

The crystal packing modes of hexane-1,6-diaminium salts with acetic, mono-, di- and trichloroacetic acids

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ARTICLE INFO

Article history:

Received 22 July 2009

Accepted 19 September 2009

Available online 26 September 2009

Keywords:

Hexane-1,6-diaminium

Conformation

Disorder

Crystal packing

Hydrogen bonds

ABSTRACT

The crystal structures of three salts of hexane-1,6-diamine: acetate ($C_6H_{18}N_2^{2+} \cdot 2(C_2H_3O_2)^-$), dichloroacetate ($C_6H_{18}N_2^{2+} \cdot 2(C_2HCl_2O_2)^-$) and trichloroacetate ($C_6H_{18}N_2^{2+} \cdot 2(C_2Cl_3O_2)^-$) have been determined by X-ray diffraction at 100(1) K. In all three cases the cations are symmetrical, and occupy the special positions, on the centres of inversion in the space group $P2_1/c$. The conformation of the cation is fully extended (*ttttt*) in the case of acetate and trichloroacetate, while it is folded (*tg⁺tg⁻t*) in the dichloroacetate. The C–C bond lengths in the anions are systematically longer with the growing number of chlorine atoms. Together with the recently described chloroacetate [15], these structures were used to the analysis of the influence of the chlorine atoms on the crystal packing. In this case, chlorine atoms play – if any – only secondary role in the determination of the crystal structures. The patterns of relatively strong N–H \cdots O hydrogen bonds are quite robust throughout the series. The changes in the packing involve the mutual disposition of the charged cationic and anionic layers, but they seem to be more dependent on the conformation of the cation than on the presence of chlorine atoms.

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1. Introduction

α,ω -Diamino aliphatic alkanes are the basic compounds, which readily form salts with both, strong organic and inorganic acids. It results usually in formation of the appropriate dication, which is quite flexible and tends to interact with counterions through the network of hydrogen bonds, striving to a high symmetry framework. This tendency can be used in a crystal engineering, for designing materials with layered structure (e.g. [1] and references therein).

Hexamethylenediamine is used in industry for the polymers production, in particular in processes which produce nylon66 (in reaction with adipic acid) and polyurethane.

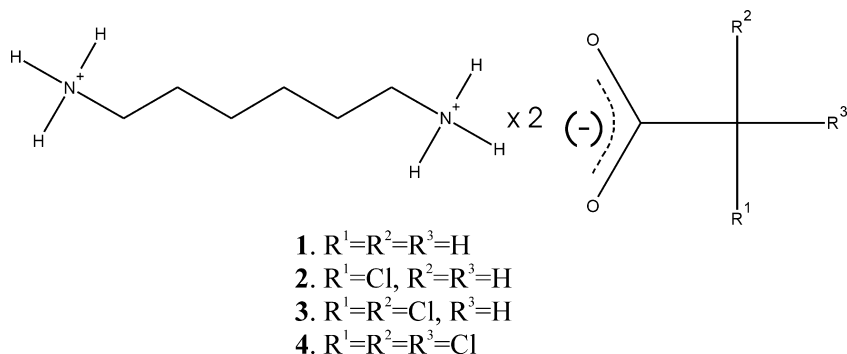
In the Cambridge Structural Database [2] (Version 5.30, October 2008, no multiple entries, no errors) there are 106 crystal structures having hexane-1,6-diaminium cation – 38 organics and 68 organometallics – significantly more than structures with pentane-1,5-diaminium (48) and heptane-1,7-diaminium (10) dications. It confirms the general rule, that the compounds with even number of carbon atoms in an aliphatic chain are relatively more willing to crystallize, what can be recognized as another example of even–odd effect [3,4]. Among 38 organic structures, in 27 cases (71%) dication exists in a fully extended conformation *ttttt* (*t* stands for *trans*), while other conformational possibilities are represented by no more than three examples. The situation is quite different for

organometallics: only in 26 of 68 structures (38%) the dications have all-*trans* conformation. Also in this case, however, there are no clear preferences for other conformations. It is noteworthy that in organometallics the dications of the one structure can present different chain arrangement more often than in organic structures (11 and 2, respectively). In the organic batch there are 18 cases (48%) of dications situated at the inversion centre and 4 in another special position, while in the organometallic batch 28 (41%) and 11, respectively.

The structures of different salts are occasionally disordered – among a total of 106 entries, there are 31 reported as disordered (7 organic, 24 organometallic). Among the 7 organic structures, the disorder is found in the following fragments: 4 cations [5–8], 2 solvents [9,10] and 1 counterion [11]. The organometallic disordered batch repeats this pattern – we found 13 cations, 7 solvents and 5 counterions disordered. Moreover, there are single cases of host–guest systems where dications are disordered about inversion centre, because the guest must occupy special position having higher site symmetry than the molecular symmetry [5].

The structures of salts of α,ω -diamino aliphatic alkanes provide also the opportunity of studying the intermolecular interactions and their mutual hierarchy in the series of similar structures. As there are good hydrogen bond donors and usually also acceptors, the interesting question might be if any other interactions can compete with the hydrogen bonds. The influence of halogen atoms seems to be especially important. For instance, the role of covalently-bound chlorine atoms in the crystal structures can be quite

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Scheme 1. Scheme presenting the salts series of hexane-1,6-diamine with acetic acid derivatives.

different: they can act as a weak acceptor of hydrogen bonds, or take part in so-called halogen bonds (for instance [12] and references therein). There were also explanations of that role based on so-called 'chlorophobic interactions' [13,14].

In the course of our ongoing studies on the intermolecular interactions we have determined the crystal structures of a series of hexane-1,6-diaminium salts with a series of derivatives of acetic acid: acetic acid itself (hereinafter referred to as **1**, cf. Scheme 1), dichloroacetic acid (**3**) and trichloroacetic acid (**4**). Very recently Ortiz et al. [15] published the structure of the fourth salt of the series, hexamethylenediammonium bis(chloroacetate). We will largely cite this structure, as **2**, in order to compare it with our results.

2. Experimental

In order to synthesize the compounds, 1 mmol of 1,6-diaminohexane was dissolved in 2 ml of water–methanol solution (1:1) and mixed successively with 1.4 mmol of: acetic acid (**1**), dichloroacetic acid (**3**) and trichloroacetic acid (**4**) (excess of acid was used to assure complete protonation of both amino groups). The solutions were heated and then placed in a well ventilated room at ambient temperature for slow crystallization. After few days, transparent crystals suitable for X-ray diffraction were obtained for compounds (**1**) and (**4**), and the third substance was recrystallized with the addition of acetonitrile and treated as described above.

Melting points were measured using the MEL-TEMP capillary device (ELECTROTHERMAL, USA), with the temperature rising rate of 2 K/min (cf. Table 1). Crystals of the compounds (**1**) and (**3**) were melting homogeneously at given temperatures, while for the crystal of compound (**4**) the temperature indicates a moment of a decay (in this temperature the crystal seems to melt, and then a part of the sample sediments at the side of the capillary).

Diffraction data were collected at 100(1) K by the ω -scan technique, on a KUMA-KM4CCD diffractometer [16] with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz-polarization effects as well as for absorption [16]. Accurate unit-cell parameters were determined by a least-squares fit of 1041 (**1**), 6610 (**3**), and 7278 (**4**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [17] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [18]. Scattering factors incorporated in SHELXL97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + A \cdot P^2 + B \cdot P]$, where $P = [\text{Max}(F_o, 0) + 2F_c^2]/3$. The final values of A and B are listed in Table 1. In the case of **3** an empirical extinction correction was also applied, according to the formula: $F'_c = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$, where x refined at 0.0143(14). All non-hydrogen atoms were refined

Table 1

Crystal data, data collection and structure refinement.

Compound	1	2	3
Formula	$C_6H_{18}N_2 \cdot 2(C_2H_3O_2)$	$C_6H_{18}N_2 \cdot 2(C_2HCl_2O_2)$	$C_6H_{18}N_2 \cdot 2(C_2Cl_3O_2)$
mp(K)	427	420	391
Formula weight	236.31	374.08	442.96
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	5.5831(8)	9.9693(3)	9.7153(10)
b(Å)	13.9610(18)	10.8779(3)	11.9043(8)
c(Å)	8.2907(11)	7.8315(2)	9.3345(10)
β (°)	101.652(13)	95.538(3)	116.564(16)
V(Å ³)	632.91(15)	845.32(4)	965.61(16)
Z	2	2	2
D_x (g cm ⁻³)	1.24	1.47	1.53
F(0 0 0)	260	388	452
μ (mm ⁻¹)	0.095	0.712	0.2905
Crystal size(mm)	0.4 × 0.4 × 0.2	0.4 × 0.4 × 0.2	0.6 × 0.2 × 0.2
θ range(°)	2.90–26.81	3.22–28.21	2.34–27.74
hkl range	$-3 \leq h \leq 7$ $-6 \leq k \leq 17$ $-10 \leq l \leq 8$	$-12 \leq h \leq 13$ $-14 \leq k \leq 14$ $-9 \leq l \leq 9$	$-12 \leq h \leq 12$ $-15 \leq k \leq 15$ $-12 \leq l \leq 11$
Reflections			
Collected	2128	8757	9728
Unique (R_{int})	1215(0.028)	1862(0.042)	2148(0.014)
With $I > 2\sigma(I)$	911	1630	1872
No. of parameters	121	131	165
Weighting scheme			
A	0.037	0.0593	0.0343
	0	0.2194	1.0481
R(F)[$I > 2\sigma(I)$]	0.035	0.029	0.031
wR(F^2) [$I > 2\sigma(I)$]	0.071	0.080	0.076
R(F) [all data]	0.050	0.034	0.037
wR(F^2) [all data]	0.075	0.082	0.080
Goodness of fit	0.991	1.077	1.047
max/min $\Delta\rho$ (e Å ⁻³)	0.17/–0.19	0.54/–0.30	0.84/–0.78

anisotropically, hydrogen atoms were located in subsequent difference Fourier maps and their positional and isotropic displacement parameters were freely refined. The trichloroacetate anion in **4** was found disordered, the chlorine atoms are found in two alternative positions. The site occupancy factors for both sets refined at 0.917(2) and 0.083(2) for more and less occupied parts, respectively. Interestingly enough, even though the s.o.f. of the second set is quite low, the appropriate atoms could be anisotropically refined, only weak constraints for two C–Cl distances were applied. Relevant crystal data are listed in Table 1, together with refinement details.

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