Crystal Structure of a Hydrate Complex of Phthalic Acid [phth = *o*-phthalate]

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In an attempt to grow crystals of sodium acid phthalate, the title compound, (phth)₂(H₂O)₃ (**1**) [phth=phthalate], was obtained which crystallizes in the monoclinic system; space group *C2/c*, $\beta = 113.65(3)^\circ$, $V = 1812.9(6)\text{\AA}^3$, $Z = 4$, $D_c = 1.415\text{ g/cm}^3$, the final $R = 0.0781$ and $wR = 0.2367$. O-H groups of phthalate rings form strong hydrogen bonds with lattice water which stabilizes the crystal structure.

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A structure analysis of sodium acid phthalate hemihydrate was undertaken as part of an investigation of a series of salts of phthalic acid.¹ The aim of the investigation was an attempt to correlate the structural features and anomalous properties observed in these compounds by Mattson and Ehlert.² A discussion of the problem appeared in part I of this series by SMITH³

Compound **1** was prepared as follows. All of the reagents were of AR grade and used without further purification. Potassium hydrogenphthalate (0.2040 g, 1 mmol) was dissolved in a 10 mL EtOH/H₂O (*v:v* = 1:1) solution, and then the resultant solution basified with 1 mol L⁻¹ KOH to pH = 8. Transparent crystals were obtained upon evaporation in a yield of up to 31.23%. *Anal.* Calcd for **1**: C, 49.72; H, 4.66% Found: C, 49.31; H, 4.56%. A crystal having dimensions of 0.20 × 0.18 × 0.17 mm was chosen for X-ray diffraction studies. The measurements were made on a Rigaku-RAXIS-IV diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073\text{ \AA}$) at 291(2)K. The structure was solved by direct methods using SHELXS-97,⁴ and refined by full-matrix least-squares techniques anisotropically for all non-H atoms. All H atoms were added according to theoretical calculation, H6F and H5E were refined using a riding model. The crystal data and experimental parameters are listed in Table 1. A chemical diagram of the title compound is shown in Fig. 1, the final positional parameters for all non-hydrogen atoms are given in Table 2 and selected bond lengths and bond angles are summarized in Table 3. The hydrogen-bonding distances and angles are presented in Table 4.

Fig. 1 Structural chemical diagram.

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The molecular structure of the title complex is illustrated in Fig. 2. The complex asymmetry unit consists of one phthalate and one and a half H₂O molecules.

Compound **1** crystallizes in space group *C2/c*. Its structure may be described as an infinite one-dimensional chain. In the complex, the adjacent phthalate rings in the chain are almost coplanar with a dihedral angle of 4.169°. The mean plane of C1 to C8 is $-5.769x + 0.619y + 6.860z = 4.4091$; the deviations of the four O atoms (O1, O2, O3 and O4) from the mean plane are 1.2097, -1.0222, 0.0930, and -0.1937 Å, respectively. The average distances of C=O and C-C are about 1.2305 and 1.307 Å, which are almost the same values as the normal distance (According to the international tables for crystallography Vol. C, the bond distances of C=O and C-O are 1.226 and 1.305 Å,

Table 1 Crystal and experimental data

Formula:	C ₁₆ H ₁₈ O ₁₁
Formula weight	386.30
Crystal size (mm):	0.20 × 0.18 × 0.17
Crystal system:	monoclinic
Space group:	<i>C2/c</i> $Z = 4$
<i>a</i> =	13.585(3) Å
<i>b</i> =	21.219(4) Å $\beta = 113.65(3)^\circ$
<i>c</i> =	6.8659(14) Å
<i>V</i> =	1812.9(6) Å ³
<i>D_x</i> =	1.415 g/cm ³
$\theta_{\max}$ =	25.25° with Mo K_α
No. of reflections measured =	2824
No. of reflections used =	1627
No. of parameters =	136
<i>R</i> =	0.0781
$(\Delta/\sigma)_{\max}$ =	0.000
$(\Delta\rho)_{\max}$ =	0.352 e Å ⁻³
$(\Delta\rho)_{\min}$ =	-0.250 e Å ⁻³
Measurement:	Rigaku-R-AXIS-IV
Program system:	Sheldrick SHELXS-97
Structure determination:	direct methods
The final positional Refinement:	full matrix

CCDC 650415 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
O(1)	991(2)	6528(1)	8366(4)	46(1)
O(2)	946(2)	6578(1)	5070(4)	43(1)
O(3)	3175(2)	4792(1)	8751(5)	52(1)
O(4)	1614(2)	5277(1)	6971(5)	49(1)
O(5)	2113(2)	6263(1)	2682(5)	49(1)
O(6)	0	4504(1)	7500	26(1)
C(1)	2646(3)	6478(2)	8011(5)	34(1)
C(2)	3223(3)	7039(2)	8427(7)	46(1)
C(3)	4335(3)	7033(2)	9358(7)	52(1)
C(4)	4883(3)	6467(2)	9884(8)	54(1)
C(5)	4319(3)	5906(2)	9480(7)	47(1)
C(6)	3197(3)	5902(2)	8528(5)	35(1)
C(7)	1432(2)	6521(1)	7007(4)	32(1)
C(8)	2590(3)	5302(2)	8013(5)	35(1)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

O(1)-C(7)	1.296(3)
O(2)-C(7)	1.231(3)
O(3)-C(8)	1.317(4)
O(4)-C(8)	1.230(4)
C(4)-C(5)	1.382(5)
C(5)-C(6)	1.397(5)
C(6)-C(8)	1.481(5)
C(2)-C(1)-C(6)	119.6(3)
C(2)-C(1)-C(7)	117.6(3)
C(6)-C(1)-C(7)	122.8(3)
C(5)-C(4)-C(3)	119.9(3)
C(5)-C(4)-C(1)	119.0(3)
C(1)-C(4)-C(3)	119.9(3)
O(2)-C(7)-O(1)	125.0(3)
O(4)-C(8)-O(3)	122.1(3)
O(3)-C(8)-C(6)	115.0(3)

respectively).

It is to be noted that there are two kinds of hydrogen bonds (C-H...O, O-H...O) involving uncoordinated oxygen atoms of carboxyl, carbon atoms and oxygen atoms of H_2O other than the intramolecular hydrogen bonds (C5-H5A...O3). The bond distance and angles are: O(1)-H(1B)...O(1)^{#1} 2.468(5), $\angle\text{O(1)-H(1B)...O(1)}^{\#1}$ 157(9) $^\circ$, O(5)-H(5F)...O(1)^{#3} 2.793(4), $\angle\text{O(5)-H(5F)...O(1)}^{\#3}$ 167(4) $^\circ$, O(5)-H(5E)...O(2) 2.782(4), $\angle\text{O(5)-H(5E)...O(2)}$ 173(5) $^\circ$, O(3)-H(3B)...O(5)^{#2} 2.604(4), $\angle\text{O(3)-H(3B)...O(5)}^{\#2}$ 172.5 $^\circ$, O(6)-H(6F)...O(4) 2.876(3), $\angle\text{O(6)-H(6F)...O(4)}$ 173(6) $^\circ$, C(5)-H(5A)...O(3) 2.762(4), $\angle\text{C(5)-H(5A)...O(3)}$ 99.7 $^\circ$. The symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+3/2$ #2 $x, -y+1, z+1/2$ #3

Table 4 Hydrogen bonds [$\text{\AA}$ and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(5)-H(5A)...O(3)	0.93	2.45	2.762(4)	99.7
O(6)-H(6F)...O(4)	0.86(2)	2.02(2)	2.876(3)	173(6)
O(5)-H(5E)...O(2)	0.90(2)	1.88(2)	2.782(4)	173(5)
O(1)-H(1B)...O(1) ^{#1}	0.82(2)	1.70(4)	2.468(5)	157(9)
O(3)-H(3B)...O(5) ^{#2}	0.82	1.79	2.604(4)	172.5
O(5)-H(5F)...O(1) ^{#3}	0.96(5)	1.85(5)	2.793(4)	167(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+3/2$ #2 $x, -y+1, z+1/2$ #3 $x, y, z-1$.

Fig. 2 Molecular structure along with atom labeling.

Fig. 3 Hydrogen-bonding interactions of compound 1.

$x, y, z-1$ (Table 3). Extensive hydrogen-bonding are show in Fig. 3. A 3D network structure is formed by hydrogen bonds.

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