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Ammonium Hydrogen Phthalate Hemihydrate(?)*

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Abstract. $NH_4(C_8H_5O_4).\frac{1}{2}H_2O(?)$, monoclinic, $C2/c$, $Z = 8$, $a = 13.564$ (8), $b = 21.173$ (11), $c = 6.840$ (5) Å, $\beta = 112.8$ (8)°, $\rho_o = \rho_c = 1.41$g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least squares to $R = 7.3\%$ for 518 counter reflexions. The planes of the carboxyl groups are inclined to that of the aromatic ring at 7 and 85°. A random disorder of N and O atoms at the general position is assumed.

Introduction. The original purpose of this series was described in part I (Smith, 1975*a*). The title compound was an additional product of the synthesis of anhydrous ammonium hydrogen phthalate (Smith, 1975*b*). The crystal structure determination was undertaken to obtain more data on the possible shapes that the phthalate ion may adopt.

The crystals are tiny prismatic needles. Careful examination under a microscope was necessary to distinguish them from the anhydrous salt, and this made chemical analysis difficult. The density, determined by flotation, is the same as that of the anhydrous salt, thus precluding separation by that means. The observed density indicates $\frac{1}{2}$ a molecule of water of crystallization per asymmetric unit. A small batch was separated under a microscope and used for chemical analysis which indicated ~ 6% nitrogen; but the possibility that the sample contained some of the anhydrous salt cannot be excluded; the small sample size also lowers the reliability of the analysis. The title compound contains 7.2% N.

A well formed crystal, $0.02 \times 0.02 \times 0.09$ mm, was found and used for diffraction study (repeated attempts to obtain larger ones having failed). Preliminary photographic data yielded rough cell constants and the other unit-cell data. No evidence for a supercell was found in these photographs. Accurate cell dimensions

were obtained from several intense high-angle reflexions (Cu $K\alpha_1$ radiation, no monochromator) on a Picker FACS1 diffractometer. A unique set of data in the range $0 \le 2\theta \le 110°$ (Cu $K\alpha$ radiation, graphite monochromator) was collected in the coupled $\omega/2\theta$ scan mode with 3 min scans through 2° in 2θ; background was measured for 40 s on either side of the peak. The data were reduced to $|F|$ and σF with $p = 0.06$ (Doedens & Ibers, 1967). Of the 1127 reflexions not affected by systematic absence, only 518 had $I \ge 3\sigma I$ and were used in subsequent calculations. No absorption corrections were applied [μ(Cu $K\alpha$) = 9 cm^{-1}].

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971); E statistics strongly favoured space group $C2/c$. At the initial stages of refinement the $\frac{1}{2}$ water molecule of crystallization was assumed to occupy the special position $0,0.55,0.25$, and was thus required to possess a twofold axis. With Cromer & Mann's (1968) scattering factors the heavy atoms were refined with isotropic temperature factors for the C atoms and anisotropic ones for N and O to $R = 7.7\%$. The inclusion of the four H atoms attached to the aromatic ring in the calculated positions reduced R to 7.5%. At this stage it was noted that the atom at the special position had a large thermal vibration and was tetrahedrally surrounded by two independent O atoms, both at 2.88 (1) Å. Neither of these O atoms was expected to have its own H attached to it in view of the shape of the carboxylic acid groups of which they were part; both were 0.075 ± 0.010 Å closer to the C atoms than were the other pair. An electron density map was calculated and showed two independent peaks ~0.75 Å from the special position and disposed along the same vectors as the O atoms; only one independent peak is expected for a water molecule. The situation at the general position was the reverse of this with short contacts to O(4), O(2) and O(1) of 2.61 (1), 2.76 (1) and

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2·81 (1) Å respectively, disposed along three of the corners of a tetrahedron; O(4) and O(1) were respectively 1·31 (1) and 1·29 (1) Å from the C atoms and are expected to carry protons; this would mean that a simple N at this location would have five protons surrounding it; only four, disposed towards the corners of the tetrahedron suggested by the O atoms, were found in the electron density map.

Several explanations of the above difficulties are worthy of consideration: (1) The analysis was troublesome and the proposed formula may be wrong; the chemical nature of the phthalate ion is not in doubt, however, and its novel shape warranted refinement. (2) The real space group *might* be *Cc* with pseudo-symmetry; however, refinement in *C*2/*c* led to a phthalate ion with sensible thermal parameters, bond angles and bond distances, suggesting that little, if any, deviation from *C*2/*c* existed in the portion of the molecule of chemical interest. (3) It was concluded that an ammonium ion occupied the special position. No feature of the electron density map was larger than 0·5 e Å^{-3}; the chemically required $\frac{1}{2}$ ammonium and $\frac{1}{2}$ water required by density must therefore both occupy the position originally ascribed to the ammonium ion.

Although no evidence was observed for a supercell, the crystal was very small and the possibility remains that such a cell exists; nonetheless, random disorder was assumed for further refinement. Given this situation, half of the O(4)–O(1) pairs in the unit cell would still carry two H atoms and the remaining half would only carry one between them, having yielded the other to an ammonia molecule to form the ammonium

ion at the special position. Water molecules could then associate with pairs of the former type and ammonia molecules with pairs of the latter type (to give ammonium ions); in both cases four H atoms would surround the atom at the general position. The term NO atom is used in the further discussion of this site.

The peak in the remaining corner of the tetrahedron suggested by the disposition of O atoms about the NO

Table 2. *Unit-cell data for barium dihydrogen diphthalate*

Ba^{2+}(HOOC.C$_6$H$_4$.COO$^-$)$_2$, space group *P*2$_1$/*c*

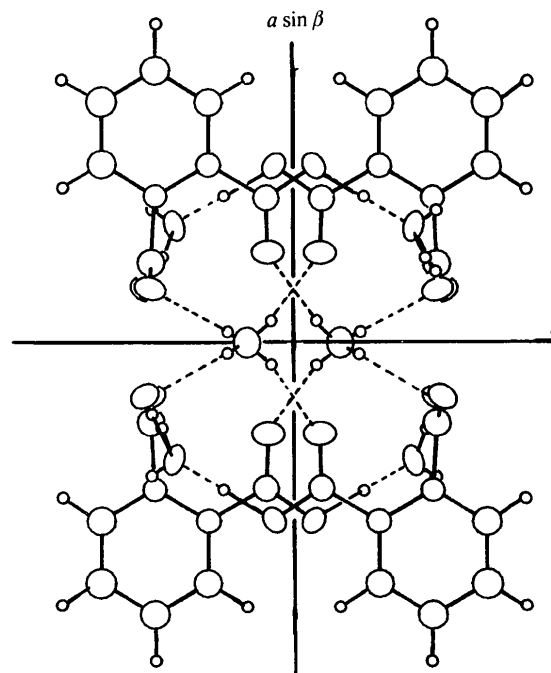|	
$a = 11\cdot4$ Å	$\rho_o = 2\cdot10$ g cm^{-3}
$b = 4\cdot50$	$\rho_c = 2\cdot10$
$c = 29\cdot2$	$Z = 4$
$\beta = 100^\circ$	

Fig. 1. A packing diagram for ammonium hydrogen phthalate hemihydrate(?) seen down c.

Table 1. *Final positional parameters and their e.s.d.'s* ($\times 10^4$)

	x	y	z
N	0	5494 (5)	2500
NO	2111 (5)	6263 (3)	2670 (10)
O(1)	976 (5)	3480 (3)	3340 (10)
O(2)	968 (5)	3423 (3)	110 (10)
O(3)	1640 (5)	4723 (3)	2000 (10)
O(4)	3190 (5)	5211 (3)	3760 (10)
C(1)	3203 (7)	4095 (4)	3550 (20)
C(2)	2643 (7)	3527 (4)	3020 (10)
C(3)	3209 (8)	2962 (5)	3420 (20)
C(4)	4328 (9)	2959 (5)	4350 (20)
C(5)	4893 (8)	3529 (5)	4910 (20)
C(6)	4325 (8)	4092 (5)	4480 (20)
C(7)	1441 (8)	3485 (5)	2010 (20)
C(8)	2615 (8)	4703 (5)	3040 (20)
H(3)	2790	2550	3010
H(4)	4720	2540	4600
H(5)	5720	3540	5600
H(6)	4750	4510	4880
NH(1)	400	5240	2200
NH(2)	200	5700	3400
O(1)H	1550	6390	460
O(4)H	2650	5740	3210
NOH(1)	1300	6500	3100
NOH(2)	2400	6500	2800

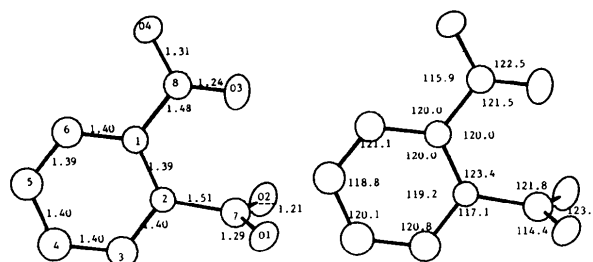
Fig. 2. The atom-numbering scheme, bond angles (°) and distances (Å) in the phthalate ion. Standard deviations: ~0·01 Å, 0·08°.

atom was 0·7 Å from it and is ascribed to an H atom. For the remaining hydrogen-bonded NO—O linkages one would expect an H some 0·8 Å from the NO atom in the direction of the O(2) atom, with a more complicated situation for the other two hydrogen bonds. In fact, only cylinders of electron density were observed along all three vectors and the remaining H atoms were thus placed at the midpoints of the vectors. The inclusion of the remaining six H atoms reduced R to a final value of 7·3%.*

Discussion. Final positional parameters are given in Table 1. Fig. 1 is a packing diagram and Fig. 2 is a view of the phthalate ion showing the atom numbering, bond angles and distances. The most interesting feature of the molecule is the hitherto unobserved disposition of the carboxylic acid groups, the planes of which are almost perpendicular to, and almost coplanar with, that of the aromatic ring (the angles being 85 and 7°). It may be interesting to compare the shape of the phthalate ion in this salt to that in barium dihydrogen diphthalate, unit-cell data for which are given in Table 2; the very short b axis requires that the phthalate ion be almost planar in the Ba salt.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32400 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

As a conclusion to this series this author is unable to relate the contribution of the O atoms to the total intensities of the monochromating reflexions in various acid phthalates to the size of the anomalous peaks observed in them at energies close to the $K\alpha$ radiation of O (Mattson & Ehlert, 1966).

Corrigendum

The author thanks Fiedler (1976) who queried the x coordinate of C(4) in part II of this series (Smith, 1975c); it should read 0·422 (2) and not 0·442 (2).

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Alkalifreies wasserhaltiges β-Al₂O₃

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Abstract. Ideal formula $3H_2O \cdot 11Al_2O_3$, hexagonal, $P6_3/mmc$, $a = 5\cdot600$ (1), $c = 22\cdot702$ (1) Å, $Z = 1$, $D_x = 3\cdot166$ g cm⁻³. Crystals were obtained by boiling β-Al₂O₃ crystals in concentrated H_2SO_4. The spinel blocks characteristic of the β-Al₂O₃ or magnetoplumbite-type structures are joined by an intermediate layer containing an O atom, O(5), and a water molecule distributed at random in the 6(h) positions with $x = 0\cdot3746$ (8) and 0·6474 (16) respectively. An H atom

might be connected to each O(5) atom to form a hydrogen bond between O(5) and the nearest water molecule. The Al—O(5)—Al angle is 157·6° instead of 180° as in pure β-Al₂O₃.

Einführung. Die hier untersuchten Kristalle stammen aus dem Arbeitsmaterial von Saalfeld, Matthies & Datta (1968) und besitzen keinen spektralanalytisch nachweisbaren Rest von Na_2O, jedoch einen gewissen Unterschuss an H_2O gegenüber der Idealzusammensetzung. Die Gitterkonstanten wurden mit Hilfe einer Weissenberg-Aufnahme (Cu $K\alpha_1$ 1,54050, Cu $K\alpha_2$

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