Hexamethylenediammonium bis(chloroacetate): a three-dimensional hydrogen-bonded framework structure

Alejandro Ortíz,[a] Braulio Insuasty,[a] Justo Cobo,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

In the title compound, $C_6H_{18}N_2^{2+} \cdot 2C_2H_2ClO_2^-$, the cation lies across an inversion centre in the $P\bar{1}$ space group. The ions are linked by two two-centre N—H···O hydrogen bonds and by one three-centre N—H···(O)$_2$ hydrogen bond to form a three-dimensional framework structure. The significance of this study lies in the analysis of the complex hydrogen-bonded structure and in the comparison of this structure with those of other simple hexamethylenediammonium salts.

Comment

A substantial number of salts containing the hexamethylenediammonium cation, $[H_3N(CH_2)_6NH_3]^{2+}$, are recorded in the Cambridge Structural Database (CSD, Version 5.29 of January 2008; Allen 2002), but there are very few entries for unsolvated salts containing simple mono-negative anions which do not contain further potential hydrogen-bond capability. Accordingly, it is of interest to investigate the hydrogen-bonded structure of such a simple salt, and we therefore report here the structure of the title compound, (I) (Fig. 1).

(I)
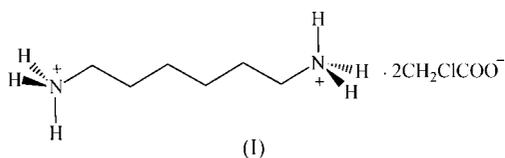
Compound (I) was prepared from the reaction between hexamethylenediamine and chloroacetic acid, where the desired product was hexamethylenediglycine intended for use as a flexible linker in the coupling of fullerene units.

In compound (I), the cation lies across a centre of inversion in the $P\bar{1}$ space group, selected for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and it adopts a nearly planar all-*trans* conformation. The three independent C—C distances within the cation are virtually identical (Table 1). By contrast, in the corresponding chloride salt, where the cation lies in a general position (Borkakoti *et al.*, 1978), there is a marked alternation in the C—C distances between those which are shorter than the mean value and those which are longer, with the distances ranging from 1.507 (4) to 1.538 (4) Å. In the 3,5-dinitrobenzoate salt, the cation lies across a centre of inversion in the $P2_1/c$ space group (Wang & Wei, 2007), and again the C—C distances show a marked alternation of long and short bonds, with distances ranging from 1.499 (5) to 1.539 (3) Å. The saccharinate salt contains two independent cations, both lying across centres of inversion in the $P2_1/c$ space group (Wang *et al.*, 2006). One of the cations exhibits a similar alternation of C—C bond lengths in the range 1.483 (4) to 1.518 (5) Å. The other was refined as disordered, but the reported C—C distances range from 0.970 (10) to 1.571 (6) Å, and no conclusion can be drawn from this apparently inadequate disorder model. These three determinations (Borkakoti *et al.*, 1978; Wang & Wei, 2007; Wang *et al.*, 2006) were all based on diffraction data collected at ambient temperature. The near constancy of the C—C distances found for (I) at 120 K suggests that the bond-length alternation observed in the other salts may possibly be an artefact of the larger thermal motion at ambient temperature.

The two independent C—O distances in the anion are fairly similar, as expected, but the conformation of the anion is such that the C—Cl bond nearly eclipses one of the C—O bonds, as indicated by the relevant torsion angles (Table 1).
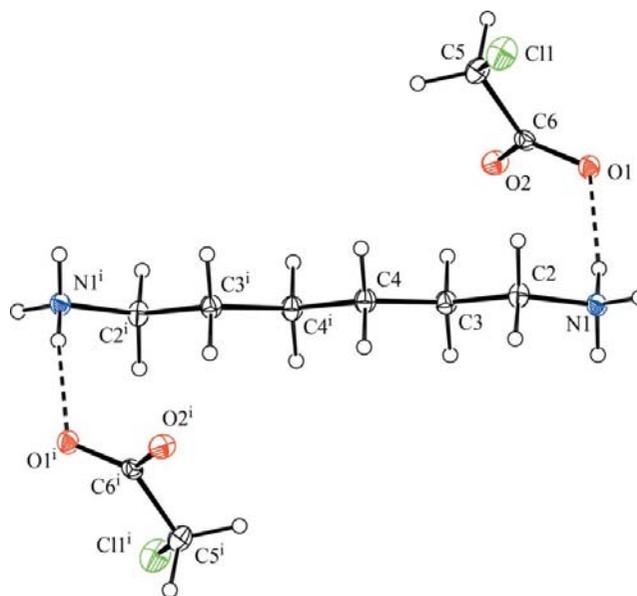

Figure 1
The independent ionic components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]
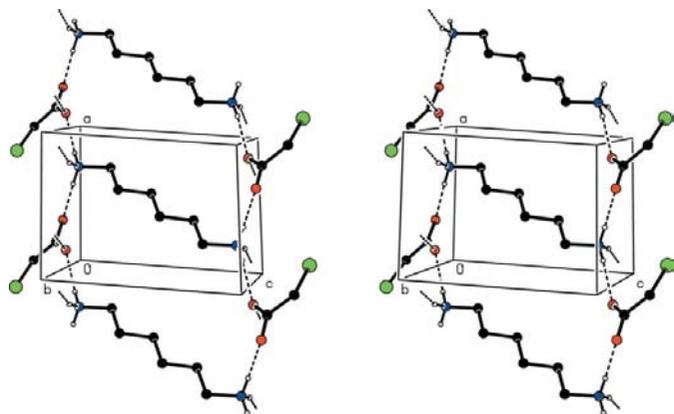
organic compounds

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_4^4(26)$ rings along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted.
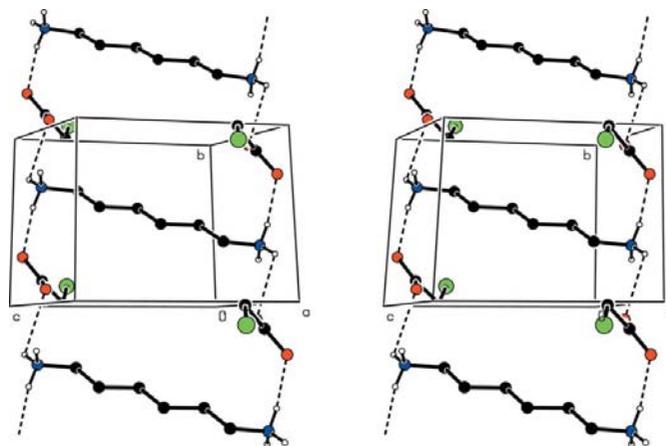

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_4^4(26)$ rings along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

The ionic components of (I) are linked into a complex three-dimensional framework structure. Within the selected asymmetric unit (Fig. 1), ammonium atom N1 acts as hydrogen-bond donor, *via* atom H1A, to carboxylate atom O1. In addition, these aggregates are linked by a second two-centre N—H⋯O hydrogen bond involving atom H1B and a planar but markedly asymmetric three-centre N—H⋯(O)$_2$ hydrogen bond involving atom H1C (Table 2). However, the formation of the framework structure is readily analysed in terms of three one-dimensional substructures, two of them in the form of rather similar chains of edge-fused rings.

Atom N1 at (x, y, z) acts as hydrogen-bond donor, *via* atoms H1B and H1C, respectively, to carboxylate atoms O2 in the anion at $(1 - x, 1 - y, -z)$ and O1 in the anion at $(2 - x, 1 - y, -z)$. Propagation of these two hydrogen bonds by translation and inversion then leads to the formation of a chain of edge-fused $R_4^4(26)$ (Bernstein *et al.*, 1995) rings running parallel to the [100] direction in which the rings are centred at $(n, \frac{1}{2}, \frac{1}{2})$, where n represents zero or an integer (Fig. 2). The Cl atoms lie on the exterior of the chains. This structural motif can alternatively be regarded as a molecular ladder, with an antiparallel pair of $C_2^2(6)$ chains acting as the uprights of the ladder and the cations providing the rungs.

In the longer component of the three-centre interaction, ammonium atom N1 at (x, y, z) acts as hydrogen-bond donor, *via* atom H1C, to carboxylate atom O2 in the anion at $(x, -1 + y, z)$. Propagation by translation and inversion of this hydrogen bond, together with that within the asymmetric unit, generates a second chain of edge-fused $R_4^4(26)$ rings, this time running parallel to the [010] direction with the rings centred at $(\frac{1}{2}, n, \frac{1}{2})$, where n represents zero or an integer (Fig. 3).

In the final substructure, ammonium atom N1 at (x, y, z) acts as hydrogen-bond donor to carboxylate atom O1 within the asymmetric unit and to carboxylate atom O2 in the anion at $(1 - x, 1 - y, -z)$, so forming an $R_4^4(12)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, 0)$. Propagation of this motif by inversion then generates a chain of rings running parallel to the [001] direction with the rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$, where n represents zero or an integer (Fig. 4). The combination of the chains along [100], [010] and

[001] suffices to generate a continuous three-dimensional framework structure. Because each of the sub-structures is itself a chain of rings, the overall three-dimensional structure is of considerable complexity, with many ring motifs embedded within it.

The hydrogen-bonded structure of hexamethylene-diammonium bis(3,5-dinitrobenzoate) is only two-dimensional (Wang & Wei, 2007), but three-dimensional hydrogen-bonded structures are present in hexamethylenediammonium disaccharinate (Wang *et al.*, 2006), in hexamethylenediammonium dichloride (Borkakoti *et al.*, 1978) and presumably also in the isomorphous dibromide salt (Binnie & Robertson, 1949). The corresponding diiodide salt (CSD refcode HXMAMI; Han, 1963) has markedly different cell dimensions from the chloride and bromide salts, but no H-atom coordinates are
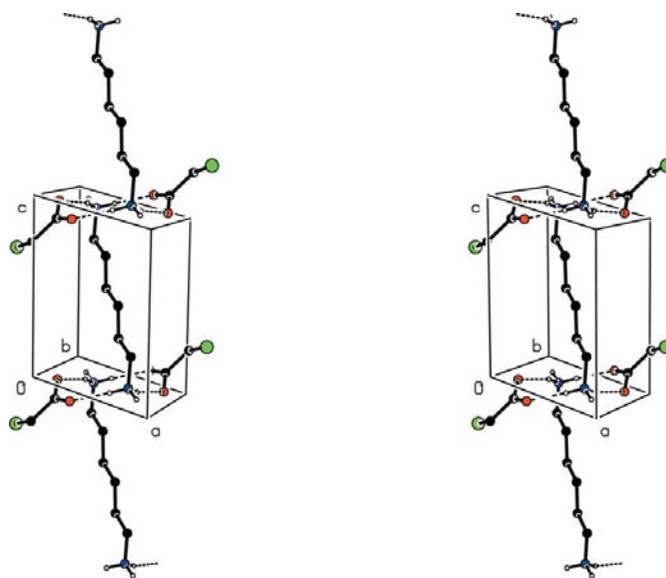

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

recorded in the CSD and the reported R factor is 0.23. Accordingly, no conclusions can safely be drawn about the hydrogen-bonded structure of this compound.

It is of interest to note that in the title compound, where the anion contains only two potential hydrogen-bond acceptor sites, the overall hydrogen-bonded structure is three-dimensional, whereas in the bis(3,5-dinitrobenzoate) salt (Wang & Wei, 2007), where the anion contains six potential hydrogen-bond acceptor sites, the hydrogen-bonded structure is nonetheless only two-dimensional. In both of these salts, only carboxylate O atoms are involved in the hydrogen bonding, and each structure utilizes all of the N—H bonds, but the overall supramolecular arrangements are very different. This suggests that attempts to make structural predictions for crystal engineering purposes, even for such simple salts, may have only limited success.

Experimental

A solution of hexamethylenediamine (4.0 g, 0.03 mmol) in a mixture of water (2 ml) and ethanol (4 ml) was cooled to 273 K, chloroacetic acid (6.5 g, 0.06 mmol) was added in small portions, and the mixture was stirred at room temperature for 4 h. The resulting solution was added to acetone (20 ml), producing a colourless crystalline precipitate of (I). This product was collected by filtration and dried, giving crystals suitable for single-crystal X-ray diffraction (yield 84%; m.p. > 623 K).

Crystal data

$C_6H_{18}N_2^{2+}\cdot 2C_2H_2ClO_2^-$
$M_r = 305.20$
Triclinic, $P\bar{1}$
$a = 6.5779 (18)$ Å
$b = 7.3593 (10)$ Å
$c = 8.425 (2)$ Å
$\alpha = 97.277 (12)°$
$\beta = 95.631 (15)°$

$\gamma = 111.037 (12)°$
$V = 373.03 (15)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.44$ mm^{-1}
$T = 120 (2)$ K
$0.42 \times 0.12 \times 0.09$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.836$, $T_{max} = 0.961$

10725 measured reflections
1718 independent reflections
1273 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 1.09$
1718 reflections

82 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.99 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}$(carrier).

Data collection: COLLECT (Nonius, 1999); cell refinement: DIRAX/LSQ (Duisenberg et al., 2000); data reduction: EVALCCD (Duisenberg et al., 2003); program(s) used to solve structure: SIR2004 (Burla et al., 2005); program(s) used to refine structure: OSCAIL

Table 1
Selected geometric parameters (Å, °).

C2—C3	1.503 (2)	C5—Cl1	1.7742 (19)
C3—C4	1.510 (2)	C6—O1	1.253 (2)
C4—C4^i	1.509 (3)	C6—O2	1.236 (2)
Cl1—C5—C6—O1	−16.3 (2)	Cl1—C5—C6—O2	165.29 (13)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O1^{ii}	0.88	1.95	2.801 (2)	163
N1—H1$B\cdots$O2^{ii}	0.88	1.86	2.739 (2)	177
N1—H1$C\cdots$O1^{iii}	0.88	1.99	2.814 (2)	154
N1—H1$C\cdots$O2^{iv}	0.88	2.59	3.020 (2)	111

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

(McArdle, 2003) and SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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