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Ethylenediamine Tartrates. II. The Crystal and Molecular Structure of Ethylenediamine Ditartrate Dihydrate, $[2(C_4H_5O_6)^-][(C_2H_{10}N_2)^{2+}].2H_2O$

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During a study of the critical temperature of the crystal growth of anhydrous ethylenediamine (+)-tartrate by cooling the solution from 41·5 to 40 °C at a rate of 0·025 °C per day, a small number of well formed crystals were observed. These crystals were found to be a novel form of ethylenediamine tartrate, namely ethylenediamine ditartrate dihydrate. This dihydrated form crystallizes in the tetragonal space group $P4_12_12$ with unit-cell constants $a = 7{\cdot}531$ (4), $c = 30{\cdot}065$ (8) Å and $Z = 4$. Three-dimensional data were collected on an automatic diffractometer. The structure was solved by direct methods based on a cosine-invariant computation, and all the H atoms were located on a difference Fourier map. Refinement by block-diagonal least squares led to a final R value of 0·040 for 964 observed reflexions. The ethylenediammonium ion, located on a twofold axis of rotation, exists in the *gauche* conformation. The hydrogen tartrate ions, bound head-to-tail by a strong O–H···O hydrogen bond (2·526 Å), form infinite chains which are interlinked in pairs to form ribbons of negatively charged ions, with one set of ribbons parallel to **a** and another parallel to **b**. The ethylenediammonium ions are linked to these ribbons by a network of N–H···O and O–H···O hydrogen bonds.

Introduction

The present study forms part of a research project on the conformational analysis of tartrates and tartaric acids occurring in the solid state.

The conformation of the tartrate ion has been reported in a number of structures (Sadanaga, 1950; van Bommel & Bijvoet, 1958; Okaya, Stemple & Kay, 1966; Ambady, 1968; Ambady & Kartha, 1968; Hinazumi & Mitsui, 1972; Carlström, 1973; Yadava & Padmanabhan, 1973; Pérez, 1976*a*). Although it is possible to point out some common features of the overall shape, there still exist slight differences in certain equivalent bond lengths, valency angles and torsion angles. The majority of the available structural data has been obtained from room-temperature X-ray diffraction experiments. A systematic investigation of the differences which arise between equivalent bond lengths is somewhat hampered for the time being. However, valency angles appear to be less severely affected by the effects of thermal motion and an analysis of their variations or a statistical study of their distributions is possible.

The α-hydroxyl O atom is often found to lie in the same plane as the carboxyl group of the same half of the molecule or ion. However, some rotations of the carboxyl group away from the CCO(H) plane have been revealed. Ambady (1968) and Ambady & Kartha (1968) related the torsions and deformations to the environment of the carboxyl group with respect to the neighbouring cation and the hydrogen-bond network. In the crystal structure of anhydrous ethylenediamine (+)-tartrate, a rotation of 20° of the carboxyl group from perfect planarity was attributed to the resulting influence of hydrogen bonds holding together the carboxyl O atoms and the N atoms of the ethylenediammonium ion (Pérez, 1976*a*).

Our twofold interest in the crystal structures of tartrates resides in the collection of information about the molecular geometry in order to provide enough data to perform a statistical analysis as well as in studies of the conformational similitudes and/or differences which arise from the ionic or molecular character and of the hydrogen-bond schemes of the structures.

The present X-ray structure analysis has been performed on a novel (+)-tartrate salt of ethylenediamine: ethylenediamine ditartrate dihydrate $[2(C_4H_5O_6)^-][(C_2H_{10}N_2)^{2+}].2H_2O$.

Preparation

Monoclinic single crystals (which exhibit piezoelectricity) of anhydrous ethylenediamine (+)-tartrate (abbreviated to EDT) were grown in a supersaturated solution of ethylenediamine tartrate by the 'cooling' process. Studies of the crystal growth of EDT revealed

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that the substance has a critical temperature of 41 °C, above which anhydrous EDT forms, while a hydrated EDT remains stable in the presence of the saturated solution below the transition temperature. The hydrated EDT is unstable to moderate heat or to low relative humidity (Kohman, 1950; Klier & Shaki, 1955; Taylor, 1956; Walker & Kohman, 1952).

During a study of the critical temperature of the crystal growth of EDT by cooling the solution from 41·5 to 40 °C at a rate of 0·025 °C per day, a small number of well formed crystals were observed. After chemical characterization and preliminary X-ray investigation these crystals were found to be ethylenediamine ditartrate dihydrate. Furthermore, the crystals were shown to be stable up to around 100 °C where a reversible transition occurs (Pérez & Bonpunt, 1974).

Experimental

Weissenberg and precession photographs indicated that the crystals were tetragonal, space group either $P4_12_12$ or $P4_32_12$ (systematic absences: $00l$ $l \neq 4n$, $h00$ $h \neq 2n$). The unit-cell dimensions were obtained as part of the alignment process on an automatic diffractometer by a least-squares fit to the settings of 20 well centred reflexions. Crystallographic data are given in Table 1.

Table 1. *Crystal data*

$[2(C_4H_5O_6)^-][(C_2H_{10}N_2)^{2+}].2H_2O$; $M_r = 396{\cdot}3$; $F(000) = 840$ e
Tetragonal, $P4_12_12$, $Z = 4$; $D_o = 1{\cdot}54$, $D_c = 1{\cdot}529$ g cm^{-3}
$a = 7{\cdot}531$ (4), $c = 30{\cdot}065$ (8) Å; $V = 1705{\cdot}2$ Å^3
μ(Cu $K\alpha$) = 8·5 cm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å; $t = 20$ °C

Intensities were measured on a Siemens automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation (with a scintillation counter) for all the reflexions within one octant of the Cu sphere limited by $2\theta \leq 120°$. A 'five-points' measuring procedure was employed. The intensity of one reference reflexion, measured after each group of 50 reflexions, was found to decrease by about 5% of its initial value over the duration of the data collection. The data reduction was performed in the usual manner with the programs of Ahmed, Hall, Pippy & Huber (1966). In all, 1882 reflexions were measured, of which 129 were assigned zero intensity as the net count of each was less than $2{\cdot}5\sigma$, where σ is the standard deviation estimated from counting statistics. However, in the tetragonal space group the number of independent reflexions was reduced to 1031, of which 60 were assigned zero intensity. Because of the small absorption coefficient, no absorption correction was applied. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C, O and N, and from Stewart, Davidson & Simpson (1965) for H.

Structure determination and refinement

A set of normalized structure factors $|E|$ was obtained after isotropic temperature correction. The statistical averages are listed in Table 2.

Table 2. *E Statistics*

	Centrosymmetric	Experimental	Non-centrosymmetric
$\langle \|\|E\|^2 - 1\| \rangle$	0·968	0·763	0·736
$\langle E \rangle$	0·798	0·875	0·886

At the time this structure was studied, versions of the programs available for crystal structure determination could only accommodate triclinic, monoclinic and orthorhombic space groups. It was thus decided to solve the structure in the $P2_12_12_1$ orthorhombic space group instead of $P4_12_12$. Such a treatment decreases the amount of information on the symmetry relations between the molecules in the unit cell. This loss of information has to be taken into account in a way described elsewhere (Pérez, 1973). The first attempt to solve the structure was with *MULTAN* (Germain, Main & Woolfson, 1970). None of the solutions provided gave an absolute figure of merit (ABSFOM) greater than 0·80, which suggests a wrong determination. The *MEDIBOR* program, based on a cosine-invariant computation (Busetta & Comberton, 1974), was then used. All the E's down to a minimum value of 1·60 were used. Of the 16 different solutions provided by this computation, only one appeared to be self consistent (ABSFOM = 0·975). This permitted the location of two tartrate ions in space group $P2_12_12_1$ (they are related by the 4_1 axis in the space group $P4_12_12$). The R value computed at this stage was 0·46. In order to find the ethylenediamine ion, a new generation of phases was initiated with the phases given by the tartrate ions and with a convenient variable set of symbolic phases for defining the ethylenediamine ion. This process is a good application of the method for determining structures with molecular islands (Busetta, 1973). The resulting E map calculated with the new set of phases with the best figures of merit revealed the remaining ethylenediamine ion and water molecules. The R value was 0·30. In $P2_12_12_1$, a block-diagonal least-squares refinement of the non-hydrogen atomic coordinates and anisotropic temperature factors led to an R value of 0·08. At this stage the mean deviation between the computed and the real phases was $\langle \Delta\varphi \rangle = 6°$, which is very low for reflexions with $E \geq 1{\cdot}60$.

After a change of origin to comply with space group $P4_12_12$, the refinement of the structure proceeded smoothly. The atomic coordinates were refined with individual isotropic thermal parameters by full-matrix least squares with unit weights. The refinement con-

verged to an R value* of 0·12. The refinement was continued with anisotropic thermal parameters and a block-diagonal matrix. On convergence of anisotropic refinement, all H atoms were located from successive difference Fourier syntheses. At this stage, the H atoms were included in the refinement with isotropic temperature factors and a weighting function derived from an error analysis was performed on $\sin\theta/\lambda$ and $|F_o|$ (Ahmed *et al.*, 1966). After several cycles of block-diagonal least-squares refinement, an ultimate R_w index* of 0·04 was obtained. At this stage the computed value of the standard deviation of unit weight σ_F* was 1·96. At the end of the refinement, the average parameter shift was less than $0{\cdot}4\sigma$. A final difference Fourier map showed no significant residual density, the extreme fluctuations being 0·19 and −0·16 e Å^{-3}. Seven reflexions, probably 'suffering from extinction', were removed from the last cycles of the refinement, and were not included in the calculation of the R values.

Results and discussion

The positional and thermal parameters with their standard deviations are presented in Table 3.† The standard deviations of the interatomic bond distances and angles for non-hydrogen atoms amount to 0·004 Å and 0·3°, respectively, and 0·03 Å for bond distances involving H atoms. These values are derived from the calculated e.s.d.'s of the fractional coordinates.

The ethylenediammonium ion

The ion is schematically shown in Fig. 1 with numbering of the atoms and the intramolecular bond distances and valency angles uncorrected for thermal vibration. In this structure the ethylenediammonium ion is located on a twofold axis which is perpendicular to the C(12)–C′(12) bond, and exists in the *gauche* conformation. The torsion angle Φ = N(11)–C(12)–

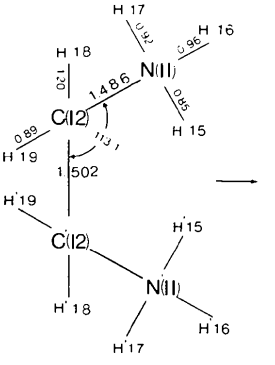

Fig. 1. Intramolecular features of the ethylenediammonium ion. (Primed atoms are derived by twofold rotation from the non-primed atoms having the same number.)

* $R = \Sigma\Delta F/\Sigma F_o$, $R_w = [\Sigma(\Delta F)^2/\Sigma F_o^2]^{1/2}$, $\sigma_F = [\Sigma(\Delta F)^2/(m-n)]^{1/2}$, m = number of reflexions, n = number of refined parameters.

† The structure factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32181 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional coordinates, thermal parameters* (×10⁴ *for* O, N, C *and* ×10³ *for* H) *and their e.s.d.'s*

The anisotropic and isotropic thermal parameters are the coefficients of the expressions $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)]$ and $T = \exp[-8\pi^2(U_{11}(\sin^2\theta/\lambda^2)]$ respectively.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	−2728 (3)	2557 (4)	1427 (1)	276 (13)	565 (17)	365 (11)	57 (12)	49 (11)	−126 (12)
O(2)	−2897 (3)	1861 (3)	708 (1)	191 (11)	449 (15)	356 (11)	33 (11)	−32 (10)	−94 (11)
C(1)	−2044 (4)	2004 (4)	1090 (1)	209 (16)	206 (16)	344 (15)	−21 (13)	−2 (14)	−32 (14)
C(2)	−136 (4)	1410 (4)	1053 (1)	183 (15)	217 (16)	299 (14)	−6 (13)	−15 (14)	−25 (13)
O(3)	698 (3)	1520 (3)	1476 (1)	357 (14)	339 (14)	380 (11)	74 (11)	−94 (11)	50 (11)
C(3)	846 (4)	2642 (4)	732 (1)	164 (15)	212 (16)	391 (16)	23 (12)	6 (14)	21 (15)
O(4)	732 (3)	4408 (3)	892 (1)	340 (15)	202 (13)	717 (16)	36 (10)	95 (13)	40 (12)
C(4)	2751 (4)	2004 (4)	665 (1)	178 (15)	248 (16)	344 (16)	1 (13)	0 (13)	−8 (14)
O(5)	2973 (3)	441 (3)	545 (1)	240 (13)	304 (14)	896 (19)	−7 (11)	127 (14)	−218 (14)
O(6)	3979 (3)	3080 (3)	738 (1)	176 (11)	333 (14)	705 (16)	−8 (10)	−9 (12)	−124 (13)
W(13)	−2611 (4)	5686 (4)	2846 (1)	593 (20)	765 (22)	392 (13)	362 (17)	7 (14)	−47 (15)
N(11)	−1025 (4)	3498 (4)	2226 (1)	268 (15)	279 (15)	311 (13)	−11 (12)	33 (12)	34 (12)
C(12)	−513 (4)	1924 (5)	2495 (1)	265 (18)	350 (19)	310 (14)	20 (15)	13 (15)	56 (16)

	x	y	z	U_{11}		x	y	z	U_{11}
HC(2)	−17 (4)	23 (4)	92 (1)	20 (3)	H(16)	−153 (5)	309 (5)	195 (1)	44 (5)
HC(3)	16 (5)	268 (4)	44 (1)	27 (4)	H(17)	−6 (5)	424 (5)	218 (1)	35 (5)
HO(2)	−417 (7)	252 (7)	77 (1)	89 (8)	H(18)	84 (6)	118 (6)	239 (1)	81 (7)
HO(3)	87 (5)	59 (5)	153 (1)	47 (5)	H(19)	−30 (7)	216 (7)	278 (1)	89 (8)
HO(4)	119 (7)	436 (7)	120 (1)	97 (5)	H(20)	−345 (6)	644 (6)	290 (1)	61 (6)
H(15)	−176 (5)	412 (4)	237 (1)	28 (4)	H(21)	−195 (7)	564 (7)	305 (2)	104 (9)

C′(12)–N′(11) is −71°. In the structure of EDT (Pérez, 1976*a*) the ethylenediammonium ion was in a quasi-*trans* conformation, the corresponding Φ being 172°. These experimental results agree with some theoretical predictions (Hadjiliadis, Diot & Theophanides, 1972) and with the results of gas electron diffraction studies (Yokozeki & Kuchitsu, 1971) on the rotational isomerism of ethylenediamine, as well as with other experimental results on the conformation of ethylenediamine as found in the solid state (Jamet-Delcroix, 1967). Thus the *gauche* and *trans* forms appear to be the most probable conformers.

All bond distances and angles are normal except for the angle C′(12)–C(12)–N(11) of 113·1 (3)°, which is considerably larger than the expected tetrahedral angle of 109° observed in the ethylenediammonium ion (Pérez, 1976*a*) and in ethylenediamine (Jamet-Delcroix, 1967, 1973).

The average H–N(11) distance is 0·91 Å, the corresponding bond angles being consistent with a tetrahedral arrangement around the N atom.

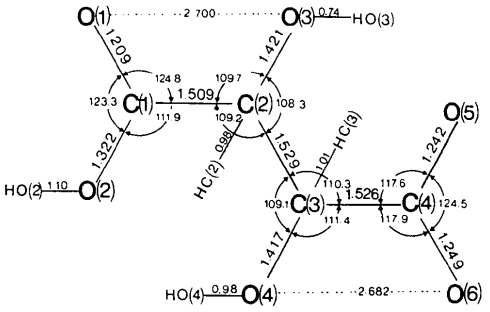

Fig. 2. Intramolecular features of the hydrogen tartrate ion.

Table 4. *Torsion angles* (°)

O(1)–C(1)–C(2)–C(3)	−115·7
O(1)–C(1)–C(2)–O(3)	2·7
O(2)–C(1)–C(2)–O(3)	−177·5
C(1)–C(2)–C(3)–O(4)	58·2
C(1)–C(2)–C(3)–C(4)	−176·6
O(3)–C(2)–C(3)–O(4)	−61·0
O(3)–C(2)–C(3)–C(4)	64·2
O(4)–C(3)–C(4)–O(6)	−2·8
O(4)–C(3)–C(4)–O(5)	176·8

The hydrogen tartrate ion

The intramolecular features of the hydrogen (+)-tartrate ion are shown in Fig. 2, where the numbering of the atoms is the same as that used for EDT (Pérez, 1976*a*).

Each half of the ion consists of a carboxyl group, an α-hydroxyl O and a tetrahedral C, and is slightly non-planar (χ^2 = 139 and 180). These two halves are so orientated that the four C atoms assume a zigzag configuration which is slightly non-planar (χ^2 = 200). Just as in other α-hydroxycarboxylic acids (Jeffrey & Parry, 1952) or in other tartrate ions or molecules, the α-hydroxyl O atom lies nearly in the same plane as the carboxyl group. Details of the internal rotations of the tartrate ion in this structure are given in Table 4.

The geometry of the non-ionized end is asymmetric. The H atom is found to be bonded to the O atom of the

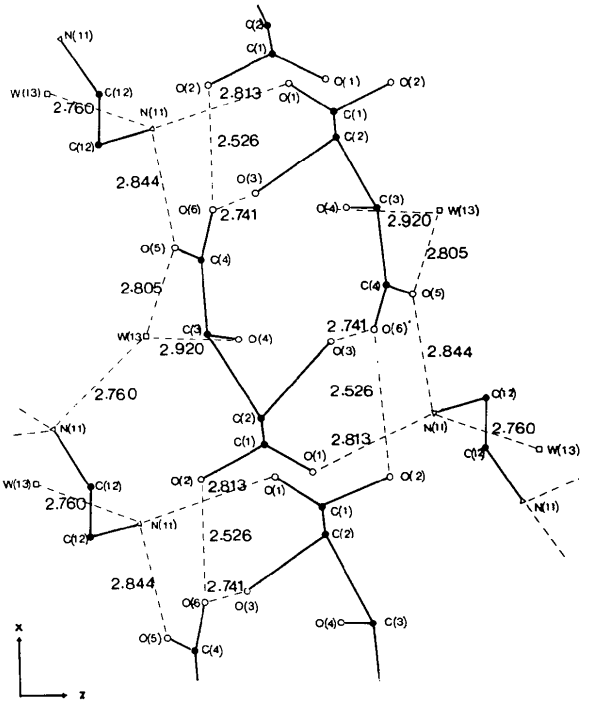

Fig. 3. Hydrogen bonding of ethylenediamine ditartrate dihydrate, showing only one of the ditartrate ribbons. Similar ribbons parallel to **b** are not shown here.

Table 5. *Hydrogen bonding*

i *j* *k*	D_{ik} (Å)	D_{jk} (Å)	θ_{ijk} (°)
O(2)–HO(2)···O(6)(−1 + *x*, *y*, *z*)	2·526 (3)	1·45 (4)	163 (4)
O(3)–HO(3)···O(6)($\frac{1}{2}$ − *x*, $-\frac{1}{2}$ + *y*, $\frac{1}{4}$ + *z*)	2·741 (4)	2·01 (4)	171 (4)
N(11)–H(15)···*W*(13)(*x*, *y*, *z*)	2·760 (4)	1·97 (4)	156 (3)
W(13)–H(20)···O(5)($-\frac{1}{2}$ − *y*, $\frac{1}{2}$ + *x*, $\frac{1}{4}$ + *z*)	2·805 (4)	1·94 (4)	176 (4)
N(11)–H(16)···O(1)(*x*, *y*, *z*)	2·813 (3)	1·85 (3)	173 (3)
N(11)–H(17)···O(5)($\frac{1}{2}$ − *x*, $\frac{1}{2}$ + *y*, $\frac{1}{4}$ − *z*)	2·844 (4)	1·94 (4)	165 (3)
W(13)–H(21)···O(4)($\frac{1}{2}$ − *y*, $\frac{1}{2}$ + *x*, $\frac{1}{4}$ + *z*)	2·920 (5)	2·18 (5)	156 (5)

carboxyl group opposite the α-hydroxyl O atom. On the whole, there is good agreement with the molecular geometry of α-hydroxycarboxylic acid groups in other tartrates (Carlström, 1973; van Bommel & Bijvoet, 1958; Okaya, Stemple & Kay, 1966; Hope & De la Camp, 1972; Bootsma & Schoon, 1967; Kroon & Kanters, 1972). However, the bond distance C(1)–C(2) [1·509 (4) Å] is slightly shorter than the average distance of 1·520 [$\hat{\sigma}(\bar{X}) = 0{\cdot}002$] Å, which was computed from 14 equivalent distances quoted for the α-hydrocarboxylic acid group of *meso*- or (+)-tartrates (Pérez, 1976*b*). The ionized end of the tartrate ion is symmetric within experimental error. Contrary to what was observed in lithium hydrogen oxalate monohydrate (Thomas, 1972) and (−)-adrenaline hydrogen (+)-tartrate (Carlström, 1973), where the distortion of the ionized carboxyl group was stated to depend on the hydrogen-bonding system, the strong hydrogen bond in which O(6) is involved (2·526 Å), as shown in Fig. 3, does not seem to influence the geometry of the carboxyl group.

Hydrogen bonding

A three-dimensional network of hydrogen bonds and short intramolecular distances stabilize the structure. This densely packed structure is in agreement with the high density (1·53 g cm^{-3}) of the crystals. The hydrogen-bonding scheme is shown in Fig. 3. Table 5 lists the intermolecular distances and angles of interest.

The tartrate ions are connected head-to-tail by strong O–H···O hydrogen bonds (2·526 Å). They form infinite chains parallel to **a** and other chains parallel to **b**. Because of the 2_1 symmetry, each chain has another chain parallel to it, and the pair are interlinked by O–H···O hydrogen bonds (2·741 Å) to form a tartrate ribbon. Thus one set of the ribbons runs parallel to **a** and the other parallel to **b**. The ethylenediamine ions and the water molecule interlink the perpendicular sets of ribbons through O–H···O bonds to form a closely-knit three-dimensional network.

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