

Redetermination of sperminium tetrachloride

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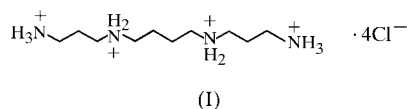
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In the title compound, 1,5,10,14-tetraazoniatetradecane tetrachloride, $C_{10}H_{30}N_4^{4+} \cdot 4Cl^-$, the sperminium tetracation lies on a centre of symmetry. The two central C—N—C torsion angles are *gauche* and of opposite signs, and all the other torsion angles are *trans*. All NH groups participate in the three-dimensional hydrogen-bond network, which is additionally strengthened by C—H...Cl interactions.

Comment

Spermine, putrescine and spermidine are biologically important aliphatic biogenic polyamines that take part in the determination and stabilization of secondary and tertiary structures of nucleic acids. In biological systems, they exist as polycations that interact with nucleic acid polyanions. The structures of the salts of these amines are therefore important in the modelling of nucleic acids. The crystal structure of sperminium tetrachloride was determined by Giglio *et al.* (1966), with 1500 visually estimated reflections collected by means of the Weissenberg method. The positions of the H atoms were calculated geometrically, and the quality of the structure determination is, by today's standards, rather poor (an *R* factor of 0.105 and reported s.u. values on bond lengths of ~ 0.01 Å). Since spermine is important because of both its biological activity and its chelating properties, we performed a redetermination of the crystal structure of sperminium chloride, (I).



Giglio *et al.* (1966) described the structure in the standard space group $P2_1/c$, with a large β angle of 121.5 (2)°. We transformed this cell into the more convenient $P2_1/n$ [transformation matrix (100/0 $\bar{1}$ 0/ $\bar{1}$ 0 $\bar{1}$)], with a β angle of 93.21 (1)°. The very good agreement between our unit-cell parameters and the results obtained almost 40 years ago by means of

precession photographs should be stressed; all differences are within 3σ .

The geometry of the centrosymmetric cation does not differ significantly from that described by Giglio *et al.* (1966). The conformation of the sperminium cation can be described as *ttgtttgttt* (where *t* denotes *trans* and *g gauche*) and is different from the all-*trans* conformation (*tttttttttt*) found in the phosphate hexahydrate (Iitaka & Huse, 1965; Cohen *et al.*, 1997) and in hydrogen sulfate dihydrate (Ilioudis *et al.*, 2002). Still another type of conformation of this cation, *gttttttttg*, was observed in the tetranitrate, where the terminal N—C—C—C torsion angles are *gauche* [65.0 (4)°; Jaskólski, 1987]. In (I), the C4—N5—C6—C7 angle is 66.7 (2)°, and there are three approximately planar fragments in the cation, *viz.* N1/C2/C3/C4/N5/C6 (and its symmetry-related counterpart) and N5/C6/C7/C7'/C6'/N5'; the dihedral angle between the neighbouring planes is 63.22 (15)°.

Bond lengths and angles are typical. Because of the steric stress caused by the *gauche* conformation, the C4—N5—C6 and N5—C6—C7 bond angles are significantly wider than the perfect tetrahedral values. Such widening has not been observed in other sperminium salts.

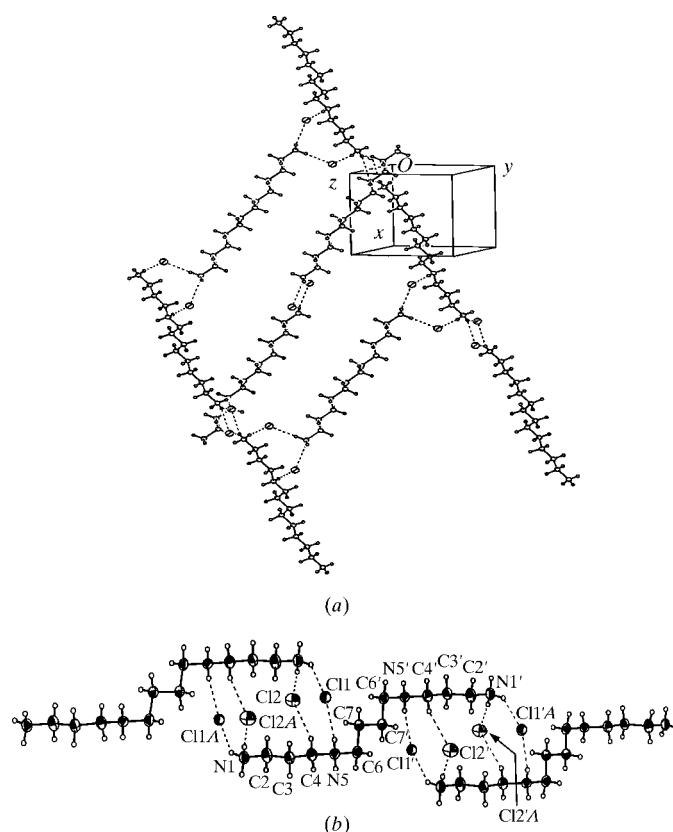


Figure 1

The two main packing motifs (Siemens, 1989) in (I). (a) The two-dimensional grid, as seen approximately along the [001] direction, and (b) a chain of molecules along the [110] direction, together with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii. A prime (') denotes the symmetry operation $(2-x, 1-y, 1-z)$. [Additional symmetry code: (A) $1-x, -y, 1-z$.]

The crystal packing is determined by N—H...Cl⁻ hydrogen bonds. All but one of the NH groups act as hydrogen-bond donors for strong and directional bonds; the only exception is the N1—H12 group, which takes part in a bifurcated hydrogen bond in which the H...Cl distances are longer and the N—H...Cl angles are smaller than those in the other cases (Table 1). A number of secondary C—H...Cl hydrogen bonds also stabilize the crystal structure.

The crystal packing is complicated, as there are many different hydrogen bonds in the structure, but some general rules can be described. There are chains of molecules along [1 $\bar{2}$ 0], connected by bifurcated hydrogen bonds. These chains are connected *via* other cations into a two-dimensional grid by means of N5—H51...Cl1 and N1—H11...Cl1 hydrogen bonds (Fig. 1*a*). The second characteristic motif involves molecules connected by the [110] vector. These molecules are connected to one another by a system of eight hydrogen bonds involving four chloride anions (Fig. 1*b*).

It might also be noted that the coordination around the two chloride anions is different. Atom Cl1 acts as an acceptor in four N—H...Cl hydrogen bonds (two strong and two weak), with approximately tetrahedral coordination. On the other hand, atom Cl2 accepts only two strong N—H...Cl hydrogen bonds, but the coordination of this anion is completed by two relatively strong C4—H...Cl hydrogen bonds. The structure of (I) might therefore be regarded as another case in which a CH group acts as a substitute donor that mimics a stronger one (NH in this case).

Experimental

The title compound was obtained by slow diffusion of dioxane into a methanol solution of the spermine complex with lanthanum chloride.

Crystal data

C₁₀H₃₀N₄⁴⁺·4Cl⁻
M_r = 348.18
 Monoclinic, *P*2₁/*n*
a = 8.569 (1) Å
b = 7.913 (1) Å
c = 13.002 (1) Å
 β = 93.21 (1)°
V = 880.24 (17) Å³
Z = 2

Data collection

Kuma KM-4 CCD four-circle diffractometer
 ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1989)
*T*_{min} = 0.936, *T*_{max} = 0.943
 8391 measured reflections

D_x = 1.314 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 2927 reflections
 θ = 4–20°
 μ = 0.66 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.25 × 0.10 × 0.10 mm

1902 independent reflections
 1382 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.025
 θ _{max} = 27.0°
h = -10 → 10
k = -10 → 10
l = -10 → 16

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.030
wR(*F*²) = 0.053
S = 1.00
 1902 reflections
 142 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.016$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$

Table 1
 Hydrogen-bonding 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—H11...Cl2 ⁱ	0.864 (19)	2.28 (2)	3.144 (2)	176.3 (16)
N1—H12...Cl1 ⁱ	0.83 (2)	2.61 (2)	3.2848 (19)	139.3 (16)
N1—H12...Cl1 ⁱⁱ	0.83 (2)	2.70 (2)	3.2945 (18)	129.1 (16)
N1—H13...Cl2 ⁱⁱⁱ	0.864 (18)	2.283 (18)	3.1351 (18)	168.9 (15)
C4—H41...Cl2	0.905 (16)	2.853 (17)	3.707 (2)	157.9 (13)
C4—H42...Cl2 ^{iv}	0.940 (17)	2.801 (17)	3.701 (2)	160.7 (12)
N5—H51...Cl1	0.855 (17)	2.350 (18)	3.1873 (17)	166.6 (16)
N5—H52...Cl1 ^v	0.845 (17)	2.308 (18)	3.1414 (15)	168.8 (15)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1618). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1989). *J. Appl. Cryst.* **22**, 396–397.
 Cohen, A. E., Craven, B. M. & Klooster, W. T. (1997). *Acta Cryst.* **B53**, 787–794.
 Giglio, E., Liquori, A. M., Puliti, R. & Ripamonti, A. (1966). *Acta Cryst.* **20**, 652–659.
 Iitaka, Y. & Huse, Y. (1965). *Acta Cryst.* **18**, 110–121.
 Ilioudis, C. A., Georganapoulou, D. G. & Steed, J. W. (2002). *CrystEngComm*, **4**, 26–36.
 Jaskólski, M. (1987). *Acta Cryst.* **C43**, 1375–1378.
 Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Versions 169. Oxford Diffraction Ltd, Wroclaw, Poland.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.