PART - I

General Information
on
Ammonium Hydrogen
d - tartarate
and
Techniques and
Graphical Analysis

CHAPTER 1

General Information on d-AHT crystals

GENERAL INFORMATION

1.1 INTRODUCTION:

Ammonium-hydrogen-d-tartrate (d-AHT) is a piezoelectric crystal (1)(2) (Zalina & Ersova, 1958, Mason 1950). In literature, some information is available regarding its structure and composition. Its piezoelectric and other properties are not studied in detail. The growth of crystals was carried out by solution method. General information available so far is presented here. The crystal will henceforth be referred to as d-AHT.

1.2 PREPARATION:

d-AHT is usually prepared in the laboratory by producing a chemical reaction of ammonium hydroxide with tartaric acid, (3) (Howley, 1971). The single crystals of d-AHT were obtained by preparing saturated solutions at higher temperature (50 Deg C) and gradually cooling the solution of this salt. The crystals were small in size. The solubility of d-AHT in distilled water is 3.24 gm/100 cc at 25 deg C (4)(5) (Clifford, 1964; Weast, 1964). Its chemical formula is reported in the literature as NH_4H tartrate (6) (Bommel and Bijvoet, 1958) $NH_4HC_4H_4O_6$ (ammonium acid D-tartrate) (7) (Wycoff, 1951), $C_4H_4NH_6$ (8), $C_4H_4O_6(NH_4)H$(9) (Lasheen, 1964) (ammonium hydrogen d-tartrate). NH_4H tartrate belongs to isomorphic series of hydrogen tartrates such as - RbH,KH and C_5H tartrates. Tartrate crystals show many interesting physical properties such as ferroelectricity piezoelectricity etc. The group of acidic tartrates, in general, possesses low solubilities and is not available in nature.

1.3 CRYSTAL STRUCTURE:

The crystal structure of d-AHT was analyzed by x-rays (6) (Bommel and Bijvoet, 1958). The crystals are orthorhombic with a= 7.648 A°, b= 11.066 A° and c= 7.843 A°; space group $P2_12_12_1$; 4 molecules per unit cell (Z=4). Tables 1.1, 1.2, represent data on bond distances and angles. The crystals are elongated prisms in the [100] direction, and belong to the orthorhombic disphenoidal crystal class (10) (Growth). The bond lengths and angles of tartrate anion in d-AHT are schematically shown in Fig 1.1. Fig 1.2 represents the orthorhombic structure of d-AHT projected along its C_0-axis (right-hand axis) and packing drawing along its C_0-axis respectively. The large black circles are ammonium, the smaller ones are carbon atoms whereas the larger oxygen atoms are dot and short line shaded (7). The crystal structure of d-AHT consists of layers perpendicular to the [010] direction. The hydrogen bonds of one tartaric ion with its surroundings within the layer are shown in Fig 1.3.

TABLE 1.1

Bond distances (A Angstron) and angles (Deg) of d-AHT

BOND	A^o (ang)	ANGLE	A^o
C_1-O_1	1.306(4)	$O_1-C_1-O_2$	124.7(3)
O_2	1.213(4)	$O_1-C_1-C_2$	112.1(3)
O_3	1.527(4)	$O_2-C_1-C_2$	123.2(3)
		$C_1-C_2-C_3$	110.4(3)
C_2-O_3	1.421(4)	$C_1-C_2-O_3$	109.3(3)
C_3	1.526(4)	$C_3-C_2-O_3$	110.0(3)
H_1	1.03 (3)	$H_1-C_2-C_1$	105.0(3)
		$H_1-C_2-C_3$	113.6(16)
C_3-O_4	1.411(4)	$H_1-C_2-O_3$	108.5(18)
C_4	1.536(4)	$O_5-C_4-O_6$	125.0(3)
	1.06 (3)	$C_3-C_4-O_5$	117.0(3)
		$C_3-C_4-O_6$	118.0(3)
C_4-O_5	1.255(4)	$C_2-C_3-C_4$	108.5(3)
O_6	1.260(4)	$C_2-C_3-O_4$	111.7(3)
		$C_4-C_3-O_4$	113.3(3)
O_1-O_6	2.560(3)	$H_2-C_3-C_4$	109.4(20)
H_5	0.85(4)	$H_2-C_3-C_2$	105.1(19)
		$H_2-C_3-O_4$	108.5(19)
O_3-O_6	2.741(3)	$H_3-O_3-C_2$	105.4(27)
H_3	0.95 (5)	$H_4-O_4-C_3$	111.6(32)
		$H_5-O_2-C_1$	112.0(32)
O_4-O_5	2.810(4)	$C_4-O_5-H_4$	102 (1)
H_4	0.82 (3)	$C_4-O_6-H_3$	135 (1)
		$C_4-O_6-H_5$	114 (1)
O_5-H_4	2.00(4)	$O_3-H_3-O_6$	164 (4)
		$O_4-H_4-O_5$	170 (4)
O_6-H_3	1.82(5)	$O_1-H_5-O_6$	169 (4)
H_5	1.72(4)	H_6-N-H_7	121 (6)
		H_6-N-H_8	93 (5)
$N-H_6$	0.87(7)	H_6-N-H_9	99 (7)
H_7	0.76(6)	H_7-N-H_8	112 (5)
H_8	0.86(7)	H_7-N-H_9	111 (6)
H_9	0.84(8)	H_8-N-H_9	118 (6)

TABLE 1.2

NITROGEN - OXYGEN DISTANCES		
N-O_1	I	3.134 A°
N-O_5	I	2.967 A°
N-O_2	II	2.855 A°
N-O_3	II	3.089 A°
N-O_4	III	2.888 A°
N-O_5	III	2.909 A°
N-O_2	IV	2.879 A°
N-O_3	IV	3.155 A°

1.4 PROPERTIES AND USES:

The d-AHT crystals exhibit diamagnetic anisotropy (9) (Lasheen, 1964). The molecular susceptibilities and anisotropy are related to the molecular shape and constitution and to the bond character, which in general markedly decreases the anisotropy. This decrease varies not only with the nature of the substituents but with their positions on the nucleus. The Krishnan-Banerjee (11) (1935) method was used in the determination of the magnetic anisotropy of the crystal. Susceptibility measurements were also carried out by Joussot Dubien et al (12) (1956).

The crystal is weakly piezoelectric, but the detailed study about this property is not available in literature. Mason (1950) measured the electromechanical coupling which was obtained to be strong (8% to 30% or higher). Table 1.3 briefly reports the physical properties of d-AHT. This material possesses low toxicity and is useful as baking powder (3) (Howley, 1971). Its potentiality as a piezoelectric crystal is not yet fully explored. A detailed and systematic study has been undertaken by the present author in reporting,

a) the growth of synthetic single crystals of d-AHT using different salt solutions of ammonium (NH_4Cl, NH_4Br, NH_4I, NH_4-$COOCH_3$, etc) as feed solutions and determining the best ammonium halide as feed solution.

b) the microhardness and hardness anisotropy related to four different faces __ as grown and cleavage faces of the crystal.

c) chemical dissolution of the as-grown and cleavage faces of the crystal using three new etchants and thereby calculating the parameters.

TABLE 1.3

Information about some physical properties of d-AHT:

i)	Molecular weight	167.12
ii)	Colour	Colourless
iii)	Specific gravity	1.636
iv)	Melting point	Decomposes before melting
v)	Solubility in 100 cc of distilled water	2.35 gm at 15° C. 3.24 gm at 25° C
vi)	Crystal structure:	
a)	System	Orthorhombic
b)	Class	Sphenoidal (Orthorhombic disphenoidal)
c)	Space group	$P2_12_12_1$
d)	Lattice parameters	a = 7.648 A° b = 11.066 A° c = 7.843 A°
e)	Number of molecules in unit cell	Z4
vii)	Habits (observed in gel growth)	a) Needle shaped b) Orthorhombic disphenoidal c) Sphenoidal
viii)	Electromechanical property	Weakly piezoelectric Electro-mechanical coupling 8 to 30%
ix)	Magnetic property	Exhibits diamagnetic anisotropy

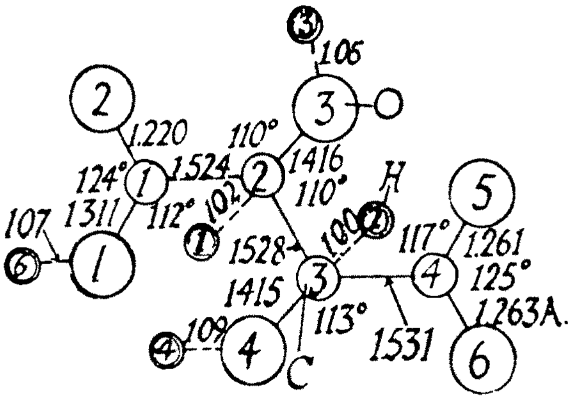

Fig. 1.1 Bond dimensions in the tartrate anion in $NH_4HC_4H_4O_6$

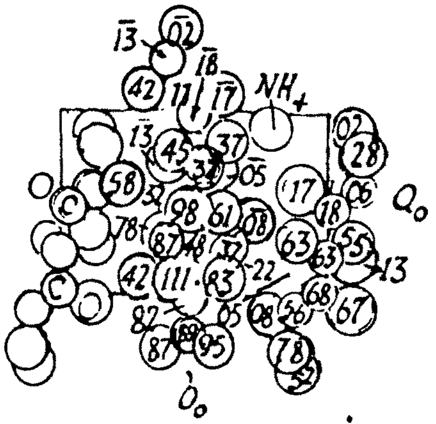

Fig. 1.2 a

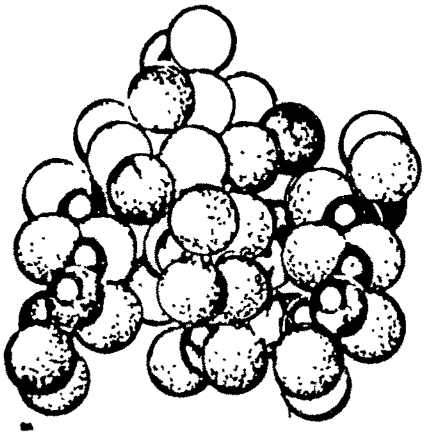

Fig. 1.2 b

Fig. 1.2 a (left) The orthorhombic structure of NH_4 HC_4H_4 O_6 projected along its C_o axis. Right-hand axes.

b (right) A packing drawing of the orthorhombic NH_4 HC_4 H_4O_6 arrangement seen along its C_o axis. The larger black circles are ammonium, the smaller ones carbon. The larger oxygen atoms are dot and short-line shaded.

Fig. 1.3

Hydrogen bridges between a tartrate ion and its surroundings.

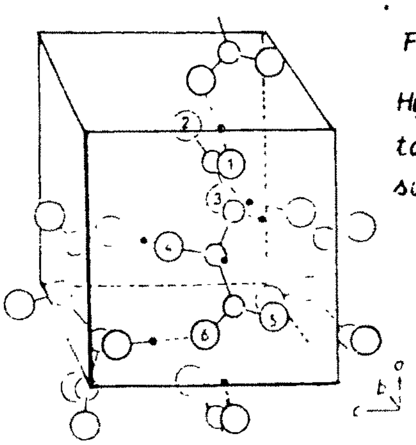

Fig. 1.3

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1.2 a) (Left) The orthorhombic structure of $NH_4HC_4H_4O_6$ projected along its C_o-axis-Right hand axis.

b) (Right) A packing drawing of the orthorhombic $NH_4HC_4H_4O_6$ arrangement seen along its C_o-axis. The large black circles are ammonium, the smaller ones carbon. The larger oxygen atoms are dot-and- short line shaded.

1.3 Hydrogen bridges between a tartrate ion and its surroundings.

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