

## Potassium hydrogen diphtalate dihydrate: a new structure and correction to the literature

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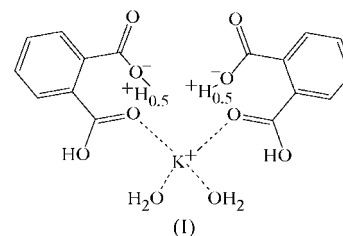
The title compound,  $K^+ \cdot [(C_8H_5O_4)_2H]^- \cdot 2H_2O$  or  $K^+ \cdot C_{16}H_{11}O_8^- \cdot 2H_2O$ , was prepared by slow evaporation of an aqueous solution of potassium hydrogen phthalate. The molecular complex consists of a potassium cation coordinated to a proton-bound hydrogen phthalate dimer and two water molecules. The potassium cation resides on a twofold axis in a distorted square-antiprism coordination geometry. The compound is isomorphous with the ammonium analogue, previously misidentified. As potassium hydrogen phthalate is frequently used in the manufacture of buffers, organic carbon standards, acidimetric standards and various other products, the crystallization of a compound with a different stoichiometry from a solution containing the acidimetric standard has important practical implications.

### Comment

The hydrated potassium salt of the proton-bound hydrogen *o*-phthalate dimer, (I), was obtained in an attempt to grow crystals of potassium hydrogen *o*-phthalate (commonly abbreviated to KAP for potassium acid phthalate) from an aqueous solution at room temperature. Instead of precipitating the usual six-sided {010} plates characteristic of KAP, heavily etched elongated prisms were observed. As these irregular crystals lacked the perfect basal cleavage planes characteristic of KAP, the sample was indexed and found to belong to the *C*-centered monoclinic crystal system, space group *C2/c*, as opposed to the primitive orthorhombic system of KAP.

The crystal habit of (I) is a combination of the pinacoids {010} and {110} elongated along [001], lacking other identifiable faces. The molecular formula was determined to be  $[K^+ \cdot H^+(o-C_6H_4COOHCOO^-)_2] \cdot 2H_2O$ , a molecular complex containing a potassium cation, a proton-bound hydrogen phthalate dimer and two water molecules (Fig. 1). The hydrogen phthalate dimer is bridged by two symmetry-related

H atoms, each with half-site occupancies. The conformation of the hydrogen phthalate ion is characterized by the nearly orthogonal carboxylate groups making an angle of  $84.2^\circ$  with one another.



The eight-coordinate potassium cation occupies a site on the twofold axis in a distorted square-antiprism coordination geometry, with approximate  $\bar{8}2$  symmetry (Fig. 2). The coordination sphere is composed of two water molecules and the hydrogen phthalate dimer in the molecular complex, and additionally two hydrogen phthalate ions from adjacent molecular complexes along the *C*-centered [001] staggered-rotation channels (Fig. 3). The potassium ions are enveloped by spiraling proton-bound hydrogen phthalate dimers and water molecules. The dominant interchannel interactions are of the van der Waals type between aryl rings.

It is surprising that this substance has not been reported until now, given the abundant research conducted on KAP

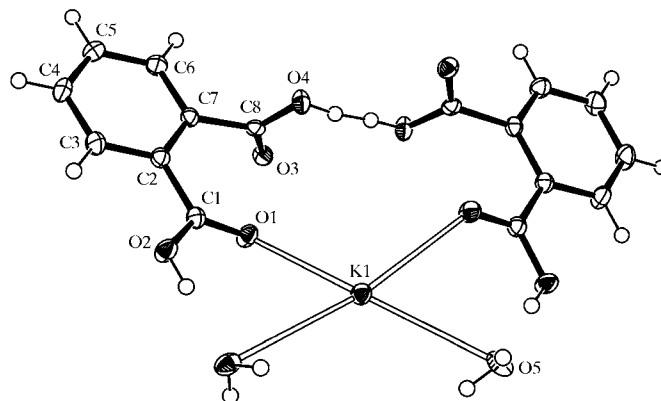


Figure 1

A view of the molecular complex of the title compound, with displacement ellipsoids at the 50% probability level.

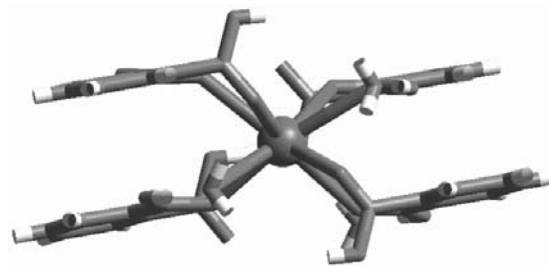
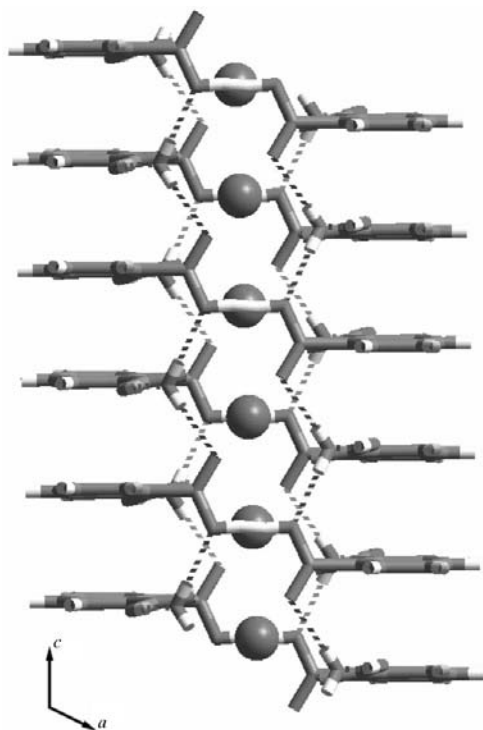


Figure 2

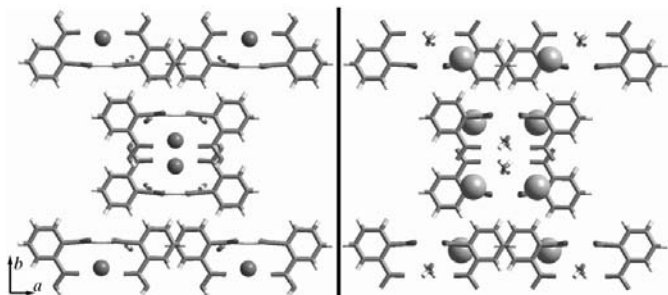
The coordination sphere of the potassium cation, illustrating the distorted square-antiprism coordination geometry.

and other phthalic acid salts (Okaya, 1965; Gougoutas *et al.*, 1980; Smith, 1975; Eremina *et al.*, 1993; Kariuki, 1995). As KAP is frequently used in the manufacture of buffer solutions, acidimetric standards and various other products, the possible contamination arising from the crystallization of a compound with a different stoichiometry has obvious practical implications for any analytical applications utilizing KAP.

Smith (1977) reported a structure that bears a remarkable resemblance to the present compound (Fig. 4), but is described under the unusual banner 'ammonium hydrogen phthalate hemihydrate(?)' and is characterized as  $\text{NH}_4(\text{C}_8\text{H}_5\text{O}_4)_2 \cdot 0.5\text{H}_2\text{O}$  (?) [monoclinic,  $C2/c$ ,  $Z = 8$ ,  $a = 13.564$  (8) Å,  $b = 21.17$  (1) Å,  $c = 6.840$  (5) Å and  $\beta =$



**Figure 3**  
A view along [010], perpendicular to the [001] potassium ion channel. Hydrogen bonds are indicated as dotted lines.



**Figure 4**  
Packing diagrams of the title compound (left) and the ammonium analogue (right), illustrating the isomorphism. The spheres (right) indicate the position of the proposed disorder in the ammonium structure. A water molecule occupies this position in the structure of the title compound (left).

112.8 (8)°]. It was immediately evident that this was the ammonium isomorph of the present potassium salt; however, it had not been described as such.

There are several questionable features contained in the report of the ammonium structure, the first and foremost being the question mark in the title. The author used flotation methods to determine the density of the crystal, and imposed a water/ammonium disorder model to account for the observed density. While the author does well to narrate the derivation of his complex solution, the disorder model employed is forced. It seems that the author's primary emphasis was to publish what he viewed as a noteworthy conformation of the phthalate anion accepting that 'the proposed formula may be wrong'. Several data sets were collected on poorly scattering crystals of the ammonium compound prepared according to the method of Smith (1977). While the present proposed model was a correct solution,  $R1$  was only 0.10.

**Experimental**

Crystals of the title compound were obtained by slow evaporation of a solution containing acidimetric grade potassium hydrogen phthalate (Aldrich, 22 g) and deionized water (Barnsted NANOpure, 18.2 M W<sup>-1</sup> cm<sup>-1</sup>, 200 ml) in a 250 ml crystallization dish at room temperature (~296 K). After approximately four days, crystals of both KAP and the title compound were produced in the same dish. Currently, the dominance of one crystal over the other appears random, though the formation of KAP is strongly favored as the title compound is only observed in approximately 1% of growth experiments conducted. Formation of the title compound does not appear to depend on temperature, exposure to light or rate of evaporation.

*Crystal data*

$\text{K}^+ \cdot \text{C}_{16}\text{H}_{11}\text{O}_8^- \cdot 2\text{H}_2\text{O}$   
 $M_r = 406.38$   
 Monoclinic,  $C2/c$   
 $a = 13.5830$  (3) Å  
 $b = 21.1270$  (5) Å  
 $c = 6.8170$  (2) Å  
 $\beta = 116.5521$  (11)°  
 $V = 1749.93$  (8) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.542$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 239 reflections  
 $\theta = 2.4\text{--}24.4^\circ$   
 $\mu = 0.36$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 Cut block, colorless  
 0.48 × 0.31 × 0.29 mm

*Data collection*

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan ( $HKL2000$ ; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.847$ ,  $T_{\max} = 0.903$   
 3680 measured reflections

2041 independent reflections  
 1682 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\max} = 29.9^\circ$   
 $h = -19 \rightarrow 19$   
 $k = -29 \rightarrow 29$   
 $l = -9 \rightarrow 9$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.082$   
 $S = 1.00$   
 2041 reflections  
 131 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

**Table 1**

Selected interatomic distances (Å).

K1—O3 <sup>i</sup>	2.7831 (8)	K1—O1	2.8279 (8)
K1—O1 <sup>i</sup>	2.8270 (9)	K1—O5	3.0954 (10)

Symmetry code: (i)  $x, 1 - y, z - \frac{1}{2}$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2–H2···O5 <sup>ii</sup>	0.82	1.76	2.5815 (12)	174
O4–H4A···O4 <sup>ii</sup>	0.82	1.62	2.4347 (17)	173
O5–H5A···O3 <sup>iii</sup>	0.827 (17)	1.925 (18)	2.7433 (13)	169.9 (14)
O5–H5B···O4 <sup>iv</sup>	0.833 (17)	1.907 (17)	2.7330 (13)	171.4 (15)

Symmetry codes: (ii)  $1-x, y, \frac{1}{2}-z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $1-x, 1-y, -z$ .

All H atoms were initially located in a difference Fourier map. The positions of the water H atoms were refined freely. The remaining H atoms were then placed in idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.93 Å and O–H distances of 0.82 Å.  $U_{\text{iso}}(\text{H})$  values were fixed at  $1.2U_{\text{eq}}$  of the parent atoms for aromatic and water H atoms, and at  $1.5U_{\text{eq}}$  of the parent atoms for OH groups.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL2000* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *maXus* (Mackay *et al.* 1998); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1160). Services for accessing these data are described at the back of the journal.

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