Cadaverinium dichloride: a case of centro–non-centrosymmetric ambiguity

Izabela Pospieszna-Markiewicz, 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

In the title salt, also known as pentane-1,5-diammonium dichloride, $C_5H_{16}N_2^{2+} \cdot 2Cl^-$, the cation exists in an ideal fully extended conformation and lies on a mirror plane in the space group $Pbam$. In the crystal structure, layers of cations are hydrogen bonded with Cl^- anions, which occupy the space between the layers. This kind of packing leads to a short unit-cell parameter of 4.463 (1) Å. This structure is another case of centro–non-centrosymmetric ambiguity; the best results were obtained in a centrosymmetric space group, with the disordered NH_3 groups accounting for the non-centrosymmetric 'component'.

Comment

Polyamines play a major role in many cellular and genetic processes, such as DNA synthesis, gene expression, cell division, protein synthesis and plant response to abiotic stress. One of these compounds is cadaverine, which is derived from the amino acid lysine by decarboxylation catalysed by lysine decarboxylase. Cadaverine is naturally present in decaying corpses and in the roots of certain plants. Under normal physiological conditions, polyamines exist as polycations. Natural polyamines bind to polyanions, for example, to DNA, and induce various changes in their secondary structure (Karigiannis & Papaioannou, 2000).

$$^+H_3N - (CH_2)_5 - NH_3^+ \cdot 2Cl^-$$
$$(I)$$
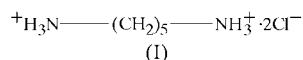
Flexible molecules (dications) of α,ω-diammonioalkanes are also used in the crystal engineering of different layered structures, either organic or organometallic. Therefore, knowledge of the packing modes of these compounds is crucial for the rational design of the new materials. Some crystal structures of halides of α,ω-diammonioalkanes, of the general formula $[NH_3-(CH_2)_n-NH_3]^{2+} \cdot 2Cl^-$, are known for $n = 1$–8, with a gap at $n = 5$. For $n = 5$, only the poorly defined structure

of cadaverinium dichloride trihydrate has been reported to date (Ramaswamy & Murthy, 1992; R factor of 0.101, no H atoms reported, three doubtful water O atoms). During our systematic investigations of the coordination template effect of various metal ions in generating new supramolecular macrocyclic and acyclic Schiff base systems derived from biogenic and biogenic-like diamines, we obtained crystals of cadaverine dichloride, (I), and decided to determine the crystal structure of this missing member of the family. In the course of these studies, we have found another case of one of the primary crystallographic problems, namely centro–non-centrosymmetric ambiguity (see, for example, Schomaker & Marsh, 1979; Marsh, 1999; Kubicki *et al.*, 2003, and references therein).

The symmetric absences allowed the orthorhombic space groups $Pbam$ and $Pba2$; the former, centrosymmetric, space group was chosen on the basis of the statistics of the $|E|$-value distribution. The probability that the structure is centrosymmetric, based on this distribution, is as high as 90%. The refinement was straightforward until the determination of the H atoms of the NH_3 groups. They could not be reasonably determined from the Fourier maps and were placed in idealized positions, but with the possibility of a 'rigid body' rotation of the whole set around the C—N bond (AFIX137 in *SHELXL97*; Sheldrick, 1997). Both NH_3 groups were optimized in the disordered dispositions, in which two sets of H atoms were connected by the mirror plane. Analysis of the hydrogen-bond network shows that the rational description of this network demands that consecutive molecules have alternative dispositions of H atoms, just as in the case without a mirror plane, *i.e.* in the space group $Pba2$. Attempts to refine the structure in that space group were not conclusive. The R
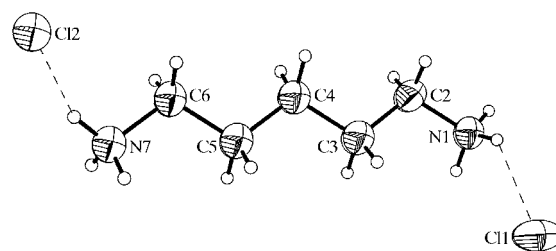
Figure 1
A view of the title salt, (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Dashed lines indicate the hydrogen bonds.
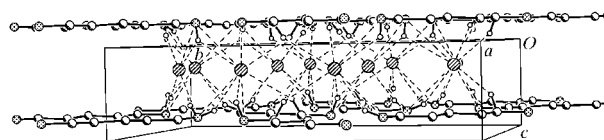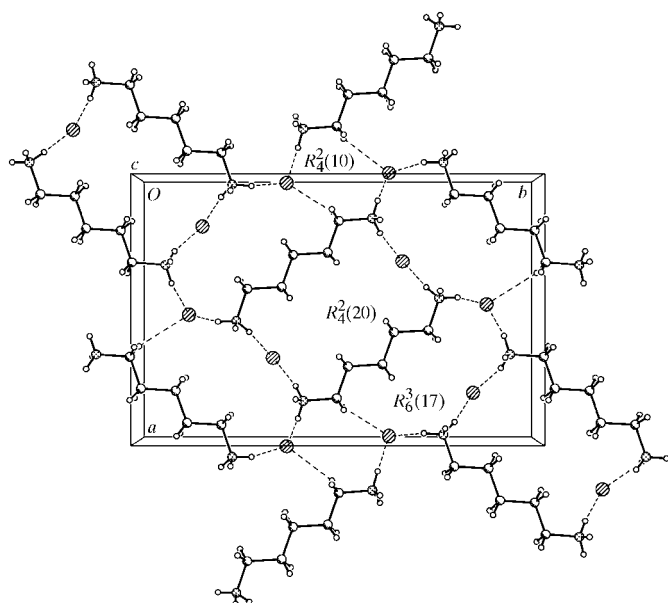

Figure 2
A packing scheme for (I), viewed approximately along the [010] direction. Hydrogen bonds are depicted as dashed lines. For clarity, only H atoms involved in hydrogen bonds are shown.

DOI: 10.1107/S0108270106018397
o399

factors, residual maps, *etc.*, were comparable with the centrosymmetric refinement, but, due to the large correlations between parameters related by a pseudo-mirror plane of symmetry, the refinement was unstable and hardly converged (more or less constant shifts as large as 0.7 were observed).

In our opinion, the best results were obtained on the assumption that the main skeleton of the structure is centrosymmetric (this is further confirmed by the regular shapes of the anisotropic displacement ellipsoids; see Fig. 1), and it is only slightly distorted by the positions of the terminal H atoms. Following this assumption, we refined the structure in the centrosymmetric space group *Pbam*, but the terminal H atoms were assumed to be disordered over two alternative positions with site-occupancy factors equal to 0.5. It may be noted that these occupancies have to be exactly equal to 0.5 in order to produce a consistent hydrogen-bond network. Similar reasons were used, for example, in evaluating the ratio of the tautomeric mixture found in a given crystal (*e.g.* Gdaniec *et al.*, 1995; Kubicki 2004, and references therein).

Fig. 1 shows a perspective view of the salt molecule, together with the labelling scheme. The cation is symmetrical and lies on a mirror plane in the space group *Pbam*. Bond lengths and angles (Table 1) are typical (*International Tables for Crystallography*, 1995, Vol. C). The cation is in a fully extended conformation and all torsion angles along the aliphatic chain are 180°. The terminal NH$_3$ groups are disordered and there are two sets of (symmetry-equivalent) positions of the H atoms.

In the crystal structure of (I), there are layers of cations parallel to the *ab* plane and the Cl$^-$ anions, hydrogen bonded to cations, occupy the space between the layers (Fig. 2). As a result of this packing stabilized by electrostatic interactions, one unit-cell parameter, perpendicular to the layer plane (in the present case, *c*) is short, *ca* 4.5 Å. Such a unit-cell parameter can be found in many analogous α,ω-diammonioalkane halogenates, for example, ethylenediammonium dichloride (4.419 Å; Bujak *et al.*, 2000), 1,3-diammoniopropyl dibromide (4.579 Å; Dou *et al.*, 1995), putrescinium (tetramethylenediammonium) dichloride (4.589 Å; Chandrasekhar & Pattabhi, 1980), hexamethylenediammonium dichloride (4.594 Å; Borkakoti *et al.*, 1978), *etc*. The structure of a layer is shown in Fig. 3. This structure is created by N—H···Cl and relatively strong C—H···Cl hydrogen bonds (Table 2).

It may be noted that C—H···Cl contacts are short and linear, and their role is important. Using Etter's graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995), there are three kinds of higher-order rings, *viz.* $R_4^2(10)$, $R_6^3(17)$ and $R_4^2(20)$. This structure is to some extent exceptional; in the majority of the structures of other α,ω-diammonioalkane halogenates, the characteristic motif $R_4^2(8)$ is present.

Experimental

Crystal data

C$_5$H$_{16}$N$_2$$^{2+}$·2Cl$^-$	$Z = 4$
$M_r = 175.10$	$D_x = 1.198$ Mg m^{-3}
Orthorhombic, *Pbam*	Mo $K\alpha$ radiation
$a = 11.9697$ (13) Å	$\mu = 0.60$ mm^{-1}
$b = 18.180$ (2) Å	$T = 295$ (1) K
$c = 4.4626$ (5) Å	Prism, colourless
$V = 971.10$ (19) Å^3	0.35 × 0.2 × 0.12 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer	1386 independent reflections
ω scans	1079 reflections with $I > 2\sigma(I)$
5851 measured reflections	$R_{int} = 0.030$
	$\theta_{max} = 29.1°$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.037$	
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1386 reflections	$(\Delta/\sigma)_{max} = 0.001$
79 parameters	$\Delta\rho_{max} = 0.43$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Figure 3
The structure of a layer of (I), together with graph-set designators. Hydrogen bonds are depicted as dashed lines.

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.479 (3)	C4—C5	1.503 (4)
C2—C3	1.482 (3)	C5—C6	1.510 (3)
C3—C4	1.527 (3)	C6—N7	1.484 (3)
N1—C2—C3	113.4 (2)	C4—C5—C6	112.6 (2)
C2—C3—C4	112.7 (2)	N7—C6—C5	111.8 (2)
C5—C4—C3	113.1 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C$\cdots$Cl1[i]	0.89	2.48	3.2133 (14)	141
N1—H1B$\cdots$Cl1[ii]	0.89	2.34	3.2133 (14)	167
N1—H1C$\cdots$Cl2[iii]	0.89	2.75	3.2342 (13)	115
N1—H1A$\cdots$Cl2[iv]	0.89	2.45	3.2342 (13)	147
C2—H2$\cdots$Cl2[v]	0.94 (2)	2.90 (2)	3.7446 (19)	150.8 (15)
C4—H4$\cdots$Cl2[v]	0.98 (2)	3.18 (2)	4.037 (2)	146.9 (14)
C5—H5$\cdots$Cl1	0.97 (2)	3.19 (2)	3.920 (2)	133.4 (16)
C6—H6$\cdots$Cl2	0.97 (2)	3.20 (2)	3.7480 (18)	117.6 (13)
N7—H7B$\cdots$Cl1	0.89	2.31	3.1869 (14)	167
N7—H7C$\cdots$Cl1[vi]	0.89	2.47	3.1869 (14)	138
N7—H7A$\cdots$Cl2	0.89	2.44	3.2225 (15)	147
N7—H7C$\cdots$Cl2[vi]	0.89	2.78	3.2225 (15)	112

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

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Borkakoti, N., Lindley, P. F., Moss, D. S. & Palmer, R. A. (1978). *Acta Cryst.* B**34**, 3431–3433.

Bujak, M., Sikorska, L. & Zaleski, J. (2000). *Z. Anorg. Allg. Chem.* **626**, 2535–2542.

Chandrasekhar, K. & Pattabhi, V. (1980). *Acta Cryst.* B**36**, 2486–2488.

Dou, S., Paulus, H. & Weiss, A. (1995). *J. Mol. Struct.* **345**, 1–10.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Gdaniec, M., Sączewski, F. & Dębowski, T. (1995). *J. Chem. Crystallogr.* **25**, 813–821.

Karigiannis, G. & Papaioannou, D. (2000). *Eur. J. Org. Chem.* pp. 1841–1863.

Kubicki, M. (2004). *Acta Cryst.* B**60**, 191–196.

Kubicki, M., Borowiak, T., Dutkiewicz, G., Sobiak, S. & Weidlich, I. (2003). *Acta Cryst.* B**59**, 487–491.

Marsh, R. E. (1999). *Acta Cryst.* B**55**, 931–936.

Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.69. Oxford Diffraction Poland Sp., Wrocław, Poland.

Ramaswamy, S. & Murthy, M. R. N. (1992). *Indian J. Biochem. Biophys.* **29**, 402–406.

Schomaker, V. & Marsh, R. E. (1979). *Acta Cryst.* **35**, 1933–1934.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.