Molecular Structure and Thermal Analysis of Potassium Hydrogenphthalate Monohydrate

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Single crystals of potassium hydrogenphthalate monohydrate, KHPhth(H$_2$O), were grown from aqueous solution using a slow cooling method and the structure was determined by X-ray diffraction analysis. The crystals belong to the monoclinic space group $P2_1/c$. Its unit cell parameters are as follows: $a = 1.1235(1)$, $b = 0.6689(1)$, $c = 1.1998(2)$ nm, $\beta = 98.85°$, $V = 0.8909(1)$ nm^3, $D_c = 1.657$ g/cm^3, $Z = 4$, $F(000) = 456$. The thermal decomposition of the complex was studied using differential scanning calorimetry (DSC), thermogravimetry-derivative thermogravimetry (TG-GTG) and FT-IR techniques. With a linear heat rate, the diagrams show three endothermic processes. RCOOK and K$_2$CO$_3$ are produced at 330 and 467 °C, respectively, according to FT-IR analysis.

Key words: Potassium Hydrogenphthalate Monohydrate, Molecular Structure, Thermal Analysis

Introduction

Potassium hydrogenphthalate (KHPhth, KHC$_8$H$_4$O$_4$) is commonly used as a primary standard to determine alkalinity because it is readily available as a pure substance and has a well-characterized reactivity near ambient temperature and pressure. Its single crystals possess piezo-electric, pyro-electric, elastic and non-linear optical properties [1 – 3]. The crystal structure of KHPhth has been determined by Okaya [4] in the orthorhombic space group $P2_1ab$ in non-standard setting. An exchange of the axes was performed by Jetten [5], which gives the space group $Pca2_1$ in the standard setting, with lattice parameters $a = 0.9609$, $b = 1.3857$, $c = 0.6466$ nm. A new kind of KHPhth structure, which contains a water molecule, is reported here. Thermal analysis using TG-DTG, DSC techniques has also been carried out to determine the thermal properties.

Results and Discussion

Structure of KHPhth(H$_2$O)

There are one water molecule, one potassium cation and one biphthalate anion in the asymmetric unit as seen in Fig. 1. As is evident from Fig. 2, seven oxygen atoms are bonded to the central potassium
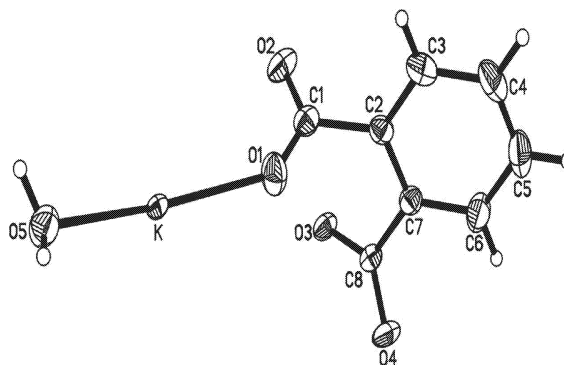

Fig. 1. The asymmetric unit of the KHPhth(H$_2$O) structure.

atom, which are O1, O2B, O3B, O3C, O4A, O4C and O5(*water*). The K-O bond lengths are as follows: K-O1, 0.2340(1), K-O2B, 0.2394(1), K-O3B, 0.2327(1), K-O3C, 0.2488(1), K-O4A, 0.2305(1), K-O4C, 0.2597(1), and K-O5(*water*), 0.2388(1) nm, with an average length of 0.2405 nm, which falls in the range of published K-O bond lengths [4, 6 – 8]. These oxygen atoms are from four different biphthalate groups and one water molecule. The metal atom takes part in a four-membered chelate ring formed by one carboxylate group: O3C-C8-O4C-K. This
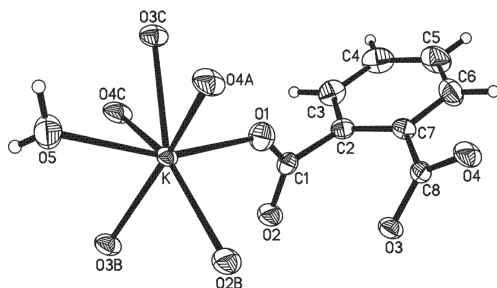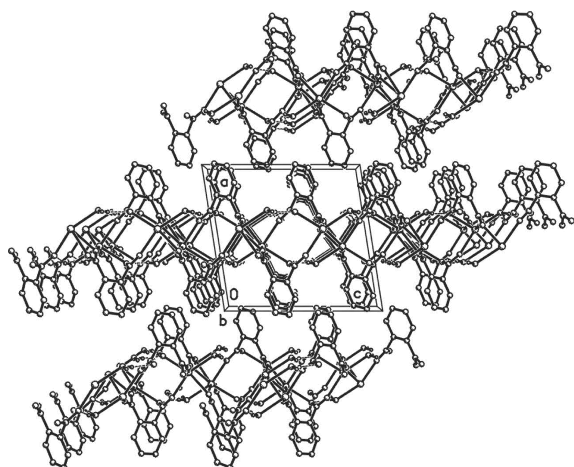
Fig. 2. The coordination sphere of the potassium ion in KHPhth(H₂O).

Fig. 3. Packing arrangement of KHPhth(H₂O).

ring is not planar. A seven-membered chelate ring is formed by two carboxylate groups, the benzene ring and the potassium atom: O3B-C8B-C7B-C2B-C1B-O2B-K. All four oxygen atoms of each phthalate group participate in coordination with potassium ion, but not with the same potassium ion.

In Fig. 3, the packing arrangement of KHPhth(H₂O) is shown. The phthalate and potassium ions are interconnected giving a complex layer structure. In Fig. 4, the distorted coordination decahedron of the potassium ion is shown.

From a consideration of the C-O bond lengths in the carboxyl groups, it is impossible to decide which of the two carboxyl groups in the phthalate moieties is ionized. In an idealized situation for non-ionized carboxyl group, a significant difference between the two C-O distances should be observed, while on coordination some lengthening of one CO-O bond should be seen. Examination of the observed carboxyl C-O bond lengths reveals that there is no significant dif-
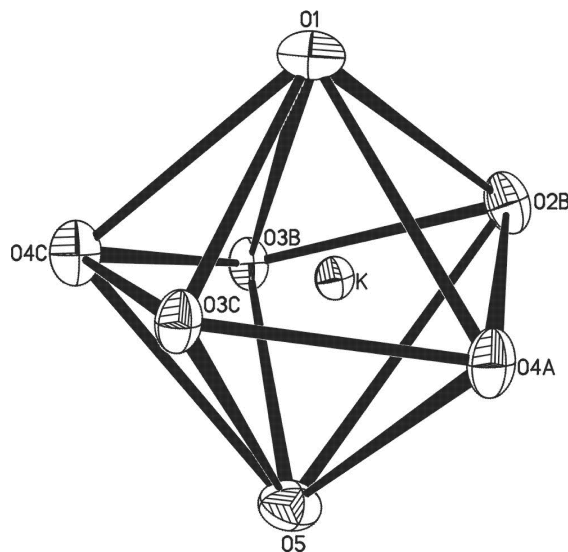

Fig. 4. The polyhedron of the potassium ion, which is a distorted decahedron.

ference between the four carboxyl C-O distances in KHPhth(H₂O): C1-O1, 0.1250(1), C1-O2, 0.1258(1), C8-O3, 0.1261(1), and C8-O4, 0.1257(1) nm. A similar situation is found in the carboxyl groups of yttrium tartrate hydrate $[Y(C_4H_4O_6)(C_4H_5O_6)\cdot 2.5H_2O]$ [9], where there is also no significant difference between any of the four carboxyl C-O distances. This is in contrast to the KHPhth crystal [4], in which the C-O distances has significant difference between C1-O1 and C1-O2, indicating that the carboxyl group does not ionize, while the equality of the bond lengths between C8-O3 and C8-O4 suggests a delocalization of the electrons in the COO⁻ group.

The equality of C-O distances may be attributed to the existence of hydrogen bonds between O in one carboxyl group and the CO-H in another one. A short H-bond of 0.213(2) nm is found for O2 and O3. This is the same as in KHPhth [4] and other alkali hydrogenphthalates [10]. In addition, the carboxyl oxygen atoms O1 and O2 and H5A, H5B of the water molecule of crystallization also form hydrogen bonds. The bond distance of H5A...O1 and H5B...O2 are 0.203(3) and 0.211(3) nm, respectively. These H-bonds together with the above mentioned H-bonds help to increase the stability of the complex layer structure of KHPhth(H₂O).

It is also difficult to judge which carboxyl group ionizes when considering the angles of the two carboxyl groups: ∠C2-C1-O1, 115.13(13)°, ∠ C2-C1-

O2, 119.07(14)°, ∠C7-C8-O3, 118.65(13)°, and ∠C7-C8-O4, 120.11(13)°. The corresponding angles in KHPhth [4] are: 122.6(2)°, 113.21(17)°, 117.46(16)°, and 117.98(19)°, where the almost equivalent C-C-O angles indicate the ionization of the C8 carboxyl group.

The two carboxyl groups are planar with a dihedral angle of 66.5°. For O1, O2, C1, C2, the plane equation is $-7.612x - 2.028y + 9.196z = 0.8690$, with a mean deviation from the plane of 0.0004 nm, and for O3, O4, C7, C8, the plane equation is $3.144x + 1.019y + 10.721z = 5.3526$, with a mean deviation from the plane of 0.00043 nm. Owing to steric hindrance caused by the two carboxyl groups in *ortho* positions, these carboxyl groups can no longer stay in the plane of the benzene ring. The angles between the ring plane and the carboxyl planes are 78.1° and 33.6° for C1 and C8 carboxyl groups, respectively.

The benzene ring is a slightly distorted regular hexagon with average C-C distance of 0.1387 nm and C-C-C angles of 119.9° like those in KHPhth [4]. All six bond distances and bond angles are within standard deviations from these average values. The equation of the ring plane is $1.399x + 4.464y + 8.475z = 7.1244$, with a mean deviation from the plane of 0.00067 nm.

Thermal analysis of KHPhth(H$_2$O)

The DSC and TG-DTG curves of KHPhth(H$_2$O) are shown in Fig. 5 and Fig. 6, respectively. In Fig. 5, three endothermic peaks can be recognized between room temperature and 450 °C. The first weak endothermic peak with a peak temperature at 224 °C has a change of enthalpy of 7.2 kJ/kg. According to the TG-DTG curves in Fig. 6, the change of weight % in this process
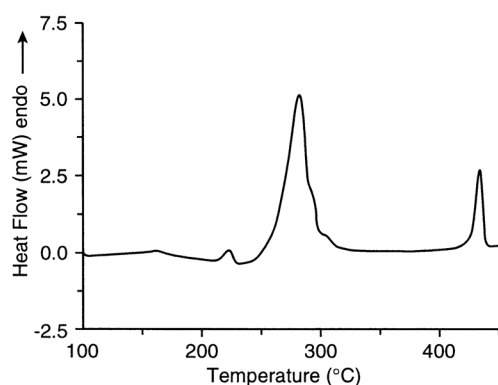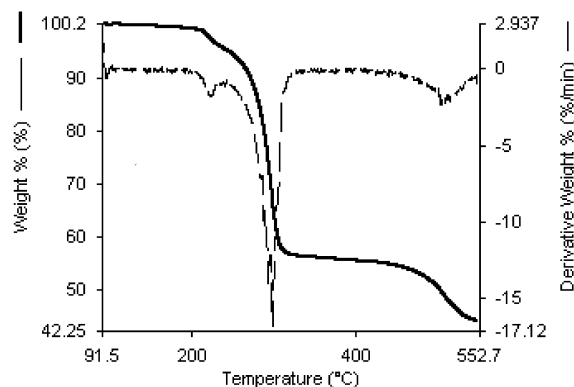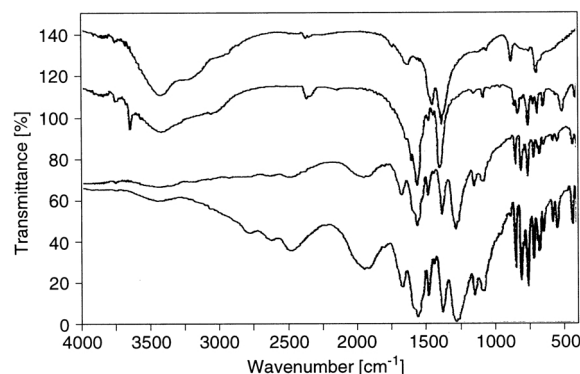

Fig. 6. TG-DTG curves of KHPhth(H$_2$O).

Fig. 7. IR spectra of KHPhth(H$_2$O) and its decomposition residues observed at room temperature, 245 °C, 330 °C, and 467 °C from bottom to top.

is 4.19 %. However, the change of weight % should be 8.11 % if it loses one mole of water. Therefore, the first step corresponds to only 0.5 mole of crystal water.

The second endothermic peak is much more intense. The change of enthalpy in this endothermic process is 183.2 kJ/kg at a peak temperature of 285 °C. This process is accompanied with a prominent weight loss (39.9 % of the total) in the TG-DTG curves.

Another endothermic peak can also be distinguished from 431 to 437 °C in the DSC curve, with a change of enthalpy of 46.5 kJ/kg. This process has a weight loss of 10.8 %. The solid residue at 550 °C was 44.2 % of the total sample weight, which is a relatively high value compared with the thermal decomposition results of potassium salts like [K(HTNR)(H$_2$O)]$_n$ [6], [K$_2$(TNR)(H$_2$O)]$_n$ [8], K(NTO)(H$_2$O) [11], and KP [12], where TNR = 2,4,6,-trinitroresorcinolate, NTO = 3-nitro-1,2,4-triazol-5 -onate, P = picrate.

Fig. 5. DSC curve of KHPhth(H$_2$O).

Table 1. Crystal data and structure refinement for KHPhth (H_2O).

Empirical formula	$C_8H_7KO_5$
Formula weight	222.24
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions (nm)	$a = 1.1235(1)$
	$b = 0.6689(1)$
	$c = 1.1998(2)$
	$\beta = 98.85(1)$
Volume (nm^3), Z	0.8909(1), 4
Density (calculated) (g/cm^3)	1.657
Absorption coefficient (mm^{-1})	0.588
$F(000)$	456
Crystal size (mm)	$0.52 \times 0.42 \times 0.16$
Index range	$0 \leq h \leq 13$
	$0 \leq k = 8$
	$-14 \leq l = 14$
Reflections collected	1990
Independent reflections	1662 [R (int) = 0.0108]
Goodness-of-fit on F^2	1.097
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0230$, $wR_2 = 0.0545$[a]
R Indices (all data)	$R_1 = 0.0271$, $wR_2 = 0.0557$[a]
Extinction coefficient	0.0245(15)
Largest diff. peak and hole (e·nm^3)	192 and -186

[a] $w = 1/[\sigma^2(F_O{}^2) + (0.0497p)^2]$, where p = $(F_O{}^2 + 2F_C{}^2)/3$.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^2 \times 10^5$) for KHPhth(H_2O).

Atom	x	y	z	U(eq)
K	5577(1)	6194(1)	6939(1)	16(1)
O(1)	3845(1)	6853(2)	5639(1)	34(1)
O(2)	3296(1)	4153(2)	4589(1)	32(1)
O(3)	4153(1)	7255(2)	3083(1)	24(1)
O(4)	3881(1)	10487(2)	2855(1)	29(1)
O(5)	6763(1)	5886(2)	8762(1)	36(1)
C(1)	3171(1)	5940(2)	4880(1)	23(1)
C(2)	2129(1)	7144(2)	4282(1)	22(1)
C(3)	990(2)	6948(3)	4596(1)	31(1)
C(4)	48(2)	8146(3)	4106(2)	37(1)
C(5)	232(2)	9565(3)	3321(2)	40(1)
C(6)	1365(2)	9815(3)	3023(2)	34(1)
C(7)	2314(1)	8597(2)	3495(1)	22(1)
C(8)	3523(1)	8804(2)	3131(1)	21(1)

The equivalent isotropic displacement parameter U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (nm) and selected angles (°) of KHPhth(H_2O).

Atoms	Bond lengths (nm)	Atoms	Angles (°)
K-O(4)A	0.2305(1)	O(1)-C(1)-O(2)	125.81(15)
K-O(3)B	0.2327(1)	O(1)-C(1)-C(2)	115.13(13)
K-O(1)	0.2340(1)	O(2)-C(1)-C(2)	119.07(14)
K-O(5)	0.2388(1)	C(7)-C(2)-C(3)	119.20(14)
K-O(2)B	0.2394(1)	C(3)-C(2)-C(1)	119.91(13)
K-O(3)C	0.2488(1)	C(4)-C(3)-C(2)	120.26(16)
K-O(4)C	0.2597(1)	C(5)-C(4)-C(3)	120.37(16)
O(1)-C(1)	0.1250(1)	C(4)-C(5)-C(6)	120.04(16)
O(2)-C(1)	0.1258(1)	C(5)-C(6)-C(7)	120.16(16)
O(3)-C(8)	0.1261(1)	O(1)-K-C(1)B	92.15(4)
O(4)-C(8)	0.1257(1)	O(5)-K-C(1)B	110.68(5)
O(5)-H(5)A	0.089(3)	O(2)B-K-C(1)B	21.71(4)
O(5)-H(5)B	0.085(3)	O(3)C-K-C(1)B	166.95(4)
C(1)-C(2)	0.1509(2)	O(1)-K-C(1)	14.39(4)
C(2)-C(7)	0.1393(2)	O(5)-K-C(1)	159.60(4)
C(2)-C(3)	0.1395(2)	C(1)-O(1)-K	137.89(10)
C(3)-C(4)	0.1384(2)	O(1)-C(1)-K	27.72(7)
C(4)-C(5)	0.1375(3)	O(2)-C(1)-K	98.08(10)
C(5)-C(6)	0.1385(2)	C(2)-C(1)-K	142.85(10)
C(6)-C(7)	0.1391(2)	C(6)-C(7)-C(2)	119.93(14)
C(7)-C(8)	0.1495(2)	C(6)-C(7)-C(8)	120.07(14)
K-C(1)	0.3373(1)	C(2)-C(7)-C(8)	119.98(13)
K-C(8)B	0.3497(1)	O(4)-C(8)-O(3)	121.21(13)
K-C(8)A	0.3500(1)	O(4)-C(8)-C(7)	120.11(13)
O1-H(5)A	0.203(3)	O(3)-C(8)-C(7)	118.65(13)
O2-H(5)B	0.211(3)	O(4)A-K-C(8)C	99.46(4)

Symmetry transformations used to generate equivalent atoms:
A $-x+1$, $-y+2$, $-z+1$; B $-x+1$, $-y+1$, $-z+1$; C x, $-y+3/2$, $z+1/2$; D x, $-y+3/2$, $z-1/2$.

To find out what the solid residues are, FT-IR was used. Fig. 7 shows the IR spectra of the solid residue of KHPhth(H_2O) at different temperature. It can be seen that the spectrum at 242 °C is almost the same as the spectrum of KHPhth(H_2O) at room temperature, which indicates that the loss of crystal water does not change much the structure of the solid residue at nearly 250 °C.

The retention of the vibration at 1605 cm^{-1} of the benzene ring framework and of the C-H out-of-plane bending vibrations at $850-650$ cm^{-1} indicate that the benzene ring does not break after the second prominent endothermic process at 330 °C. The asymmetric and symmetric vibrations of $RCO_2{}^-$ at 1605 and 1400 cm^{-1} prove the retention of potassium carboxylate groups although the absorptions of RCO_2K in KHPhth(H_2O) are at 1563 cm^{-1} and 1382 cm^{-1}. The wavenumber of RCO_2K in the solid residue increases in the asymmetric and symmetric vibration, which also proves the formation of a new kind of carboxylate.

The spectrum of the solid residue at 470 °C is more simple. The disappearance of the vibration at 1605 cm^{-1} of the benzene ring framework and the C-H out-of-plane bending vibration at $850-650$ cm^{-1} indicate that the benzene ring breaks the C-H vibration. However, the vibrations at 1451, 880 and 700 cm^{-1} of the solid residue prove the existence of K_2CO_3 [13]. Furthermore, there still exist the asymmetric and symmetric vibrations of RCO_2K at 1635 and 1383 cm^{-1}, respectively.

Experimental Section

Materials

KHPhth crystals suitable for X-ray analysis were grown from aqueous solutions using a slow cooling method [14]. Two kinds of KHPhth crystals were obtained: One was the same as Okaya [4] reported, the other contained a water molecule, which is reported here. Analysis for KHPhth(H_2O): calcd. C 43.24, H 3.17; found C 43.26, H 3.14.

Physical measurements

A Perkin-Elmer Pyris 1 DSC was used for DSC measurement. Dry, oxygen-free nitrogen was used to purge the DSC at 20 ml/min. The heating rate for the thermal decomposition analyses was 10 °C/min. Sample mass was about 0.5 mg, contained in sealed aluminum pans. A Perkin-Elmer Pyris 1 TG analyzer was used for thermogravimetric analysis. About 0.5 mg of sample was held in a platinum pan, in a flow of dry, oxygen-free nitrogen at 20 ml/min, and the heating rate was 10 °C/min. A Bruker Equinox 55 FT-IR spectrometer (KBr pellet) was used in the range of $400 - 4000$ cm^{-1} with the resolution of 4 cm^{-1}.

X-ray crystallography

A Siemens P4 four-circle diffractometer with graphite monochromatized Mo-K$_\alpha$ radiation ($\lambda = 0.071073$ nm) at 296(2) K using ω scan mode was used. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction date from 26 reflections in the θ range of $3.82 - 15.27°$. An empirical absorption correction was applied to the data. Crystallographic and refinement parameters are given in Table 1.

The structure was solved by direct methods. Anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The hydrogen atoms of the water molecule were located on a ΔF map and refined with constraints. The program, SHELXL-97 [15] was used for computations. Coordinates and equivalent atomic displacement parameters of the non-hydrogen atoms are listed in Table 2. Selected bond distances and bond angles are given in Table 3.

All equipments were calibrated before use.

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