
N11—H11B...O14	0.91	2.41	2.916 (3)	116
N11—H11B...O31 ^{vii}	0.91	2.34	3.043 (3)	134
N11—H11C...O34 ⁱⁱⁱ	0.91	2.09	2.770 (3)	131
N11—H11C...O21	0.91	2.34	3.004 (3)	130

Symmetry codes: (i) $x, y, z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z$; (iv) $x + 1, y, z + 1$; (v) $-x, -y + 2, -z - 1$; (vi) $-x, -y + 1, -z$; (vii) $x - 1, y, z - 1$.

The positions of the NH₃ H atoms were found geometrically and these atoms were treated as a rigid group with one common N—H distance refined. All other H atoms were found in a difference Fourier map and their positions were freely refined (see Table 1), with $U_{\text{iso}}(\text{H}) = 1.2$ (or 1.4 for NH₃ groups) times $U_{\text{eq}}(\text{parent})$.

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens,

1989) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3118). Services for accessing these data are described at the back of the journal.

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