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Hexane-1,6-diaminium chloride [hydrogen bis(chloroacetate)]

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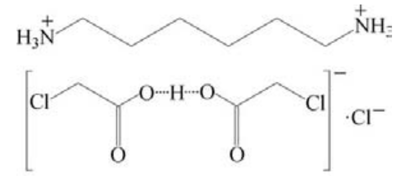
In the structure of the title compound, $C_6H_{18}N_2^{2+}\cdot H(C_2H_2ClO_2)_2^-\cdot Cl^-$, the hexane-1,6-diaminium dication is disordered over two sets of positions, with almost equal occupancies. Both alternative positions of the dication are in the fully extended conformation, situated on an inversion centre at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$). Two chloroacetic acid moieties, related by another centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), are connected by a very short symmetrical O$\cdots$H$\cdots$O hydrogen bond [O$\cdots$O = 2.452 (2) Å], with the H atom at the centre of inversion. These two fragments thus effectively form the hydrogen bis(chloroacetate) monoanion, and the overall charge is balanced by an additional chloride anion which resides on a twofold axis. The ions form a layer structure, with alternating layers of dications and anions running along the [101] direction, linked *via* hydrogen bonds. There are two N—H$\cdots$O interactions and two N—H$\cdots$Cl$^-$ interactions.

Comment

Aliphatic α,ω-diaminoalkanes have predictable basic properties because of the two amine groups at the ends of the aliphatic chain. They react with both organic and inorganic acids, resulting in salts composed of a diamine dication and suitable anion(s). The flexible cation tends to adopt a variety of conformations, which are influenced by the crystal packing. This property can be utilized in crystal engineering for the synthesis of supramolecular synthons, which control molecular aggregation and lead to particular patterns and new properties (Mahmoudkhani & Langer, 2001, 2002), and furthermore for the design of new materials possessing, for example, a layered structure (*cf.* Pospieszna-Markiewicz *et al.*, 2006).

In the Cambridge Structural Database (CSD; Allen, 2002; Version 5.30 of October 2008, no multiple entries, no error structures), there are 106 crystal structures containing the hexane-1,6-diaminium cation, *viz.* 38 organic and 68 organometallic. Among the organic structures, there are 27 with the dication in a fully extended conformation. There is no particular preference among any of the other possible conformations and none of them is represented by more than three examples. In 18 of the organic structures, the dications are situated about an inversion centre, and in four cases, some other special position. There are examples of structures having a disordered dication (*e.g.* Freeman, 1984; Visi *et al.*, 2006; Yang *et al.*, 2007; Wang *et al.*, 2006), anion (Todd & Harrison, 2007) or a solvent molecule (Liu *et al.*, 2004; Rather *et al.*, 2003).

In the course of our studies on the salts of aliphatic α,ω-diaminoalkanes with derivatives of acetic acid, we have determined the crystal structure of the title compound, (I), at 100 K. It can be compared with the crystal structures of hexane-1,6-diaminium dichloride [Binnie & Robertson (1949); redetermined by Borkakoti *et al.* (1978)], with the recently published structure of hexane-1,6-diaminium bis(chloroacetate) (Ortíz *et al.*, 2008) and with the results of our previous studies on the crystal packing mode of hexane-1,6-diaminium salts with acetic and di- and trichloroacetic acids (Paul & Kubicki, 2009).



(I)

The dication is symmetrical, with the mid-point of the central C—C bond residing on a centre of inversion at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$) (Fig. 1). The dication is disordered over two sets of positions, with the two chains crossing each other at the centre of inversion (Fig. 1). The two alternative orientations are almost equally populated; the site-occupancy factors refined at 0.512 (8) and 0.488 (8). Both disordered dications have a nearly fully extended conformation. Atom Cl on the chloroacetate anion is located almost in the plane of the carboxylate group, with O—C—C—Cl torsion angles of −11.2 (2) and 169.62 (11)°, which is in good agreement with all ten organic crystal structures containing the chloroacetate anion found in the CSD (no multiple entries, no errors, only organic).

The bond lengths in the carbon chain of the dication exhibit a similar pattern to those found in hexane-1,6-diaminium

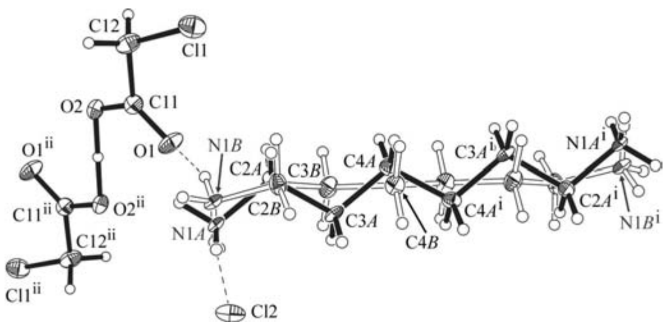


Figure 1
An anisotropic ellipsoid representation (50% probability) of the ionic components of (I), together with the atom-labelling scheme and a comparison of the two alternative positions of the cation. The part of higher occupancy is drawn with solid lines. H atoms are depicted as spheres with arbitrary radii. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (iv) $-x+1, -y+1, -z+1$; (v) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+1$.]

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dichloride (Binnie & Robertson, 1949; Borkakoti *et al.*, 1978), in which there is an alternation of C—C bond lengths. Such a pattern was not observed, however, in the structure of hexane-1,6-diaminium bis(chloroacetate) (Ortíz *et al.*, 2008). The structure of (I) was determined at 100 K, and differences in lengths between neighbouring bonds are still observable; however, they do not meet the standard test for difference (3 s.u.) and are probably a result of the disorder of the aliphatic chain.

Carboxylic acid moieties related by the centre of inversion at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) form a hydrogen-bonded dimeric monoanion (*cf.* Fig. 1), in which one carboxylate group is neutral and one negatively charged. The O···H···O hydrogen bond is short, with an O···O distance of 2.452 (2) Å, with the H atom centred on the inversion centre. Refinement resulted in a relatively high isotropic displacement parameter. This suggests that it is, in fact, disordered between two positions. This is another example of an acid salt, $M\text{H}X_2$, of a mono-carboxylic acid, HX, belonging to type A (Speakman & Mills, 1961; Ichikawa, 1972), with a short hydrogen bond and an H atom situated on an inversion centre. The mean bond length [2.466 (3) Å] given by Speakman & Mills is in good agreement with our results. The two C—O bond lengths are different [C11—O1 = 1.2284 (18) Å and C1—O2 = 1.2848 (18) Å], with the shorter bond not involved in the hydrogen bonding. The difference Fourier map of this region without any H atom clearly shows the significant spread of the residual electron density between the centrosymmetric pair of O atoms.

The three-dimensional network of hydrogen bonds is, along with the electrostatic interactions between the charged species, the main building force in the crystal structure of (I) (Fig. 2). There are three strong bonds between the NH donor groups and oxygen or chloride acceptors (Table 1). A weaker N—H···O bond can probably be regarded as a secondary interaction, with unfavourable N—H···O angles of *ca* 119°. The Cl atom of the chloroacetate anion does not participate in hydrogen-bond formation, as was observed by Ortíz *et al.* (2008).

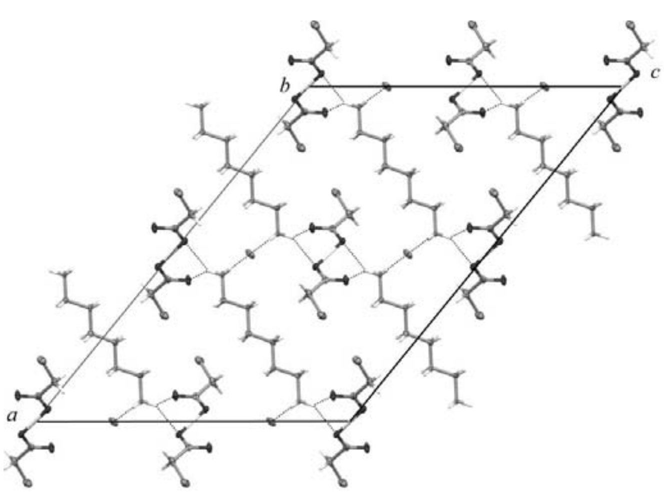

Figure 2
The molecular ladder-like packing of the ionic species viewed along the *b*-axis direction. Hydrogen bonds are depicted as dashed lines.

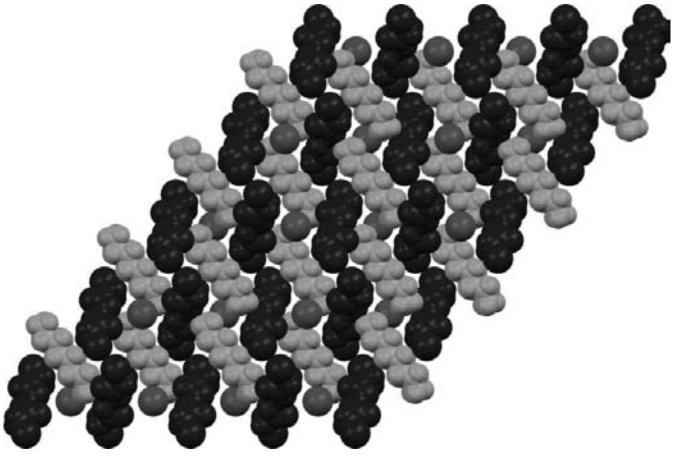

Figure 3
A space-filling representation of the crystal structure; the layers of charged species are shown with different shades of grey (the view is along the *b*-axis direction).

Similar interactions were found in other hexane-1,6-diaminium salts, *viz.* the dichloride [N···Cl = 3.145 (3)–3.191 (2) Å; Borkakoti *et al.*, 1978] and the bis(chloroacetate) [N···O = 2.739 (2)–2.814 (2) Å; Paul & Kubicki, 2009]. Likewise, in the series of tri-, di- and acetate salts, three stronger N—H···O and two weaker N—H···Cl/O interactions were observed.

Because of the dication disorder, the hydrogen-bond network of each component should be treated separately. Using graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995), there is an $R_4^2(8)$ ring motif, typical for diaminium salts, found only for the '*A*' component. However, the other typical motif – $R_4^4(26)$, which is present in tri-, di-, mono- and acetic acid salts – is absent from both forms. Similar to the structure of the bis(chloroacetate), (I) can be described as a molecular ladder, with a parallel pair of $C_4^3(14)$ (form '*A*') or $C_4^4(16)$ (form '*B*') chains acting as the uprights of the ladder, and the cations providing the rungs. Such a ladder can be observed running along the [001] direction (Fig. 2). The ends of the dicationic chains lying in the same layer are linked *via* two sets of N1*A*—H1*A*1···Cl2 and N1*A*—H1*A*3···Cl2$^{\text{i}}$ (form '*A*') or one set of N1*B*—H1*B*3···Cl2 (form '*B*') hydrogen bonds (symmetry codes as in Table 1) so that the 'upper' part of one cation is connected with the 'lower' part of the second cation. The different layers are connected *via* two sets of N1*A*—H1*A*2···O1$^{\text{iii}}$ and N1*A*—H1*A*2···O2$^{\text{ii}}$ (form '*A*') or three sets of N1*B*—H1*B*1···O1$^{\text{iii}}$, N1*B*—H1*B*2···O1$^{\text{iv}}$ and N1*B*—H1*B*2···O2$^{\text{ii}}$ (form '*B*') hydrogen bonds, where the last interaction of each form is weak and probably secondary. The space-filling representation of the structure (Fig. 3) highlights the alternating layers of dications and anions, similar to those found in the course of studies of a parallel series of hexane-1,6-diaminium salts (Paul & Kubicki, 2009).

Experimental

Hexane-1,6-diamine (1 mmol) was dissolved in a water–methanol (1:1) mixture (2 ml) and mixed successively with chloroacetic acid and hydrochloric acid (2:1, 1.4 mmol). The excess of acid was used to assure complete protonation of both amine groups. The solution was heated and then allowed to cool to ambient temperature for slow crystallization. After a few days, transparent crystals suitable for X-ray diffraction were obtained.

Crystal data

$C_6H_{18}N_2^{2+}\cdot C_4H_5Cl_2O_4^{-}\cdot Cl^{-}$
$M_r = 341.65$
Monoclinic, $C2/c$
$a = 25.702$ (5) Å
$b = 4.4419$ (4) Å
$c = 18.718$ (4) Å
$\beta = 129.14$ (3)°
$V = 1657.4$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.56$ mm^{-1}
$T = 100$ K
0.3 × 0.3 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with an Eos CCD detector
2850 measured reflections
1614 independent reflections
1301 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.062$
$S = 1.05$
1614 reflections
135 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*1···Cl2	0.89	2.12	3.003 (6)	171
N1*A*—H1*A*3···Cl2$^{\rm i}$	0.89	2.18	3.059 (7)	167
N1*A*—H1*A*2···O2$^{\rm ii}$	0.89	2.21	2.988 (7)	146
N1*A*—H1*A*2···O1$^{\rm iii}$	0.89	2.55	3.006 (7)	113
N1*B*—H1*B*3···Cl2	0.89	2.58	3.366 (5)	147
N1*B*—H1*B*1···O1$^{\rm iii}$	0.89	1.90	2.767 (6)	164
N1*B*—H1*B*2···O1$^{\rm iv}$	0.89	1.99	2.761 (6)	144
N1*B*—H1*B*2···O2$^{\rm ii}$	0.89	2.42	2.922 (6)	116
O2···H1···O2$^{\rm v}$	1.23	1.23	2.452 (2)	180

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

The disorder applies to all hexane-1,6-diaminium atoms; the two disorder components cross each other at the middle of the C4—C4′ bond, at the inversion centre. Atoms H12*A* and H12*B* of the chloroacetate unit were located in a difference map and refined freely, and all other H atoms were positioned geometrically (N—H = 0.89 Å and C—H = 0.97 Å) and were refined using a riding model, with $U_{\rm iso}$(H) values set at 1.2 (CH$_2$ groups) and 1.5 (NH$_3$) times the $U_{\rm eq}$ value of the carrier atom. C—N bond lengths were restrained to a target value of 1.49 (1) Å.

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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3035). Services for accessing these data are described at the back of the journal.

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