

Neutron diffraction study of ammonium tartrate $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$

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Abstract. A neutron diffraction study of ammonium tartrate has been carried out. Using the diffractometer in symmetrical setting, intensities of 750 reflections have been measured. The positions of all the hydrogen atoms have been determined. A good agreement is noticed between the present neutron and the earlier x-ray heavy atom parameters. The tartrate ion consists of two nearly identical planar halves, with an interplanar angle of 62° . The structure is stabilized by a network of hydrogen bonds. Details of hydrogen bonding and the ammonium ions environment are discussed.

Keywords. Ammonium tartrate neutron diffraction tartrate ion configuration; hydrogen bonding.

1. Introduction

The conformation of the tartrate ion has been the subject of several investigations. Recently, the crystal structure of ammonium tartrate by 3D x-ray photographic data has been reported by us (Yadava and Padmanabhan 1973) which contains other references on the x-ray work of tartrates. The studies reveal that the tartrate ion consists of two planar halves, each containing a carboxyl group, a tetrahedral carbon atom and a hydroxyl oxygen atom. As the hydrogen atoms could not be located in the x-ray study, a neutron study was undertaken and the results of the investigation are presented in this paper.

2. Experimental

Single crystals of ammonium tartrate were grown by slow evaporation of an aqueous solution of the salt. A crystal weighing 85 mg was chosen for data collection. The shape of the crystal was approximately cubic with dimensions $4.1 \times 3.8 \times 3.8$ mm. The crystal was mounted along the *b*-axis on the neutron diffractometer 3D-FAD (Momin *et al* 1969) at the CIRUS reactor at Trombay. The setting angles were calculated using the crystal data given in table 1.

The integrated intensities of 750 independent reflections within the limit $\sin \theta/\lambda \leq 0.55$ [$\lambda = 1.178 \text{ \AA}$] were recorded in the symmetrical setting using the $\theta - 2\theta$ step-scan mode (0.1° step in 2θ). The background was scanned for a minimum of 1° on either side of the peaks. A standard reflection was measured at regular intervals to provide a check on crystal and electronic stabilities. No significant variation was observed. The integrated intensities were reduced to

Table 1. Crystal data

Molecular formula	$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$
Lattice constants	$a = 7.083$ (1) Å
	$b = 6.128$ (3)
	$c = 8.808$ (1)
	$\beta = 92.42$ (1)°
Molecules per unit cell	$z = 2$
Systematic absences	$OkO: k = 2n + 1$
Space group	$P2_1$

F_o^2 by applying the Lorentz and absorption corrections using the program DATARED (Srikanta 1968) which includes the absorption correction program ORABS (Wehe, Busing and Levy 1962) as a subroutine. A linear absorption coefficient of 2.77 cm^{-1} was used.

3. Structure refinement

The positions of the twelve hydrogen atoms were located from a nuclear scattering density map computed using the phases calculated from the non-hydrogen atoms positions of our x-ray study (Yadava and Padmanabhan 1973). The positional parameters and isotropic temperature factors of all atoms were refined by the method of least squares using the program XFLS (Busing, Martin and Levy 1962). The function minimized was $\Sigma w (|F_o^2| - |F_c^2|)^2$, where

$$w = 1/\sigma (F_o)^2 \text{ and } \sigma (F_o)^2 \text{ was based on the counting statistics (Busing and Levy 1957).}$$

The structure was then refined with anisotropic thermal parameters and an extinction parameter G (Zachariasen 1967; Coppens and Hamilton 1970). The final value of G was 0.50×10^4 which corresponds to an equivalent mosaic spread 11 sec of arc. For the worst affected reflection 500, F_o^2/F_c^2 was 0.42. In the anisotropic refinement the parameters of the heavy atoms and the hydrogen atoms were refined in alternate cycles as it was not possible to refine all the parameters in the same cycle. The final $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$ was 0.063 and $\Sigma (|F^2| - |F_o|^2) / \Sigma F_o^2$ was 0.096. The nuclear scattering lengths for C, N, O and H used were: $bC = 0.664$, $bN = 0.940$, $bO = 0.580$ and $bH = -0.374 \times 10^{-12} \text{ cm}$ (Bacon 1972). The fractional coordinates and anisotropic thermal parameters are given in table 2. The intramolecular bond distances and angles are listed in table 3.

4. Discussion

The tartrate ion

Except for small differences, a good agreement is noticed between our earlier x-ray and the present neutron parameters of the tartrate ion. The ion (figure 1) consists of two $\text{CH}\cdot\text{OH}\cdot\text{COO}$ parts; each part containing a

Table 2. Final positional and thermal parameters. All the values are multiplied by 10^4 and their standard deviations are given in the parantheses. The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	3005 (8)	2970 (13)	7704 (6)	102 (12)	43 (13)	55 (6)	-34 (13)	22 (7)	-18 (10)
O (1)	3123 (10)	964 (9)	7389 (9)	88 (13)	128 (20)	104 (10)	-32 (15)	23 (9)	8 (12)
O (2)	1534 (9)	4032 (15)	7700 (8)	83 (14)	175 (20)	114 (11)	3 (12)	5 (8)	20 (13)
C (2)	4852 (7)	4178 (12)	8113 (6)	80 (10)	74 (14)	45 (6)	-12 (11)	11 (6)	11 (8)
O (3)	6393 (8)	2699 (7)	8267 (7)	82 (11)	117 (20)	67 (7)	26 (14)	-10 (7)	10 (11)
C (3)	5243 (7)	5883 (12)	6915 (5)	88 (10)	64 (14)	40 (6)	-18 (11)	-1 (6)	6 (8)
O (4)	5376 (9)	4810 (13)	5513 (7)	128 (14)	143 (19)	47 (8)	-27 (15)	0 (7)	-14 (10)
C (4)	7043 (7)	7216 (12)	7368 (6)	67 (9)	83 (14)	59 (7)	-25 (12)	5 (6)	-9 (9)
O (5)	7099 (9)	8088 (15)	8636 (7)	115 (13)	196 (23)	79 (9)	-36 (17)	14 (8)	-51 (14)
O (6)	8268 (8)	7396 (15)	6391 (7)	34 (11)	190 (23)	89 (8)	-44 (14)	14 (7)	7 (11)
N (1)	1053 (6)	8042 (11)	9147 (4)	109 (8)	147 (13)	73 (5)	11 (10)	0 (5)	2 (28)
N (2)	3850 (5)	1919 (12)	5683 (5)	102 (7)	154 (12)	68 (5)	-34 (9)	12 (5)	-20 (7)
H (1)	1722 (21)	9277 (30)	8510 (19)	206 (28)	212 (42)	120 (22)	-17 (32)	-28 (19)	-14 (8)
H (2)	-435 (19)	8306 (23)	9158 (16)	147 (25)	201 (35)	116 (18)	-7 (26)	28 (17)	-27 (22)
H (3)	1311 (21)	6581 (25)	8648 (17)	183 (29)	191 (36)	127 (20)	-60 (29)	-7 (18)	1 (21)
H (4)	1753 (22)	8046 (29)	165 (15)	217 (32)	226 (44)	114 (16)	59 (36)	-39 (17)	8 (24)
H (5)	7682 (23)	2767 (35)	5616 (17)	193 (28)	282 (50)	113 (18)	3 (38)	48 (20)	7 (30)
H (6)	9756 (17)	2598 (28)	6540 (15)	153 (21)	275 (41)	131 (18)	-57 (30)	-6 (15)	24 (22)
H (7)	9523 (19)	1935 (29)	4717 (18)	214 (27)	287 (39)	139 (23)	-2 (25)	84 (20)	18 (26)
H (8)	8536 (21)	345 (25)	5949 (19)	194 (26)	139 (38)	132 (21)	38 (28)	20 (19)	4 (23)
H (9)	4645 (13)	5003 (26)	9203 (11)	77 (16)	266 (41)	88 (13)	21 (25)	10 (11)	-18 (21)
H (10)	5934 (17)	1254 (25)	8196 (14)	175 (21)	165 (35)	106 (14)	25 (26)	9 (13)	-26 (19)
H (11)	4150 (18)	7058 (25)	6908 (15)	151 (22)	209 (30)	123 (18)	59 (25)	12 (15)	49 (21)
H (12)	5895 (21)	5781 (26)	4779 (15)	218 (28)	238 (38)	96 (16)	-11 (25)	17 (17)	33 (23)

Table 3. Intra molecular bond-distances (Å) and angles (°) with estimated standard deviations.

C (1)-O (1)	1.269 (10)		
C (4)-O (6)	1.247 (10)		
C (1)-O (2)	1.241 (9)		
C (4)-O (5)	1.240 (9)		
C (2)-O (3)	1.420 (9)	O (1) ... O (3)	2.641 (10)
C (3)-O (4)	1.413 (9)	O (4) ... O (6)	2.672 (9)
C (1)-C (2)	1.534 (9)	O (1) ... O (2)	2.233 (9)
C (2)-C (3)	1.522 (9)	O (5) ... O (6)	2.215 (8)
O (3)-H (10)	0.950 (12)		
O (4)-H (12)	0.961 (12)		
C (2)-H (9)	1.103 (10)		
C (3)-H (11)	1.048 (12)		
O (1)-C (1)-O (2)	125.0 (7)	C (1)-C (2)-H (9)	105.7 (8)
O (5)-C (4)-O (6)	125.9 (6)	O (3)-C (2)-H (9)	110.5 (7)
O (1)-C (1)-C (2)	117.2 (7)	C (3)-C (2)-H (9)	109.0 (8)
O (6)-C (4)-C (3)	117.4 (6)	O (4)-C (3)-H (11)	112.9 (7)
O (2)-C (1)-C (2)	117.2 (5)	C (4)-C (3)-H (11)	104.4 (8)
O (5)-C (4)-C (3)	116.6 (7)	C (2)-C (3)-H (11)	108.3 (8)
C (1)-C (2)-C (3)	110.4 (6)		
C (1)-C (2)-O (3)	11.2 (6)		
O (3)-C (2)-C (3)	109.9 (7)	H (1)-N (1)-H (2)	103.7 (9)
C (2)-C (3)-O (4)	108.4 (6)	H (1)-N (1)-H (3)	112.2 (8)
O (4)-C (3)-C (4)	112.3 (5)	H (1)-N (1)-H (4)	107.3 (9)
C (2)-C (3)-C (4)	110.8 (5)	H (2)-N (1)-H (3)	117.3 (9)
C (2)-O (3)-H (10)	109.3 (7)	H (2)-N (1)-H (4)	107.5 (8)
C (3)-O (4)-H (12)	110.5 (8)	H (3)-N (1)-H (4)	108.3 (8)
		H (5)-N (2)-H (6)	113.1 (8)
		H (5)-N (2)-H (7)	108.4 (8)
		H (5)-N (2)-H (8)	108.8 (7)
		H (6)-N (2)-H (7)	107.8 (8)
		H (6)-N (2)-H (8)	118.2 (8)
		H (7)-N (2)-H (8)	119.5 (8)

Table 4. Deviations of atoms from least-squares planes (Å).

	Plane 1	Plane 2	Plane 3
O (1)		0.002	
O (2)		0.002	
O (3)		-0.181*	
O (4)			0.123*
O (5)			-0.008
O (6)			-0.038
C (1)	-0.020	-0.004	
C (2)	0.018	0.001	
C (3)	0.020		-0.006
C (4)	-0.020		0.024

* Not included in the plane.

planar carboxyl group and a tetrahedral CH·OH—configuration. In each of the two parts the hydroxyl oxygen atom stays close to the carboxyl plane. The details of the least-squares planes fitted to the groups of atoms, O (1) O (2) C (1) C (2) and O (5) O (6) C (3) C (4) as well as C (1) C (2) C (3) C (4) are given in table 4. The planes of the two parts O (1) O (2) O (1) C (2) and O (5) O (6) C (3)

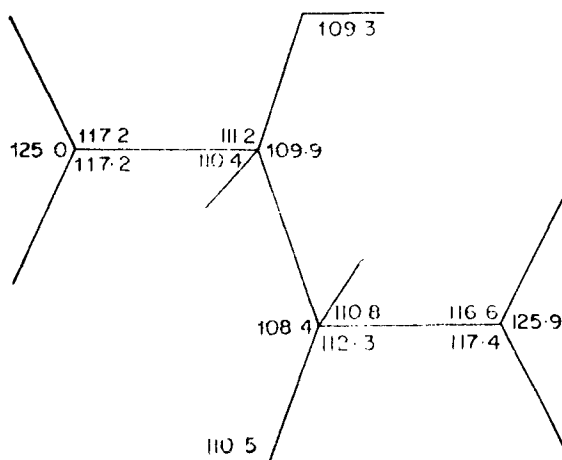
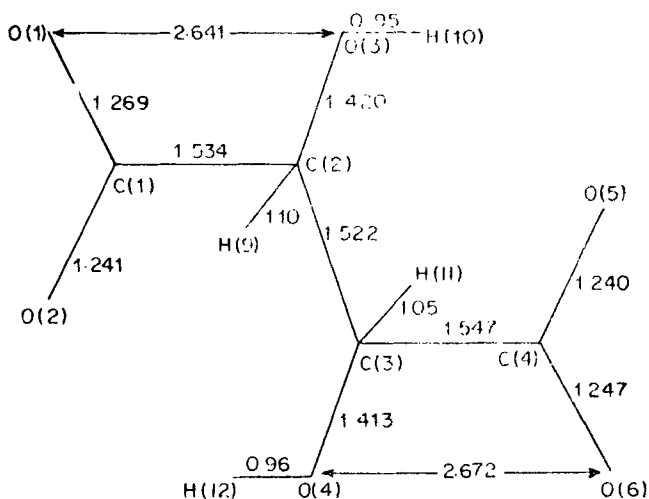


Figure 1. Features of the tartrate ion.

C (4) make an angle of 62° . The carboxyl group of C (3) C (4) O (5) O (6) appears to be less planar than that of C (1) C (2) O (1) O (2). Such a situation also exists in the structure of *d*-tartaric acid (Okaya *et al* 1966). The chemically equivalent bonds in the ion are (1) C (1) — C (2) and C (3) — C (4); (2) the four C—O bonds of the carboxyl groups; (3) the two C—O (H) bonds (4) the two O—H bonds and (5) the two C—H bonds. Within the limits of experimental error, no significant differences are observed in the equivalent bond lengths and bond angles and thus the two parts of the tartrate ion appear to be similar.

Molecular packing, hydrogen bonding and ammonium ion

The structure projected down the *c*-axis is shown in figure 2. The tartrate molecules form a zigzag chain along the *b*-axis and are held in this position by a network of hydrogen bonds through the ammonium ions. In addition, the hydroxyl

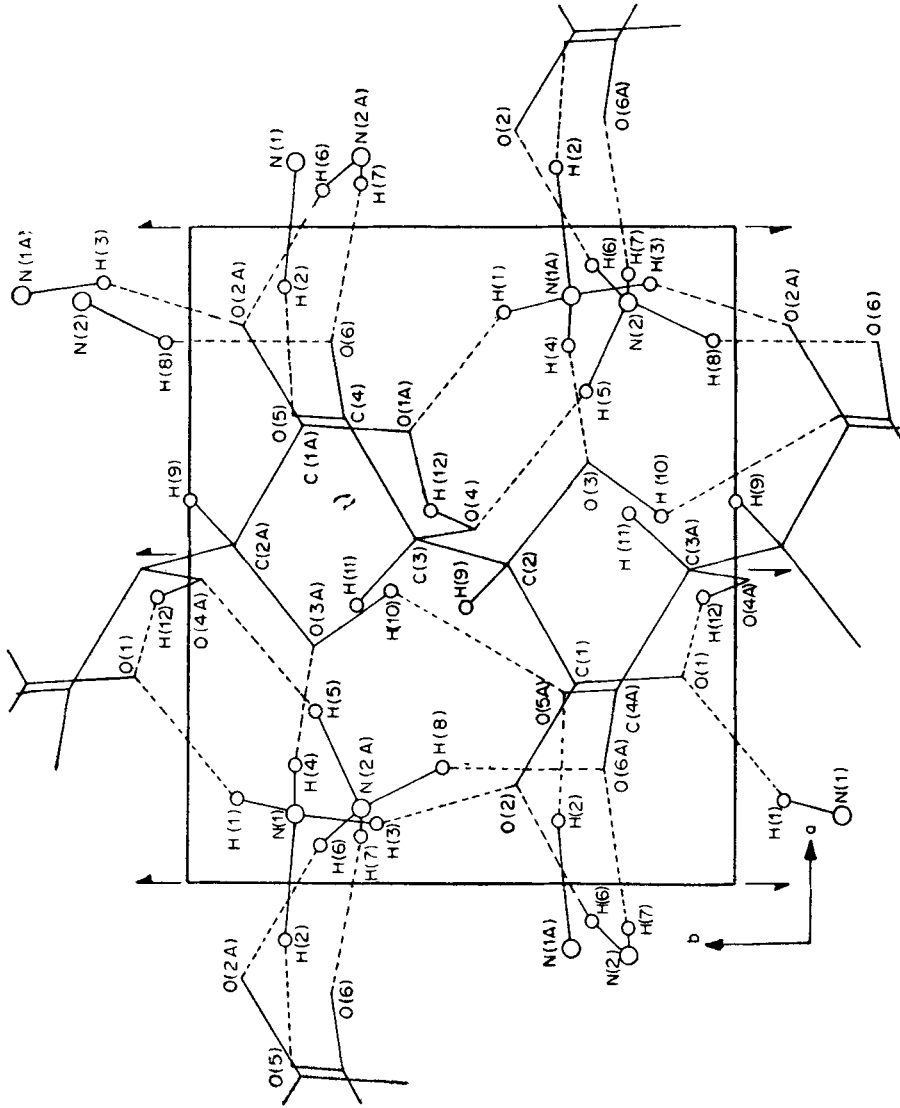


Figure 2. The crystal structure of ammonium tartrate projected down the *c*-axis. Hydrogen bonds are indicated by broken lines.

oxygen atoms are involved in hydrogen bond formation with carboxyl oxygen atoms of other tartrate ions. Thus there are two types of hydrogen bonds in the structure: (i) $N-H \cdots O$ where the nitrogen atom is from an ammonium ion and the acceptor atom is either a carboxyl or a hydroxyl oxygen of different tartrate ions and (ii) $O-H \cdots O$, where the donor oxygen atom is a hydroxyl oxygen and the acceptor atom is a carboxyl oxygen atom of another tartrate ion. The distances and angles characterising these hydrogen bonds are listed in table 5. Atom H (5) appears to be involved in a bifurcated hydrogen bond. The distance $H(5) \cdots O(3)$ (2.51 Å) indicates rather a weak interaction and the main strength is in the $H(5) \cdots O(4)$ interaction. The hydrogen bonds $O-H \cdots O$ are bent more than bonds $N-H \cdots O$.

The bond distances $O(3)-H(10)$ and $O(4)-H(12)$ are normal, but the $O-H \cdots O$ angles 135.9° and 144.3° are less than the reported values 176° and 152° in *d*-tartaric acid by Okaya *et al* (1966).

The average $N-H$ bond length in the two ammonium ions is 1.05 Å. This is close to the corresponding values reported in other neutron-diffraction studies: 1.044 Å in NH_3OHCl (Padmanabhan *et al* 1967); 1.06 Å in $(NH_4)_2SO_4$ (Schlemper and Hamilton 1966) 1.06 Å in $Cu(NH_4)_2SO_4 \cdot 6H_2O$ (Brown and Chidambaram 1969).

The ammonium ions are distorted tetrahedra with the $H-N-H$ angles varying from 103.7° to 117.3° in one ammonium ion and from 107.8° to 113.1° in the other ammonium ion. Table 5 shows that in the case of one ammonium ion the average $N \cdots O$ distance is 2.82 Å and is coordinated to four oxygen neighbours.

Table 5. Hydrogen bonding in ammonium tartrate.

$XH \cdots Y$	d_{X-H}^*	$d_{H \cdots Y}$	$d_{X \cdots Y}$	$\angle_{X-H \cdots Y}$
$N(1)-H(1) \cdots O(1)^{y+1}$	1.07	1.78	2.82	170.4°
$N(1)-H(2) \cdots O(2)^{x-1}$	1.09	1.77	2.81	161.7
$N(1)-H(3) \cdots O(2)$	1.03	1.78	2.78	173.4
$N(1)-H(4) \cdots O(3)^{z+1}$	1.07	1.86	2.86	165.3
$N(2)-H(5) \cdots O(3)$	1.01	2.51	2.96	107.6
$N(2)-H(5) \cdots O(4)$	1.01	2.06	2.03	173.6
$N(2)-H(6) \cdots O(2)^{x+1}$	1.07	1.82	2.85	169.1
$N(2)-H(7) \cdots O(6A)$	1.01	1.91	2.81	151.0
$N(2)-H(8) \cdots O(6)^{y-1}$	1.04	1.87	2.88	173.3
$O(3)-H(10) \cdots O(5)^{y-1}$	0.95	2.15	2.89	135.9
$O(4)-H(12) \cdots O(1A)$	0.96	2.06	2.88	144.3

* The distances are corrected for thermal motion with the light atom assumed to be riding on the heavier atom; e.s.d. in bond-distance 0.02 Å in bond-angles 1.6° .

In the second ammonium ion, the average N···O distance is 2.91 Å and has five nearest oxygen neighbours. This correlation between the N···O distance and coordination number agree with the observations of Khan and Baur (1972).

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