Journal of Molecular Structure 966 (2010) 107–112

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The crystal packing modes of butane-1,4-diamine salts with acetic, di- and trichloroacetic acids at 100 K

Agnieszka Paul *, Maciej Kubicki

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

ARTICLE INFO

Article history:
Received 10 November 2009
Received in revised form 3 December 2009
Accepted 5 December 2009
Available online 12 January 2010

Keywords:
Butane-1,4-diaminium
Conformation
Disorder
Crystal packing
Hydrogen bonds

ABSTRACT

The crystal structures of three salts of butane-1,4-diamine: acetate (($C_4H_{14}N_2^{2+} \cdot 2(C_2H_3O_2)^-$), dichloroacetate (($C_4H_{14}N_2^{2+} \cdot 2(C_2HCl_2O_2)^-$) and trichloroacetate (($C_4H_{14}N_2^{2+} \cdot 2(C_2Cl_3O_2)^-$) were determined by X-ray diffraction at 100 K. In all these cases the dication is either symmetrical and situated at the inversion center or disordered about the inversion center, in the $P2_1/c$ space group. The conformation of dication is *ttt* (*t-trans*) for acetate and trichloroacetate, or tg^-t and tg^+t (*g-gauche*) – for dichloroacetate, and this last salt undergoes the phase transition in higher temperature. The role of covalently bonded chlorine atoms in the determination of the crystal packing, at least in this case, is only the secondary one. The potential halogen bonds or N—H···Cl hydrogen bonds do not compete successfully with the N—H···O hydrogen bonds of different strength which – along with the coulombic interactions between the charged species – are certainly the main driving force of the crystal packing along this series of compounds. The different packing modes are pronounced in relative cation–dication arrangement in the layer structure.

1. Introduction

α,ω-Diamino aliphatic alkanes are the simple organic compounds with predictable basic properties, resulting from two amino groups attached at two ends of a carbon chain. They easily react with organic and inorganic acids, forming appropriate salts, composed of conformationally flexible (di)cations, which in the crystal structures can (and do) interact with the anions by the networks of hydrogen bonds. This tendency, together with an inclination towards forming the highly symmetrical networks can be used in crystal engineering, in designing the new materials, for example having a layer structure [1,2].

Butane-1,4-diamine, also known as putrescine, is a biogenic diamine, playing an important role in several biological processes (ex. in the stabilizing effect on secondary and tertiary structures of nucleic acids), where it appears as protonated cation interacting through the hydrogen bonds [3,4]. Similarly to hexane-1,6-diamine, putrescine is widely reacted with adipic acid to form polyamide – Nylon-4,6 – which is manufactured under a trade name Stanyl. Different studies about the crystal structures of diamine salts reveal that putrescinium dication tends to be situated at the crystallographic inversion center or presents a symmetric conformation with non-crystallographic inversion center [4–7].

In the Cambridge Structural Database ([8] Version 5.30, October 2008) the putrescinium dication was found in the crystal structures of 31 organic and 82 organometallic compounds (no multiple hits; no errors). The fully extended conformation of this ion is observed in 61% of the organic structures (at least one dication in the structure presents the *ttt* conformation) and the other possible arrangements are in minority. The even–odd effect (which manifests in this case as the preference for crystallization of the salts containing cations with the even number of carbon atoms), that was observed for diamines with longer aliphatic chains [1] is not observed for putrescine and its closest homologues, as there are 202, 113 and 48 structures having the dications of propylene-1,3-diamine, butane-1,4-diamine and pentane-1,5-diamine, respectively.

The disorder in crystal structures containing butane-1,4-diaminium dication is found in 22% and 28% of organic and organometallic structures, respectively (similarly to the structures with hexane-1,6-diaminium dication, where disorder appears in 6% and 23%, respectively). In the organic batch the disorder of solvent appears twice [9,10] while the carbon chain of diamine is disordered in the crystal structures of 5 substances [4,6,11–14]. In the organometallic batch the disorder is more common, with 13 cases of cations, 4 of counterion, 4 of solvent and 2 with both ions disordered.

In the series of the title salts – where the anions have growing number of chlorine atoms – we were able to investigate the influence of the number of chlorine atoms on the crystal packing modes and therefore the impact of halogen atoms on the crystal architecture in the cases, where the strong hydrogen bonds might be the main packing factor. We could therefore analyze the presence of

---

* Corresponding author. Tel.: +48 (0)61 8291256; fax: +48 (0)61 8291505.
E-mail address: agapaul@amu.edu.pl (A. Paul).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.12.016

so-called 'halogen bonding' (e.g., [15]), which was reported to be able to successfully compete with hydrogen bonds (e.g. [16]).

In the course of our studies on diamine salts we determined the crystal structures of the series of butane-1,4-diamine salts with acetic acid and its derivatives: acetic acid (referred as **1**), dichloroacetic acid (**2**) and trichloroacetic acid (**3**). In spite of many efforts, we were not able to obtain the crystals of the chloroacetate salt.

2. Experimental

In order to synthesize the compounds **1**–**3**, 1 mmol of butane-1,4-diamine was dissolved in 2 ml of methanol and mixed successively with 2.4 mmol of acetic acid (**1**), dichloroacetic acid (**2**) and trichloroacetic acid (**3**) (excess of acid was applied to assure complete protonation of both amino groups). The solutions were heated and afterwards placed in well ventilated room for a slow crystallization. After few days the transparent crystals of (**1**), suitable for X-ray diffraction were obtained, while the remaining salts were recrystallized from 2 ml of methanol:nitromethane (1:1) solution and treated as before.

Melting points were measured using MEL-TEMP capillary device (ELECTROTHERMAL, USA), with temperature raising rate of 2 K/min (cf. Table 1). The results suggest, that the strongest interactions occur in salt **1**, where the chlorine atoms are absent. Diffraction data were collected at 100 (**1**) K by ω-scan technique on KUMA-KM4CCD (**2**) and XCALIBUR EOS (**1**, **3**) four circles diffractometers [17] with graphite-monochromatized Mo Kα radiation ($\lambda = 0.70073$ Å). The temperature was controlled by Oxford Instruments Cryosystems cooling devices. The data were corrected for Lorentz-polarization effects and absorption [17]. The unit cell parameters were determined by a least-squares fit of 4746 (**1**), 1409 (**2**) and 6341 (**3**) reflections. 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.

In each case the function $\Sigma w(|F_o|^2-|F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + A.P^2 + B.P]$, where $P = (F_o^2 + 2F_c^2)/3$. The final values of A and B are listed in Table 1. In the case of (**1**) an empirical extinction correction was also applied, according to the formula: $F_c' = kF_c[1 + 0.001 \times F_c2\lambda3/\sin(2\theta)]^{-1/4}$, with the extinction coefficient equal 0.071(9). All non-hydrogen atoms were refined anisotropically. The dication in (**2**) was found disordered, two middle carbon atoms are disordered about the inversion center, with equal site occupancy factors. All hydrogen atoms were located in subsequent difference Fourier maps and their positional and isotropic displacement parameters were freely refined, with exception for structure (**2**), where hydrogen atoms connected to carbon C2 were located basing on the geometry of neighboring atoms.

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 753515 **(1)**, CCDC 753514 **(2)** and CCDC 753516 **(3)**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44 1223 336 033, e-mail:deposit@ccdc.cam.ac.uk, or www:www.ccdc.cam.ac.uk.

3. Results and discussion

Figs. 1–3 depict the anisotropic ellipsoid representations of the title salts. The selected geometric parameters are listed in Table 2).

3.1. Molecular geometry

The values of bond lengths and angles do not differ significantly along the series (cf. Table 2), with the exception for dication of (**2**), which is disordered about the inversion centre. In cations of (**1**)

Table 1
Crystal data, data collection and structure refinement.

Compound	1	2	3
Formula	$C_4H_{14}N_2{\cdot}2(C_2H_3O_2)$	$C_4H_{14}N_2{\cdot}2(C_2HCl_2O_2)$	$C_4H_{14}N_2{\cdot}2(C_2Cl_3O_2)$
m.p. (K)	437–439	422–424	383–385
Formula weight	208.26	345.02	414.91
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	5.7029(2)	8.4893(9)	8.7503(4)
b(Å)	12.4341(4)	6.6312(5)	7.7688(3)
c(Å)	8.5276(3)	13.6909(14)	13.9931(8)
β(°)	103.584(4)	107.832(11)	112.118(5)
V(Å^3)	587.78(4)	733.69(13)	881.24(7)
Z	2	2	2
D_x(g cm^{-3})	1.177	1.562	1.564
F(0 0 0)	228	354	420
μ(mm^{-1})	0.09	0.81	0.99
Crystal size (mm)	0.7 × 0.5 × 0.5	0.5 × 0.15 × 0.15	0.5 × 0.35 × 0.3
Θ range (°)	3.3–28.9	3.5–26.7	3.1–28.9
hkl range	$-7 \leqslant h \leqslant 7$	$-7 \leqslant h \leqslant 10$	$-11 \leqslant h \leqslant 11$
	$-15 \leqslant k \leqslant 16$	$-7 \leqslant k \leqslant 8$	$-10 \leqslant h \leqslant 10$
	$-11 \leqslant l \leqslant 11$	$-17 \leqslant l \leqslant 6$	$-18 \leqslant h \leqslant 18$
Reflections:			
Collected	6592	2302	10157
Unique (R_{int})	1433	1337	2128
With $I > 2\sigma(I)$	1268	1106	1814
No. of parameters	105	119	119
Weighting scheme:			
A	0.0495	0.0420	0.0301
	0.09	0.14	0.10
$R(F)$ [$I > 2\sigma(I)$]	0.0290	0.0311	0.0256
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0823	0.0739	0.0585
$R(F)$ [all data]	0.0336	0.0398	0.0321
$wR(F^2)$ [all data]	0.0838	0.0770	0.0597
Goodness of fit	1.075	1.056	1.076
Max/min $\Delta\rho$ (e Å^{-3})	0.34/−0.17	0.50/−0.39	0.38/−0.27