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The Crystal Structure of Ammonium Hydrogen Maleate

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Ammonium hydrogen maleate, $NH_4^+C_4H_3O_4^-$ crystallizes in the orthorhombic system with $a = 0.4616(1)$, $b = 0.8085(2)$, $c = 1.6410(5)$ nm, $Z = 4$ in space group Pbcm, and is isostructural with the analogous potassium salt. The crystal structure has been refined from diffractometer data to conventional R and R_w of 0.052 and 0.065 for 690 reflexions [$I > 3\sigma(I)$]. Minor changes in the crystal structure were observed due to formation of N—H···O hydrogen bonds.

INTRODUCTION

The crystal structure of potassium hydrogen maleate was first treated by X-ray[1] and neutron[2] diffraction so that the symmetry of the hydrogen bond could be examined and the dimensions of the maleate residue precisely determined. Neutron diffraction study was done for 0kl data and provided data on the intramolecular hydrogen bond of 244 pm. It was not possible to distinguish between a hydrogen lying in the mirror plane or disordered half hydrogens, 105 pm away from each oxygen. Three-dimensional X-ray work confirmed the hydrogen bond of 243.7(4) pm with hydrogen located in the miror plane thus indicating the symmetric hydrogen bond by using definition (ii) which refers to crystallographic symmetry[3,4]. Since the ammonium ion, NH_4^+, forms a considerable number of salts which are isostructural with the corresponding potassium and rubidium salts, ammonium hydrogen maleate was prepared. The crystals proved to be isostructural with potassium hydrogen maleate and a complete crystal structure was carried out in order to obtain further data on the hydrogen bond as well as to study the effect of ammonium ion on the structure.

EXPERIMENTAL

The crystals of the title compound were kindly supplied by Prof. Hadži, Chemistry Department, E. Kardelj University of Ljubljana. Cell dimensions were obtained by least-squares from the 2Θ values of 40 moderately highorder reflexions measured on a CAD-4 diffractometer ($MoK\alpha_1$, $\lambda = 70.926$ pm). The centrosymmetric distribution of $|E|$ values ($\langle E^2 \rangle = 1.000$; $\langle |E^2 - 1| \rangle = 0.894$; $\langle |E| \rangle = 0.810$) indicated the space group Pbcm (No. 57) rather than $Pbc2_1$ (No. 29) which is also possible for the systematic absences. A prismatic, transparent crystal was used for the data collection. Details of the crystal data, data collection and reduction are given in Table I. The data were corrected for variations in reference reflexions and Lorentz-polarization effects, but not for absorption.

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TABLE I

Crystal Data and Data Collection Summary for Ammonium Hydrogen Maleate at 293(1) K

Molecular formula	$NH_4^+C_4H_3O_4^-$
Molecular weight	133.10
Space group	orthorhombic, Pbcm (No. 57)
a (nm)	0.4616(1)
b (nm)	0.8085(2)
c (nm)	1.6410(5)
Volume (nm^3)	0.61243
D_m (flotation) ($Mg \cdot m^{-3}$)	1.46(5)
Z	4
D_x ($Mg \cdot m^{-3}$)	1.444
X-rays (pm)	MoKα, $\lambda = 71.069$
Diffractometer	CAD-4 automatic, four-circle
Scan method	$\omega - 2\Theta$
2Θ scan width (°)	$0.9 + 0.2 \tan \Theta$
Maximum scan time (s)	100
Scan rate (°min^{-1})	min.: 0.8 max.: 20.1
Aperture (mm)	$2.5 + 0.9 \tan \Theta$
Reference reflexions	$\bar{2}\ 2\ \bar{4}$; $\bar{2}\ 2\ \bar{3}$; $0\ 4\ \bar{4}$
Background	1/4 of the scan time at each of the scan limits
$2\Theta_{max}$ (°)	60
Size of the crystal (mm)	$0.4 \times 0.4 \times 0.5$
Intensity decrease (%)	1
Measured reflexions	2069 ($-h, +k, \pm l$)
Mean discrepancy on I (%)	6.2
Averaged reflexions	863
Observed reflexions [$I > 3\sigma(I)$]	690
Unobserved reflexions	173
$\sigma(I)$ based on	counting statistics
μ (mm^{-1})	0.141

The initial positions of the heavy atoms were taken from the earlier study of the potassium salt and were refined by full-matrix least squares, minimizing $\Sigma w (|F_o| - k|F_c|)^2$, where w was chosen to keep $\Sigma w (\Delta F)^2$ uniform over the ranges of $(\sin\Theta/\lambda)$ and $|F_o|$. At this stage the conventional $R = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$ was 0.078. A difference electron-density synthesis located the hydrogen atoms close to the expected position. The positions of hydrogens with isotropic temperature factors were included in the final stages of the refinement. The final R and $R_w = (\Sigma w (F)^2/\Sigma w F_o^2)^{1/2}$ were 0.052 and 0.065 respectively; the weighting function was $w = 1.00/[\sigma^2 (F_o) + 0.002 F_o^2]$. The final difference synthesis revealed no peak higher than 100 e. nm^{-3}. In the final refinement cycle, the average and maximum shift/error for the refined parameters were 0.58 and 2.84, respectively, for U of H(2). Scattering factors for O, N and C were those given in reference 5 and for H were taken from reference 6.

All calculations were performed on the DEC-10 computer at RCU Ljubljana with SHELX-76[7] system of the crystallographic programmes. Lists of structure factors and anisotropic thermal parameters are available on request.

Final atomic coordinates with U_{eq}[8] are given in Table II.

TABLE II

Fractional Atomic Coordinates ($\times 10^4$ for O, N, C; $\times 10^3$ for H) and Equivalent or Isotropic Thermal Parameters (pm^2) with Estimated Standard Deviations

	x	y	z	U_{eq}	U_{iso} ($\times 10^{-1}$)
N	7221(5)	2500	0000	482(10)	
O(1)	4663(3)	3014(2)	1759(1)	610(8)	
O(2)	2296(3)	4234(2)	762(1)	626(9)	
C(1)	2730(3)	4016(2)	1502(1)	455(8)	
C(2)	887(4)	4934(2)	2095(1)	489(9)	
H(1)	625(9)	269(5)	43(3)		145(12)
H(2)	846(8)	328(6)	—14(4)		212(20)
H	480(10)	302(6)	250		106(13)
HC	—60(6)	561(3)	186(2)		63(7)

RESULTS AND DISCUSSION

The crystal structure of ammonium hydrogen maleate is essentially the same as that of potassium hydrogen maleate. It is composed of alternate layers of NH_4^+ and planar hydrogen maleate ions (Figure 1.). The ions lie in special positions due to space group considerations. The nitrogen atom of the ammonium ion lies on a twofold axis, whereas the acidic hydrogen atom lies on a mirror plane, which also bisects the hydrogen maleate residue at the midpoint of the —C=C— bond. Some important interatomic distances and angles are listed in Table III.

The maleate residue was found to be planar, with a mean plane —0.6659 x — 0.7461 y — 0.0051 z = 0.32682 nm. The deviations from this plane are 0.2, 0.2, —0.6 and 0.2 pm for O(1), O(2), C(1) and C(2) respectively. The acidic hydrogen H is by —5.0 pm out of the plane. The two C—O bond

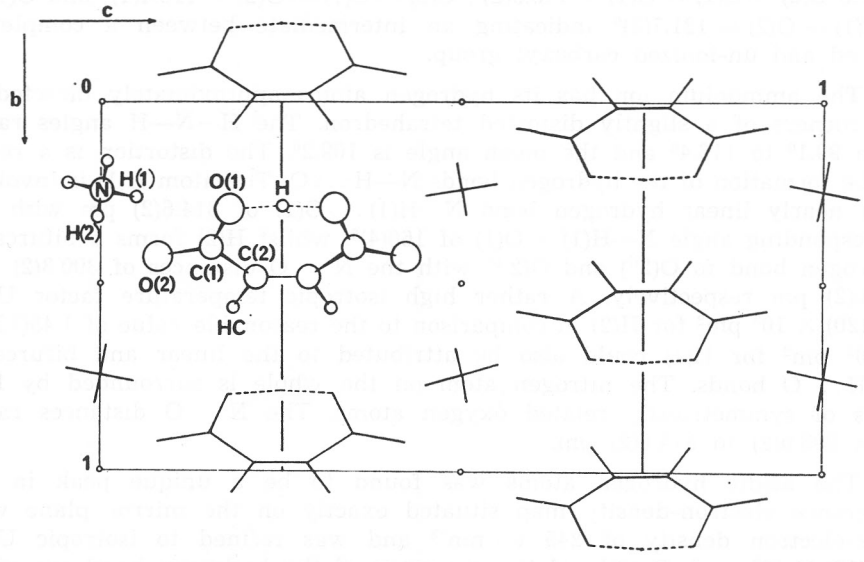

Figure 1. A view of the crystal structure along the [100] direction. The atoms of the crystal chemical unit are labelled.

TABLE III

Interatomic Distances (pm) and Angles (°) with Estimated Standard Deviations

(a) Ammonium ion

N—H(1), H(1^{i})	85(5)	H(1)—N—H(1^{i})	116(5)
N—H(2), H(2^{i})	88(5)	H(1)—N—H(2)	115(5)
N···O(1), O(1^{i})	314.6(2)	H(1)—N—H(2^{i})	105(5)
N···O(2), O(2^{i})	294.9(2)	H(1^{i})—N—H(2)	105(5)
N···O(2^{ii}), O(2^{iii})	300.3(2)	H(1^{i})—N—H(2^{i})	115(5)
N···O(2^{iv}), O(2^{v})	293.0(2)	H(2)—N—H(2^{i})	99(5)

(b) Hydrogen maleate ion

C(1)—O(1)	127.7(2)	O(1)—C(1)—O(2)	121.7(2)
C(1)—O(2)	124.3(2)	O(1)—C(1)—C(2)	119.9(2)
C(1)—C(2)	149.0(2)	O(2)—C(1)—C(2)	118.4(1)
C(2)—C(2^{vi})	132.9(2)	C(1)—C(2)—C(2^{vi})	130.8(2)
C(2)—HC	96(3)	C(1)—C(2)—HC	115(2)
		HC—C(2)—C(2^{vi})	114(2)

(c) Hydrogen bonds

H—O(1), O(1^{vi})	121.8(3)	O(1)—H—O(1^{vi})	174(4)
O(1)···O(1^{vi})	243.2(2)	C(1)—O(1)—O(1^{vi})	109.3(2)
H(1)···O(1)	232(5)	N—H(1)···O(1)	166(4)
H(1)···O(2)	228(4)	N—H(1)···O(2)	136(4)
H(2)···O(2^{ii})	243(5)	N—H(2)···O(2^{ii})	123(3)
H(2)···O(2^{iv})	228(4)	N—H(2)···O(2^{iv})	130(4)

Symmetry code i: x, 1/2 — y, — z; ii: 1 + x, y, z; iii: 1 + x, 1/2 — y, — z; iv: 1 — x, 1 — y, — z; v: 1 — x, — 1/2 + y, z; vi: x, y, 1/2 — z

lengths are C(1) — O(1) = 127.7(2) pm and C(1) — O(2) = 124.3(2) pm with the angles C(2) — C(1) — O(1) = 119.9(2)°, C(2) — C(1) — O(2) = 118.4(1)° and O(1) — — C(1) — O(2) = 121.7(2)° indicating an intermediate between a completely ionized and un-ionized carboxyl group.

The ammonium ion has its hydrogen atoms approximately directed to the corners of a slightly distorted tetrahedron. The H—N—H angles range from 99.1° to 116.4° and the mean angle is 109.2°. The distortion is a result of the formation of the hydrogen bonds N—H ... O. The atom H(1) is involved in a nearly linear hydrogen bond N—H(1) ... O(1) of 314.6(2) pm with the corresponding angle N—H(1) — O(1) of 166(4)°, whilst H(2) forms a bifurcated hydrogen bond to O(2^{ii}) and O(2^{iv}) with the N ... O distances of 300.3(2) and 293.0(2) pm respectively. A rather high isotropic temperature factor U of 2.12(20) × 10^{3} pm^{2} for H(2) in comparison to the reasonable value of 1.45(12) × × 10^{3} pm^{2} for H(1) could also be attributed to the linear and bifurcated N—H ... O bonds. The nitrogen atom on the whole is surrounded by four pairs of symmetrically related oxygen atoms. The N ... O distances range from 293.0(2) to 314.6(2) pm.

The acidic hydrogen atoms was found to be a unique peak in the difference electron-density map situated exactly on the mirror plane with peak-electron density of 245 $e \cdot nm^{-3}$ and was refined to isotropic U of 1.06(13) × 10^{3} pm^{2}. Details of the geometry of the hydrogen bond are given in Table III.

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IZVLEČEK

Kristalna struktura amonijevega hidrogen maleata

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Amonijev hidrogen maleat $NH_4^+C_4H_3O_4^-$ (AHM) kristalizira v ortorombskem kristalnem sistemu z $a = 0.4616(1)$, $b = 0.8085(2)$, $c = 1.6410(5)$ nm, $Z = 4$ v prostorski skupini Pbcm in je izostrukturen z ustrezno kalijevo soljo. Končni vrednosti R in R_w za 690 difraktometrskih podatkov sta bili 0.052 in 0.065. Kristalna struktura AHM se bistveno ne razlikuje od strukture kalijeve soli. Sestavljena je iz posameznih amonijevih ionov in hidrogen-maleatnih anionov. V strukturi sta dva tipa vodikovih vezi. V hidrogen maleatu je intramolekularna vodikova vez O···H···O dolžine 0.2342(2) nm, amonijeve in hidrogen maleatne ione pa povezujejo vodikove vezi N—H···O.