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Crystal Structure of Tris(2-hydroxyethyl)ammonium Bromide

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The crystal structure of tris(2-hydroxyethyl)ammonium bromide, $[HN(CH_2CH_2OH)_3]Br$, was determined as rhombohedral by single crystal X-ray diffractometer. The final R value was found to be 0.032 for 576 observed reflections. The crystal consists of layers of hydrogen-bonded cations, $[HN(CH_2CH_2OH)_3]^+$ and anions, Br^-. Within a layer every cation donates and every anion accepts three hydrogen bonds. In the cation, trifurcated intramolecular hydrogen bonds are formed due to the surrounding of the hydrogen atom bonded to the N atom by the 2-hydroxyethyl groups.

Introduction

Tris(2-hydroxyethyl)amine, alternatively named as triethanolamine and 2, 2$'$, 2$''$-nitrilotrisethanol, has been used as a complexing agent with di- and trivalent transition metal ions[1–4]. Tris(2-hydroxyethyl)amine is also a weak base and forms ionic salts when reacted with acids. Mootz and Co-workers[5,6] examined the crystal structure of the chloride and hydrogensulfide salts of this compound as well as itself in the frozen state.

In the course of the synthesis of some novel transition metal complexes of tris(2-hydroxyethyl)amine, we have carried out X-ray crystal analysis of Ni (II) complex of this ligand[7]. In this paper, we report the crystal structure of bromide salt of tris(2-hydroxyethyl)amine.

Experimental

Tris(2-hydroxyethyl)ammonium bromide was prepared by the reaction of tris(2- hydroxyethyl)amine with hydrogen bromide and recrystallised from an alcohol-water solution. X-ray diffraction data were obtained from a suitable colourless tabular crystal (0.6x0.6x0.34 mm) on a Nicolet P3 four-circle diffractometer with $MoK\alpha$ radiation ($\lambda = 0.71043 Å$) at 293 K. The intensity data was measured for an I-centred monoclinic cell with $\underline{a} = 9.164(6), \underline{b}=8.471(5), \underline{c} = 12.439 Å$ and beta $=96.57(4)^\circ$ and later re-indexed by application of the transformation matrix 0,-1, 0; -0.5, 0.5, -0.5; 2,0, -1 for conformity with the true rhombohedral cell referred to the hexagonal axes.

Data collection and cell refinement were carried out by Nicolet P3 software. Data collection used 2Θ scan rates of 5.33 $(Ip < 150)$ to $58.6(Ip < 2500)^{\circ}min^{-1}$, where Ip was the prescan intensity. Scan widths were 2Θ= 2.4 to 2.8°. A local program was used for data reduction[8]. The cell parameters were calculated and refined from the setting angles of 14 reflections with Θ ranging from 10.5° to 15.0°. A total 1557 reflections were measured and the number of independent reflections was 688, of which 576 with $I > 2\sigma$ (I) were observed and used for refinement. Structure refinement was carried out by full matrix least squares[9]. The parameters given by Mootz et al.[6] for the corresponding isotropic chloride were adopted as starting parameters for the non-hydrogens and it turned out that their structure had to be inverted, reducing R from about 0.06 to 0. 03, to yield the best fit with the present data.

All non-H were refined anisotropically. H attached to N (HN in Table 3) was refined isotropically. Methylene hydrogens were placed in calculated positions with $C - H = 0.95\mathring{A}$ and refined riding upon the C to which they were attached with a common group U_{iso}. The positions of the hydroxyl H could not be determined. All computations were performed on a SUN SPARC server (UNIX operating system) at the Computing Centre of the University of Aberdeen. The scattering factors for C, O, N and H atoms were taken from the International Tables for X-ray crystallography[10] and the molecular graphic was obtained by using the ORTEX graphic program[11].

Results and Discussion

The lattice parameters of tris(2-hydroxyethyl)ammonium bromide are given in Table 1. The parameters indicate that the salt has a rhombohedral crystal structure and each unit cell contains six molecules of the compound. The experimentally measured density value (1.590 g cm^{-3}) of the crystal is well consistent with the density value (1.604 g cm^{-3}) determined by X- ray diffractometry. The atomic coordinates and isotropic and anisotropic thermal parameters are given in Table 2 and 3, respectively. Table 4 lists the selected bond distances and angles of tris(2-hydroxyethyl)ammonium bromide and compares them with chloride and hydrogensulfide salts of the same cation. All ions are located on a three fold rotation axes as shown in Figure 1.

Table 1. Cell parameters of $[HN(CH_2CH_2OH)_3]Br$

a ($\mathring{A}$)	8.418(5)	$\alpha(^{\circ})$	90
b ($\mathring{A}$)	8.418(5)	$\beta(^{\circ})$	90
c ($\mathring{A}$)	23.298(1)	$\gamma(^{\circ})$	120
V ($\mathring{A}^3$)	1429(1)	R	0.032
$^{*}D(gcm^{-3}$	1.604	wR	0.040
**Z	6	Space group	R_{3C}

* experimentally determined as 1.509

** number of molecules in the unit cell

A search of the Chemical Database Service[12] reveals that the crystal structure of tris(2-hydroxyethyl)-ammonium bromide is very similar to those previously reported for the chloride and hydrogensulfide salts with the same cation by Mootz et al.[6]. In fact, the three salts are isotypic with each other. The crystal contains the puckered layer of hydrogen-bonded cations, $[HN(CH_2CH_2OH)_3]^+$, and anions, Br^-. The layers in the crystal are held together by the hydrogen bonding. Within a layer every cation donates and every anion accepts three hydrogen bonds although the length of the hydrogen bond $[O \ldots Br = 3.294(5)Å]$ is somewhat longer than those of observed in tris(2-hydroxyethyl) ammonium chloride $[O \ldots Cl = 3.156(2)Å]$ and tris(2-hydroxyethyl) ammonium hydrogensulfide $[O \ldots S = 3.172(2)Å]$ (Table 4). Table 4 also shows that the change of the anions in the structure does not significantly alter the bond distances and angles of the cation.

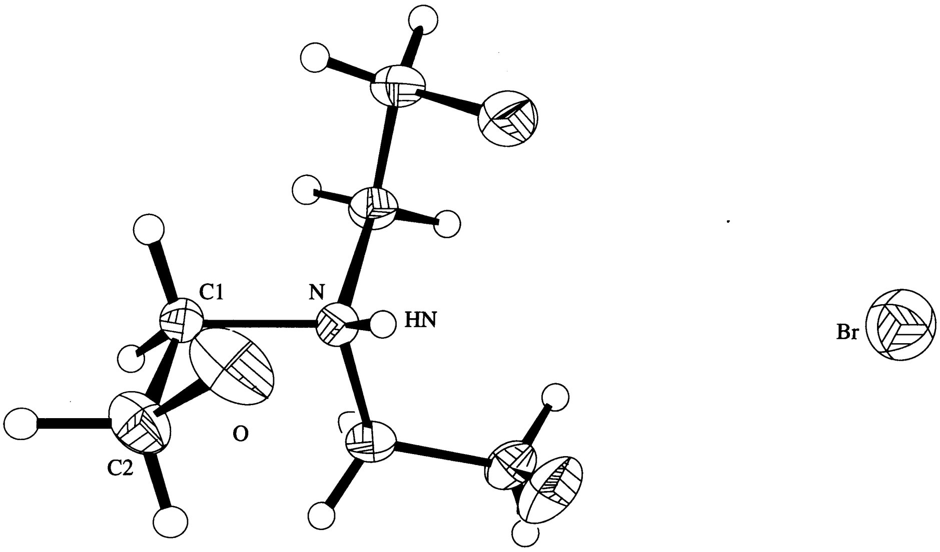

Figure 1. A cation-anion pair in the structure of $[HN(CH_2CH_2OH)_3]Br$ with non-H vibration ellipsods at the 40% probability level and H, other than hydroxyl H which were not determined, shown as spheres of arbitrary radius. The complete cation as shown is generated by the operation of a 3-fold axis passing through Br, HN and N, and only the atoms present in the asymmetric unit are labelled

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for non hydrogen atoms with e.s. d' s in parantheses

	x/a	y/b	z/c	U_{eq^*}
Br	0	0	-0.04	0.0334(2)
O	-0.2913(5)	-0.1907(7)	-0.1563(2)	0.051(1)
N	0	0	-0.0802(3)	0.025(1)
C1	-0.1859(4)	-0.1492(5)	-0.0606(3)	0.0305(9)
C2	-0.3343(7)	-0.1594(5)	-0.0996(3)	0.038(1)
$^{**}H1A$	-0.1888	-0.2635	-0.0613	
H1B	-0.2072	-0.1237	-0.0226	
$^{**}H1A$	-0.3359	-0.0474	-0.0982	
H2B	-0.4506	-0.2575	-0.0882	
HN	0	0	-0.1155	

$^*U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

** and H2 indicate the hydrogen atoms bonded to C1 and C2, respectively

Table 3. Anisotropic thermal parameters ($Å^2$) for non hydrogen atoms with e.s d's in parantheses

	U11	U22	U33	U23	U13	U12
Br	0.0326(3)	0.0326(3)	0.0350(4)	0	0	0.0163(1)
O	0.039(2)	0.071(2)	0.045(2)	-0.024(2)	-0.012(2)	0.030(2)
N	0.026(2)	0.026(2)	0.022(3)	0	0	0.013(1)
C1	0.026(2)	0.025(2)	0.033(2)	0.004(1)	0.005(1)	0.007(1)
C2	0.027(2)	0.044(2)	0.042(2)	-0.006(2)	-0.001(2)	0.017(1)

In the cation, as a result of surrounding of the hydrogen atom bonded to the N atom by the 2-hydroxyethyl groups, trifurcated strong intramolecular hydrogen bonds $[N - H(\ldots O)_3 = 2.36(6)\text{Å}]$ are formed. The geometry of the cation is mainly determined by the function of these hydrogen bonds and also resembles that of the molecules in the crystals of tris(2-hydroxyethyl)amine[5].

Table 4. Comparison of selected interatomic distances (Å) and angles (°) of the title compound with other two tris(2-hydroxyethyl) ammonium salts*.

	$^8Br^-$	$^bC1^-$	$^cSH^-$
Bond distances			
N-C1	1.507(4)	1.505(1)	1.505(2)
C1-C2	1.512(7)	1.511(2)	1.504(3)
C2-O	1.429(8)	1.420(2)	1.413(3)
HN-N	0.82(5)	0.88(4)	0.94(6)
O...HN	2.36(6)	2.36(1)	2.30(2)
N...HO	2.792(7)	2.805(2)	2.782(3)
$^{**}X^i \ldots HO$	3.294(5)	3.156(2)	3.172(2)
Bond angles			
C2-C1-N	110.4(4)	111.0(1)	110.8(2)
C1-C2-O	106.7(4)	107.0(1)	107.1(2)
C1-N-HN	107.7(6)	108(1)	107(1)
C1-N-C1^{ii}	111.2(4)	111.3(1)	111.5(1)
O...HN-N	114(7)	112(2)	112(2)
$Br^i \ldots$ O-C2	81.2(2) -	-	
O$\ldots Br^i \ldots O^{iii}$	93.1(1)	-	-

*(a) this study; (b) and (c) tris(2-hydroxyethyl)ammonium bromide and hydrogensulfide, respectively[6].

** X indicates hydrogen-bonded atoms such as Br, Cl and S

Symmetry codes : $(i) x - 2/3, y - 1/3, z + 1/6$
$(ii) - y, x - y, z$
$(iii) - 1 - y, x - y, z$

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