N-{3-[(2-Ammonioethyl)amino]-propyl}ethane-1,2-diaminium tris(trifluoromethanesulfonate): a salt of a folded triply protonated tetramine

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The structure of a trifluoromethanesulfonate salt of a non-typical triply protonated linear tetramine, $C_7H_{23}N_4{}^{3+}\cdot 3CF_3SO_3{}^-$, with a layered crystal structure is presented. One N atom remains unprotonated. The conformation of the cation is enforced by intra- and intermolecular hydrogen bonds. The crystal structure is built of ca 10 Å deep layers, within which cations and anions are hydrogen bonded. Each layer is only weakly bound to its neighbours. This study shows a rare example of an unsymmetrically protonated polyamine and the relation between the lack of protonation, intramolecular hydrogen bonding and the conformation of the cation.

Comment

Polyamines play a major role in many biological processes. Most eukaryotic cells have a polyamine transporter system on their cell membrane that facilitates the internalization of exogenous polyamines. This system is highly active in rapidly proliferating cells and is the target of some chemotherapeutics currently under development (Wang *et al.*, 2003). Polyamines are also important modulators of a variety of ion channels, including NMDA and AMPA receptors (Chen *et al.*, 2005). In the course of our studies on metal complexes with polyamines, some new salts of biogenic polyamines and their derivatives have recently been described (Pospieszna-Markiewicz *et al.*, 2006, 2007; Jazdoń *et al.*, 2007). We present here another example, (I), *viz.* the trifluoromethanesulfonate salt of an unexpectedly triply protonated 3,7-diazanonane-1,9-diamine.

$$[H_3N\!-\!\!\diagup\!\!\diagdown\!\!-\!NH\!-\!\!\diagup\!\!\diagdown\!\!\diagup\!\!-\!NH_2\!-\!\!\diagup\!\!\diagdown\!\!-\!NH_3]^{3+} \cdot 3CF_3SO_3{}^-$$

(I)
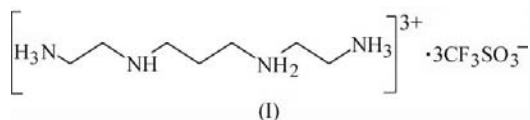
Protonated polyamines are also useful for studying the coordination properties of different anions (*e.g.* halides;

Ilioudis *et al.*, 2000). Linear symmetrical tetramines in their protonated forms usually exist as di- or tetracations. For instance, in the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002) there are 42 fragments containing triethylenetetramine cations: in 31 cases they are tetracations, in eight they are dications, while two of three remaining structures are highly disordered (Yao *et al.*, 1999; Zheng *et al.*, 2003), and in only one, namely bis(triethylenetetramine) tris[bis(nitrilotriacetato)zirconium] tetrahydrate, (II) (Haussuhl *et al.*, 2000), is the trication unequivocally determined. For sperminium (1,5,10,14-tetraazoniatetradecane), there are seven tetracations and one dication. The 3,7-diazanonane-1,9-diamine derivatives are represented by only one salt, in which the amine is tetraprotonated, namely benzene-1,2,4,5-tetracarboxylate (Su *et al.*, 2002).

At room temperature, at least two of three anions in (I) display large and eccentric displacement ellipsoids, suggesting a certain degree of disorder. Lowering the temperature to 100 K significantly reduces the ellipsoids and also improves their shapes. The 100 K structure is reported here.

The conformation of the cation is *gttggggt* (where *t* denotes *trans* and *g* gauche, *cf.* Fig. 1), as can be seen from the values of the torsion angles along the chain [71.00 (15), −178.77 (11), −175.46 (11), −66.72 (16), 62.13 (15), 71.31 (14), 90.19 (14) and −170.13 (11)°]. It is far from the all-*trans* conformation observed in some related α,ω-diaminoalkanes, *e.g.* in *n*-decylammonium chloride (Schenk & Chapuis, 1986) or 4-bromocinnamate (Ballabn *et al.*, 2006), and also the *gttttttg* conformation reported for the 3,7-diazanonane-1,9-diamine tetracation (Su *et al.*, 2002), and is probably a consequence of both inter- and intramolecular hydrogen bonds. The intramolecular N4···N8 distance is 2.8480 (16) Å (for the all-*trans*
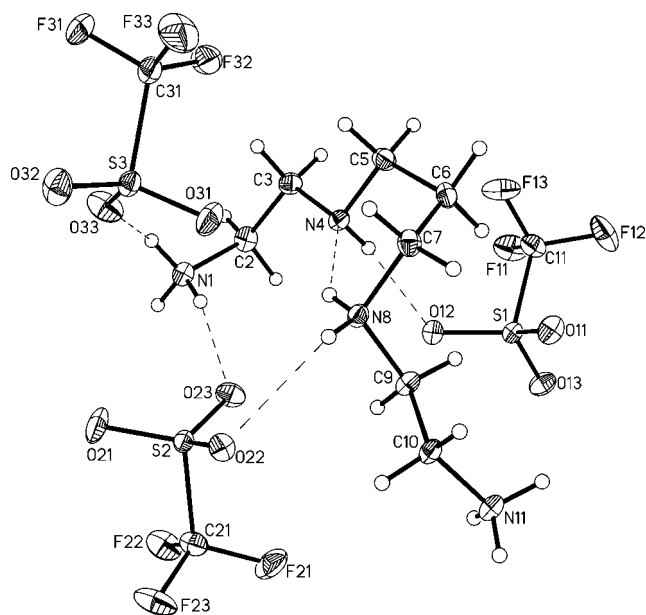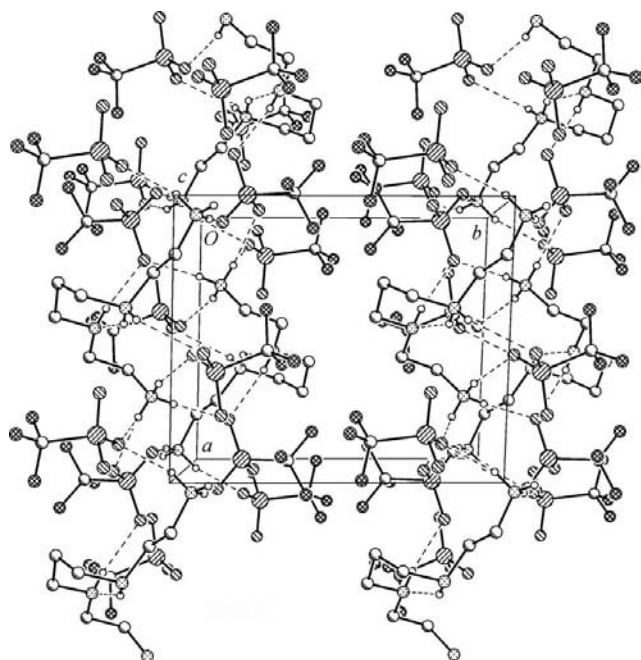

Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres with arbitrary radii. Hydrogen bonds are drawn as dashed lines.

conformation it would be almost 5 Å) and the H8A atom is obviously involved in the interaction (Table 1); this hydrogen bond closes a six-membered chair-like ring. A different situation was observed in the unsymmetrically protonated tetramine of (II) (Haussuhl *et al.*, 2000), in which the N···N distance is even shorter (2.807 Å *versus* 4 Å for all-*trans*), but, surprisingly, hardly any hydrogen-bond interactions can be found, as the intramolecular N—H···N angle is as small as 98°. It might be noted that in both cases the N atom that might
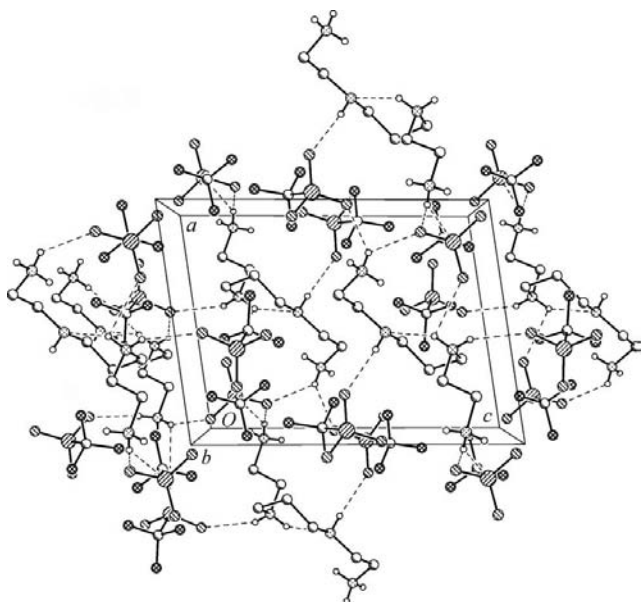
Figure 2
The geometry of the hydrogen-bonded layer as seen along the *b* direction. The hydrogen bonds are depicted as dashed lines.

Figure 3
The crystal packing as seen along the *c* direction. Dashed lines represent hydrogen bonds.

act as the hydrogen-bond acceptor has no intermolecular short contacts. The second factor that contributes to the stability of the folded conformation of the cation is the intermolecular hydrogen bonding with one of the anions (Fig. 1). The motif formed by these interactions might be described, using graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995), as $R_2^2(13)$, or $R_3^3(11)$, taking into account the intramolecular hydrogen bond. The anions are in a typical skew conformation, with the O—S—C—F torsion angles close to ±60 or 180°.

Due to the large number of hydrogen-bond donors and acceptors, the overall crystal structure would be expected to be determined by the hydrogen bonds between the ionic components (Table 1). Interestingly, this is only partly true. The crystal comprises layers expanding in the *ac* plane (Figs. 2 and 3), within which cations and anions are hydrogen bonded, while the layers are only held together by weak van der Waals interactions. The organization within a layer is quite complicated (Fig. 2). Using graph-set notation, one can find some characteristic motifs of higher rank, as all the first-rank motifs are simple dimers (*D*). The terminal NH₃ groups are involved in two kinds of interactions: they make centrosymmetric tetramers (of second order) with two anions *via* the same NH₃ group, *i.e.* N1 to N1$(2 - x, 2 - y, 1 - z)$ and N11 to N11$(-x, 2 - y, 2 - z)$, and mixed four-order rings, *i.e.* N1 to N11$(1 + x, y, z)$, all with the same $R_4^4(12)$ graph set. These rings connect molecules into chains characterized by the interlinked motifs $C_4^4(32)$. The 'internal' NH groups are also involved in ring-like structures. Two N4—H4 groups, together with the N1—H1B groups of the same molecule, and two anions close a centrosymmetric $R_4^4(14)$ ring; the N8—H8B group not involved in intramolecular hydrogen bonding makes a small $R_2^2(8)$ ring. All these motifs are interconnected to create the strongly bound layer, in which some secondary relatively short C—H···O contacts are also observed (Table 1). These layers are *ca* 10 Å deep (almost the whole *b* parameter). The shortest F···F interlayer contact is 2.89 Å, indicating that only weak unspecific interactions are involved between layers.

Experimental

An equimolar mixture of Eu(CF₃SO₃)₃ (18 mg, 30 μmol) in methanol (5 ml), 2,6-diacetylpyridine (4.9 mg, 30 μmol) in methanol (5 ml) and 3,7-diazanonane-1,9-diamine (5 μl, 30 μmol) in methanol (5 ml) was stirred at room temperature for 48 h. The solvent was evaporated under reduced pressure to yield a yellow powder. Yellow single crystals suitable for X-ray diffraction analysis were formed by slow diffusion of methanol into an acetonitrile solution of the compound (1 ml) at 278 K over a period of a few weeks.

Crystal data

C₇H₂₃N₄³⁺·3CF₃SO₃⁻	$\gamma = 91.333\ (6)°$
$M_r = 610.50$	$V = 1171.28\ (18)$ Å³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.1174\ (8)$ Å	Mo $K\alpha$ radiation
$b = 10.5925\ (7)$ Å	$\mu = 0.44$ mm⁻¹
$c = 12.2690\ (13)$ Å	$T = 100\ (1)$ K
$\alpha = 91.964\ (7)°$	$0.4 \times 0.2 \times 0.1$ mm
$\beta = 98.312\ (8)°$	

Data collection

Kuma KM-4-CCD diffractometer
9862 measured reflections
5707 independent reflections

4783 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 1.07$
5707 reflections
396 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A⋯O23	0.87 (2)	1.99 (2)	2.8239 (16)	161.4 (18)
N1—H1B⋯O12^{i}	0.89 (2)	2.01 (2)	2.8847 (17)	165.2 (17)
N1—H1C⋯O33	0.86 (2)	2.20 (2)	2.8526 (17)	132.9 (16)
N1—H1C⋯O11^{ii}	0.86 (2)	2.236 (19)	2.9516 (16)	141.0 (17)
N4—H4⋯O12	0.831 (19)	2.380 (19)	3.2049 (16)	172.0 (17)
N8—H8A⋯O23	0.856 (18)	2.573 (17)	3.0034 (16)	112.2 (13)
N8—H8A⋯O31	0.856 (18)	2.581 (17)	2.8726 (16)	101.2 (13)
N8—H8B⋯O22^{iii}	0.833 (18)	2.288 (18)	3.0254 (15)	147.6 (16)
N8—H8B⋯O22	0.833 (18)	2.413 (19)	3.0573 (15)	134.7 (15)
N8—H8A⋯N4	0.856 (18)	2.125 (18)	2.8480 (16)	141.8 (15)
C9—H9B⋯O23	0.950 (17)	2.508 (16)	3.1473 (18)	124.7 (12)
C9—H9A⋯O11	0.949 (17)	2.631 (17)	3.5090 (17)	154.0 (13)
C10—H10B⋯O22	0.932 (17)	2.576 (16)	3.2955 (17)	134.3 (12)
N11—H11A⋯O13^{iv}	0.85 (2)	2.05 (2)	2.8727 (16)	161.7 (19)
N11—H11B⋯O32^{iii}	0.88 (2)	1.96 (2)	2.7618 (16)	150.3 (17)
N11—H11C⋯O33^{v}	0.92 (2)	1.98 (2)	2.8713 (18)	162.6 (16)

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

The H-atom positions were freely refined. H atoms bound to the same non-H atom were constrained to have the same U_{iso} value, which was refined as a free variable.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; 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); software used to prepare material for publication: *SHELXL97*.

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