



## Crystal structure of potassium hydrogen phthalate revisited

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The present study provides new insight into the structure of potassium hydrogen phthalate **1**. The single crystal X-ray structure of **1** consists of a crystallographically independent potassium cation and a unique hydrogen phthalate anion. The  $\mu_4$ -heptadentate binding mode of the unique hydrogen phthalate ligand organizes the  $K^+$  ions into a layer resulting in a two-dimensional (2D) coordination polymer. As a result parallel chains of face-sharing  $\{KO_7\}$  polyhedra extending along *c* are formed. The parallel chains are flanked on either side by hydrogen phthalate wings and are interlinked by vertex sharing of three polyhedra to extend the connectivity along *a* axis. The structure of **1** is stabilised by  $\pi \cdots \pi$  stacking interactions. A comparative study of the structures of alkali metal hydrogen phthalates is described.

**Keywords:** Potassium hydrogen phthalate, X-ray structure,  $\mu_4$ -Heptadentate binding, Two-dimensional, Coordination polymer

As part of our ongoing research program of metal-carboxylates we recently reported on the structural aspects of water rich bivalent metal phthalates<sup>1</sup>. In our studies of *s*-block metal carboxylates we have recently demonstrated that the mode of linking of  $\{MO_n\}$  ( $M=Ba$ ,  $n=9$ ) polyhedra can be either discrete or face-sharing depending on the nature or binding modes of ligands around the central metal<sup>2</sup>. In view of our long standing interest in the structural aspects of *s*-block metal carboxylates<sup>3,4</sup>, we have undertaken a study of the structural features of the noncentrosymmetric potassium hydrogen phthalate **1** (also known as potassium acid phthalate and abbreviated as KHP) to comprehend the mode of linking of  $\{KO_x\}$  polyhedra in the crystal structure.

Compound **1** is a well-known primary standard for acid-base titrations<sup>5</sup> as this anhydrous compound contains a free  $-COOH$  group and is commercially available in a high state of purity. In synthetic inorganic chemistry KHP is used as a source of hydrogen phthalate or phthalate ligand for example for the synthesis of the molecular solid bis(hydrogenphthalato)diazinc(II) or the one-dimensional (1D) ladder coordination polymer piperazinediium bis( $\mu_2$ -phthalato)zincate(II) monohydrate<sup>6</sup>. In addition, KHP can also be employed as a thermal standard<sup>7</sup>. The crystal structure of **1** was first reported by Okaya<sup>8</sup> in the noncentrosymmetric orthorhombic space group  $P2_1ab$ . Potassium hydrogen phthalate is referred to by the abbreviation KHP in

nonlinear optics literature. In recent years KHP has been extensively studied by several research groups for its nonlinear optical properties by growing both pure and doped crystals from aqueous solution due to the commercial availability of this water soluble noncentrosymmetric solid. Many reports of growth of doped crystals of KHP have appeared in the literature for example incorporation of S-donor ligands like thiourea<sup>9</sup> and or bivalent metal ions like zinc<sup>10</sup> and a recent claim of incorporation of resorcinol<sup>11</sup>. Interestingly, the sodium analogue namely sodium hydrogen phthalate crystallizes in the noncentrosymmetric orthorhombic  $B2ab$  space group as sodium hydrogen phthalate hemihydrate<sup>12</sup> unlike **1** which is anhydrous in nature. In the present work we have recrystallized commercial samples of KHP in the presence and absence of thiourea for the single crystal study. The results of these investigations are described in this report.

### Materials and Methods

All the chemicals used in this study were of reagent grade and used as received without any further purification. Double distilled water was used for recrystallization of **1**. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400  $cm^{-1}$  at a resolution of 4  $cm^{-1}$ . UV-visible spectra of aqueous solutions of the samples were recorded using Agilent 8453 UV-visible

spectrophotometer (200–1100 nm) using a quartz cell. The crystal structure of potassium hydrogen phthalate recrystallized in the presence of thiourea was determined using a Bruker D8 Quest Eco X-ray diffractometer. Intensity data were collected at room temperature (RT) using monochromated Mo ( $K\alpha$ ) ( $\lambda = 0.7107 \text{ \AA}$ ) radiation. The program suite APEX3 (Version 2019.1) was used (i) to integrate the frames, (ii) to perform absorption correction and (iii) to determine the unit cell. The structure was solved with SHELXS and subsequent refinements were performed with SHELXL<sup>13</sup>. All non-hydrogen atoms were refined anisotropically. H atoms attached to the aromatic ring of the phthalate ligand were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. Technical details of data acquisition and selected crystal refinement results are given in Table 1.

Table 1 — Crystal data and structure refinement for **1**

Identification code	KHP
Empirical formula	$C_8H_5O_4K$
Formula weight	204.22
Temperature	293(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	$a = 9.6089(5) \text{ \AA}$ $b = 13.3044(7) \text{ \AA}$ $c = 6.4735(3) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$827.58(7) \text{ \AA}^3$
Z	4
Density (calculated)	$1.639 \text{ mg/m}^3$
Absorption coefficient	$0.616 \text{ mm}^{-1}$
F(000)	416
Crystal size	$0.632 \times 0.193 \times 0.165 \text{ mm}^3$
Theta range for data collection	$2.615$ to $25.650^\circ$
Index ranges	$-11 \leq h \leq 11$ , $-16 \leq k \leq 16$ , $-7 \leq l \leq 7$
Reflections collected	8061
Independent reflections	1541 [R(int) = 0.0207]
Completeness to theta = $25.242^\circ$	98.70%
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	1541 / 1 / 120
Goodness-of-fit on $F^2$	1.116
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0197$ , $wR2 = 0.0531$
R indices (all data)	$R1 = 0.0206$ , $wR2 = 0.0539$
Absolute structure parameter	0.113(13)
Largest diff. peak and hole	0.154 and $-0.211 \text{ e.\AA}^{-3}$
CCDC number	1976019

### Recrystallization of potassium hydrogen phthalate

The recrystallization was performed both in the presence and in the absence of thiourea. An aqueous solution of potassium hydrogen phthalate (2.040 g, 10 mmol) in  $\sim 25 \text{ mL}$  of water was added into an aqueous solution of thiourea (0.760 g, 10 mmol) in  $\sim 25 \text{ mL}$  of water. The reaction mixture was stirred well for 4 h and filtered. The filtrate was left undisturbed for slow evaporation of the solvent. The crystalline product thus obtained was washed with small amounts of cold water and air dried. Yield of isolated product was  $\sim 1.1 \text{ g}$ . In another experiment, potassium hydrogen phthalate (1.020 g, 5 mmol) was dissolved in water ( $\sim 50 \text{ mL}$ ). The clear solution was left undisturbed for slow evaporation of the solvent. The crystalline product thus obtained was washed with small amounts of cold water and air dried. Yield of isolated product was  $\sim 0.85 \text{ g}$ .

## Results and Discussion

### Description of the crystal structure of KHP

From the X-ray study, the molecular formula of potassium hydrogen phthalate is ascertained as  $K(C_8H_5O_4)$ . KHP crystallizes in the noncentrosymmetric orthorhombic space group  $Pca2_1$  (Space group No. 29) and its structure consists of a crystallographically independent  $K^+$  cation and a unique hydrogen phthalate anion with all atoms located in general positions (Supplementary Data, Fig. S1). The geometric parameters of the unique hydrogen phthalate ligand are in the normal range (Supplementary Data, Table S1). The unit cell parameters obtained in this work are in excellent agreement with earlier reported data<sup>8, 14–17</sup>. In the Cambridge Structural Database (CSD)<sup>18</sup> a total of 13 hits are available to date for the structure of potassium hydrogen phthalate in  $Pca2_1$  space group<sup>19</sup>. The very first report on potassium acid phthalate by Okaya<sup>8</sup> in 1965 described the structure in the  $P2_1ab$  (older notation for space group No. 29) space group. In all the later studies the space group is designated as  $Pca2_1$ . Of the thirteen entries in the CSD, eight datasets (variable temperature) were reported by Harte et al.<sup>15</sup> and Riley et al.<sup>16</sup> to study the temperature effect on the short H-bond (four datasets) and proton transfer, respectively. In spite of several studies on the structure of KHP, it is surprising to note that the two-dimensional architecture of the  $K^+$  ions and the mode of linking of  $\{KOx\}$  polyhedra has not been described in detail. Hence we present this aspect in our structure discussion below.

The central potassium exhibits seven coordination and is bonded to four symmetry related hydrogen phthalates (Fig. 1) via the carboxylate oxygen atoms O1, O1<sup>i</sup>, O1<sup>ii</sup>, O2<sup>ii</sup>, O2<sup>iii</sup>, O3<sup>i</sup>, O3<sup>ii</sup> (for symmetry relation see Table 2) resulting in a distorted monocapped trigonal prismatic {KO<sub>7</sub>} polyhedron (Fig 1). One oxygen of hydrogen phthalate viz. O4 which carries H4 is not involved in metal binding.

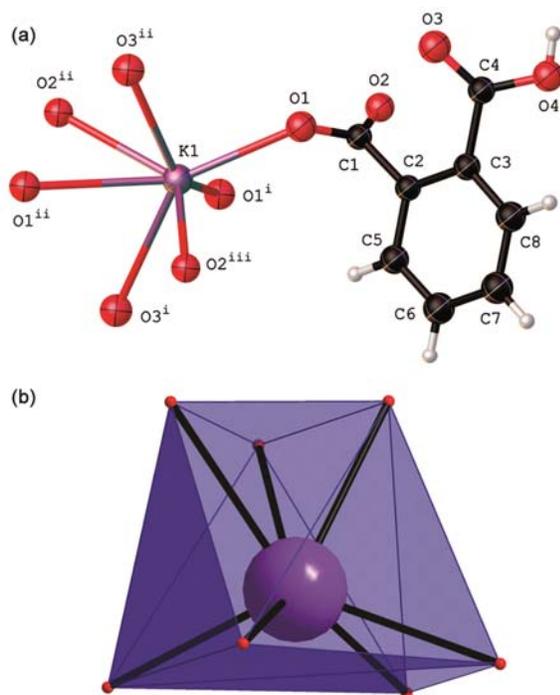


Fig. 1 — The crystal structure of **1** showing the atom labelling for the crystallographically independent K<sup>+</sup> ion which exhibits seven coordination and the unique hydrogen phthalate (**top**). For clarity, only the O atoms of the symmetry generated ligands are shown. Symmetry code: i)  $-x+1/2, y, z-1/2$ ; ii)  $x-1/2, -y+1, z$ ; iii)  $-x+1/2, y, z+1/2$ . The distorted monocapped trigonal prismatic {KO<sub>7</sub>} polyhedron (**bottom**)

The K-O bond distances vary between 2.6353(16) and 3.1396(19) Å while the O-K-O bond angles range from 44.96(4) to 147.96(6)<sup>o</sup> (Table 2). These values are in good agreement with reported data<sup>14-17</sup>. The observed bond lengths and angles indicate severe distortion from a regular {KO<sub>7</sub>} polyhedron.

The unique hydrogen phthalate with a carboxylate anion (O1, O2) and a -COOH group (O3, O4) disposed *ortho* to each other, functions as a μ<sub>4</sub>-bridging ligand and each unique linker is bonded to four symmetry-related potassium ions. The O1 atom of the carboxylate group binds to three symmetry-related K<sup>+</sup> ions and functions as a μ<sub>3</sub>-bridge resulting in three different K···K separations of 3.894, 4.347 and 4.914 Å, respectively (Fig. 2) while O2 binds to two symmetry-related K<sup>+</sup> ions resulting in a K···K separation of 3.894 Å. In the unionized carboxylic acid group (O3, O4) only the O3 atom is bonded to two symmetry related potassium ions with a K···K separation of 3.894 Å (Fig 2). The net result is a μ<sub>4</sub>-heptadentate bridging coordination mode (Supplementary Data, Fig. S2) for the unique hydrogen phthalate ligand. When the K<sup>+</sup> ions are organised with the three different K···K separations, a two-dimensional connectivity of the metals extending along the direction of both *a* and *c* axes (crystallographic *ac* plane) can be observed (Fig. 3, in Supplementary Data, Fig S3). The coordination of the μ<sub>4</sub>-bridging hydrogen phthalate ligands to each K<sup>+</sup> ion in the layer results in the formation of parallel chains of face-sharing {KO<sub>7</sub>} polyhedra flanked by hydrogen phthalate ligands which extend along *c* axis (Fig 4). The face sharing architecture of the polyhedra can be explained due to the binding of more than one K<sup>+</sup> ion by O1, O2 and O3. A closer scrutiny reveals that the parallel chains of {KO<sub>7</sub>} polyhedra along *c* are

Table 2 — Selected bond lengths (Å) and angles (°) for **1**

Bond lengths (Å)					
K1-O1	2.6353(16)	K1-O3 <sup>ii</sup>	2.8757(18)	K1-K1 <sup>iv</sup>	3.894
K1-O1 <sup>i</sup>	2.769(2)	K1-O1 <sup>ii</sup>	2.9896(17)	K1-K1 <sup>iii</sup>	4.347
K1-O2 <sup>ii</sup>	2.7908(17)	K1-O3 <sup>i</sup>	3.1396(19)	K1-K1 <sup>v</sup>	4.914
K1-O2 <sup>iii</sup>	2.8161(17)				
Bond angles (°)					
O1-K1-O1 <sup>i</sup>	89.80(5)	O1 <sup>i</sup> -K1-O3 <sup>ii</sup>	138.11(5)	O3 <sup>ii</sup> -K1-O1 <sup>ii</sup>	65.73(5)
O1-K1-O2 <sup>ii</sup>	129.60(5)	O2 <sup>ii</sup> -K1-O3 <sup>ii</sup>	67.34(5)	O1-K1-O3 <sup>i</sup>	138.48(5)
O1 <sup>i</sup> -K1-O2 <sup>ii</sup>	86.87(5)	O2 <sup>iii</sup> -K1-O3 <sup>ii</sup>	88.16(5)	O1 <sup>i</sup> -K1-O3 <sup>i</sup>	64.86(5)
O1-K1-O2 <sup>iii</sup>	89.88(6)	O1-K1-O <sup>ii</sup>	147.96(6)	O2 <sup>ii</sup> -K1-O3 <sup>i</sup>	83.56(4)
O1 <sup>i</sup> -K1-O2 <sup>iii</sup>	133.21(5)	O1 <sup>i</sup> -K1-O <sup>ii</sup>	118.01(6)	O2 <sup>iii</sup> -K1-O3 <sup>i</sup>	85.70(5)
O2 <sup>ii</sup> -K1-O2 <sup>iii</sup>	126.89(4)	O2 <sup>ii</sup> -K1-O <sup>ii</sup>	44.96(4)	O3 <sup>ii</sup> -K1-O3 <sup>i</sup>	137.82(3)
O1-K1-O3 <sup>ii</sup>	83.09(5)	O2 <sup>iii</sup> -K1-O <sup>ii</sup>	82.30(5)	O1 <sup>ii</sup> -K1-O3 <sup>i</sup>	72.09(5)
Symmetry transformations used to generate equivalent atoms: i) $-x+1/2, y, z-1/2$ ; ii) $x-1/2, -y+1, z$ ; iii) $-x+1/2, y, z+1/2$ ; iv) $-x, -y+1, z+1/2$ ; v) $-x, -y+1, z-1/2$					

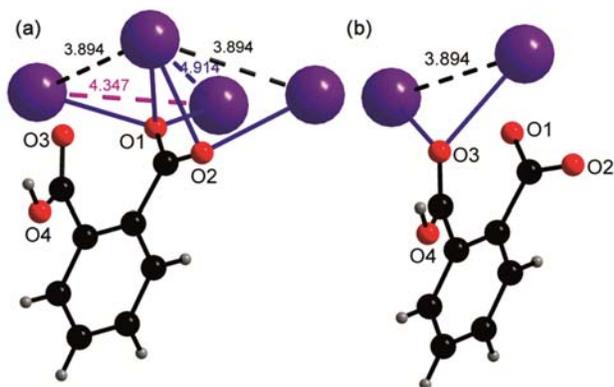


Fig. 2 — Binding mode of the (O1, O2) carboxylate (**left**); Binding mode of the free -COOH (O3, O4) group (**Right**). O1 is bonded to three K<sup>+</sup> while O2 and O3 are bonded to two K<sup>+</sup> ions. See also Fig. S1

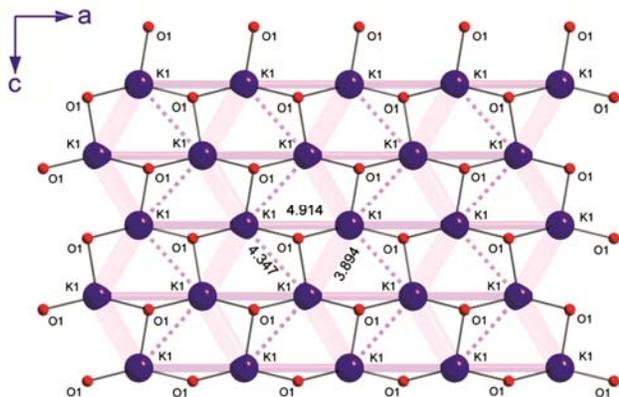


Fig. 3 — Two dimensional connectivity of K<sup>+</sup> ions showing the three different K...K separation. For clarity only the  $\mu_3$ -bridging O1 atom is shown. For a figure showing all the seven O atoms around each K, see Fig. S3

interlinked at the O1 site and extend along *a* axis. The O1 oxygen is bonded to three symmetry related K<sup>+</sup> ions. In view of this, the vertex O1 is shared by three {KO<sub>7</sub>} polyhedra (Supplementary Data, Fig. S4). By viewing the structure along *a* axis it can be evidenced that the organic ligands function like wings for the {KO<sub>7</sub>} polyhedral chain (Fig. 4).

The H4 atom of the -COOH group functions as a hydrogen donor and is accepted by the carboxylate oxygen of a symmetry related hydrogen phthalate resulting in a O4-H4...O2 hydrogen bonding interaction accompanied by a D...A distance of 2.551(2) Å and DHA angle of 170.4° (Supplementary Data, Table S2). This short bond links the hydrogen phthalate anions into a zig zag chain extending along the direction of the *c* axis (Fig. 5). It is interesting to note that the hydrogen bonding between the adjacent ligands is within the 2D layer in the *ac* plane. Study

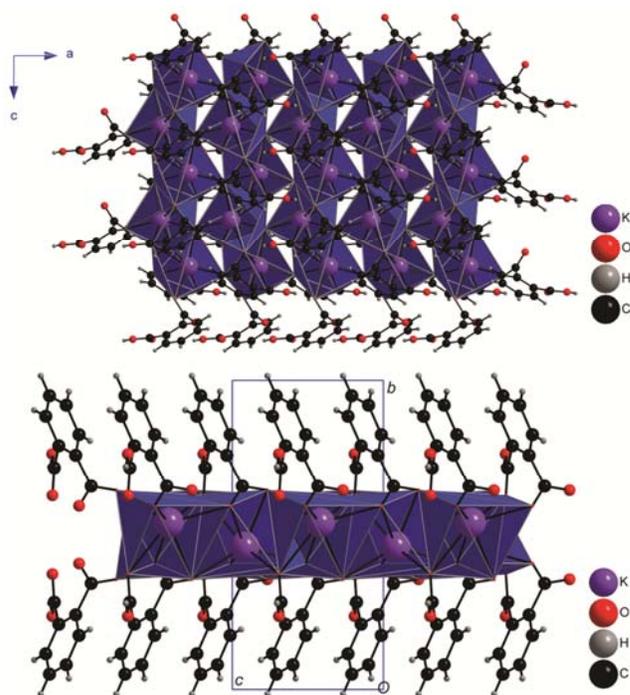


Fig. 4 — A view along *b* axis shows parallel chains of face-sharing {KO<sub>7</sub>} polyhedra flanked on either side by hydrogen phthalate wings which extend along *c* axis. The parallel chains are interlinked at O1 and thus extend along *c* (**top**). A view along *a* showing the hydrogen phthalate wings on either side of the polyhedral chain (**bottom**)

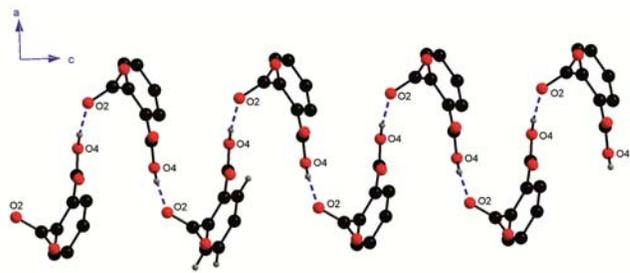


Fig. 5 — A portion of the infinite H-bonded chain of hydrogen phthalates extending along *c* due to the O4-H4...O2 interaction (**bottom**)

of the hydrogen bonding interactions in the hydrogen phthalates of Li<sup>20,22</sup> and K<sup>15</sup> has been the subject of much research. For KHP the effect of temperature on this short H-bond has been studied in detail by Harte et al.<sup>15</sup>.

An analysis of the short ring interactions using the program Platon<sup>23</sup>, reveals two Cg...Cg (Cg is ring centroid) distances between adjacent aromatic rings measuring 4.991 and 5.141 Å, respectively (Supplementary Data, Table S3). Both these distances which are perpendicular to each other alternate along *c* and *b* axis respectively (Supplementary Data, Fig. S5).

The shorter Cg...Cg distance of 4.991 Å corresponds to the stacking of the six membered rings along the *c* axis in the layer while the longer Cg...Cg contact is between neighboring aromatic rings in the adjacent layers in the (1 0 1) plane (Fig. 6). The longer Cg...Cg interaction extends the structure in the third dimension by linking the adjacent layers and is an inter layer interaction. Since  $\pi\cdots\pi$  stacking interactions between benzene rings can exist at Cg...Cg distances upto 7.0 Å<sup>24</sup>, these interactions in the title compound can be considered as further stabilizing its structure.

In view of the above mentioned interesting structural features and the isostructural nature of the hydrogen phthalates of K, Rb and Cs (*vide infra*) the supramolecular aggregation<sup>25,26</sup> of the isotopic compounds especially KHP can be explained as follows. In aqueous medium hydrated potassium ions condense with the carboxylate site of hydrogen phthalate forming a charge neutral 1:1 compound. This at the supersaturation, aggregates to satisfy the other coordination centre, namely the undissociated carboxylic acid group.

#### Synthetic aspects and spectral studies of KHP

An aqueous reaction of phthalic acid with alkali metal hydrogen carbonate (or hydroxide) in equimolar ratio affords the alkali metal hydrogen phthalate in good yields. This synthetic route is well documented for all the alkali metal hydrogen phthalates especially for Rb<sup>27</sup> and Cs<sup>28</sup>. Due to its ready availability a commercial sample of potassium hydrogen phthalate was recrystallized in the presence and absence of thiourea in this work and the crystalline material was further studied by infrared and absorption spectra. The presence of a free -COOH group could be readily inferred from a characteristic signal at ~1680 cm<sup>-1</sup> in

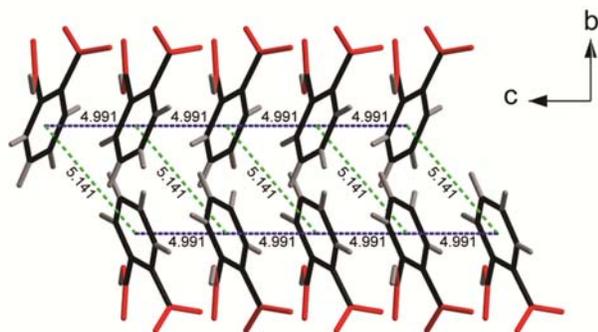


Fig. 6 —  $\pi\cdots\pi$  stacking interactions of the aromatic rings showing intra layer (4.991 Å) and inter layer (5.141 Å) interaction. For clarity the K<sup>+</sup> ions are not shown

the IR spectrum. The UV-visible absorption spectrum was very nearly same as that of the free acid in view of the closed shell electronic configuration of K<sup>+</sup>. A comparison of the IR spectra of both crystals reveals that both spectra are identical. The optical spectra of crystals of **1** grown in the presence and absence of thiourea also exhibit a similar relationship namely both spectra are identical indicating that the absence of thiourea in the isolated crystal. The absence of any thiourea was further confirmed by a Lassaigne's test. The results of the spectral studies are in accordance with the crystal structure of KHP. The interlinked chains of face-sharing {KO<sub>7</sub>} polyhedra cannot accommodate any S-donor ligands in the crystal structure leading to the fractional crystallization of the less soluble potassium hydrogen phthalate (Supplementary Data, Fig. S6). Incorporation of any metal ions other than Rb<sup>+</sup>, Cs<sup>+</sup> or Tl<sup>+</sup> in place of the heptacoordinated potassium can also be ruled out based on structural arguments as can be evidenced from the comparative study of the structural chemistry of alkali metal hydrogen phthalates described below.

#### Comparative structural chemistry of alkali metal hydrogen phthalates

A comparative study of the structural aspects of the alkali metal hydrogen phthalates<sup>12,20-22,27-30</sup> (Table 3) reveals several interesting features. In this series of alkali metal compounds excepting the hydrogen phthalates of Li and Na which are hydrated the remaining compounds are anhydrous. Although the hydrogen phthalates of Li and sodium are referred to as dihydrate (entry no. 2), monohydrate (entry no. 3), methanol solvate and hemihydrate (entry no. 5) these terms do not refer to any lattice water or lattice methanol solvent. In all these compounds the water molecules or the solvent methanol are coordinated to the central metal. Excepting two Li compounds (entry nos. 3 and 4) which are triclinic, all other compounds in Table 3 crystallize in the orthorhombic crystal system; starting from sodium (entry nos. 5-9) all hydrogen phthalates including that of thallium<sup>30</sup> crystallize in non-centrosymmetric space groups<sup>12,27,28,30</sup>. In addition to the differing degrees of hydration of the alkali metal hydrogen phthalates, it is interesting to note that the coordination number of the central metal varies from four for Li to eight for Cs. The degree of hydration reduces accompanied by an increase in the coordination number as one goes down the group. All compounds in Table 3 starting from K are not only anhydrous but also crystallize in the same non-centrosymmetric space group (No. 29).

Table 3 — Structural details of alkali metal hydrogen phthalates						
S. No.	Molecular formula	Space group (*)	{MO <sub>x</sub> } unit	Binding mode of (C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	D	CSD refcode
1	(NH <sub>4</sub> )(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	<i>Pcab</i> (61)	--	--	0	AHPHAL
2	Li(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub>	<i>Pnma</i> (62)	{LiO <sub>4</sub> }	μ <sub>2</sub> -bidentate	1	LHPHTL
3	Li(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sup>#</sup>	<i>P</i> $\bar{1}$ (2)	{LiO <sub>4</sub> }, {LiO <sub>4</sub> }	μ <sub>2</sub> -bidentate, μ <sub>3</sub> -tridentate	2	LIHPAL
4	Li(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )CH <sub>3</sub> OH <sup>#</sup>	<i>P</i> $\bar{1}$ (2)	{LiO <sub>4</sub> }, {LiO <sub>4</sub> }	μ <sub>4</sub> -tetradentate, μ <sub>2</sub> -bidentate	3	LIHPHM01
5	Na(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> ) <sub>1/2</sub> H <sub>2</sub> O	<i>B2cb</i> (41)	{NaO <sub>6</sub> }	μ <sub>4</sub> -pentadentate	2	NAHPHT
6	K(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	<i>Pca2</i> <sub>1</sub> (29)	{KO <sub>7</sub> }	μ <sub>4</sub> -heptadentate	2	This work
7	Rb(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	<i>P2</i> <sub>1</sub> <i>ab</i> <sup>‡</sup> (29)	{RbO <sub>7</sub> }	μ <sub>4</sub> -heptadentate	2	RBHPHT
8	Cs(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	<i>Pca2</i> <sub>1</sub> (29)	{CsO <sub>8</sub> }	μ <sub>4</sub> -octadentate	2	ZZZSWU02
9	Tl(C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> )	<i>P2</i> <sub>1</sub> <i>ab</i> <sup>‡</sup> (29)	{TlO <sub>6</sub> }	μ <sub>4</sub> -hexadentate	2	DOKRIE01

(\*) Space group Number ; M= alkali metal; D=dimensionality; # two unique Li and two unique hydrogen phthalate; ‡ non-standard setting

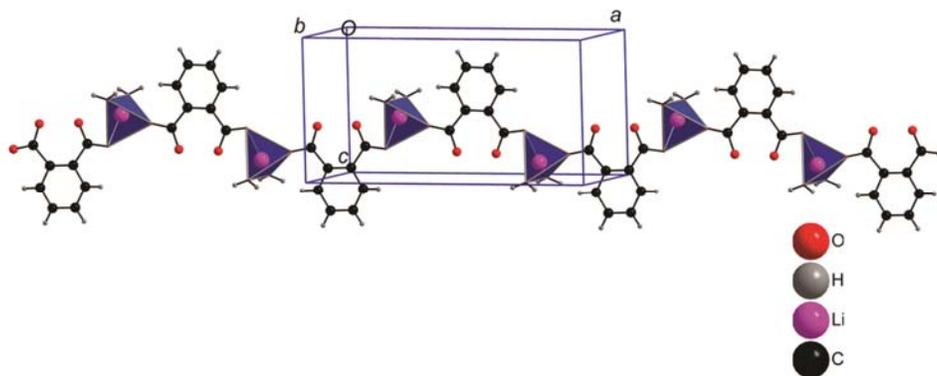


Fig. 7 — A portion of the 1-D polymeric chain extending along *a* axis showing the discrete {LiO<sub>4</sub>} tetrahedra due to the bridging bidentate binding of hydrogen phthalate in Li(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>

The binding mode of the hydrogen phthalate ligand shows some variation and it can be seen that for the heavier congeners which are anhydrous, the denticity of the ligand is high (μ<sub>4</sub>-heptadentate for K<sup>+</sup> or μ<sub>4</sub>-octadentate for Cs) unlike for the Li compound (entry no. 2) where hydrogen phthalate exhibits a μ<sub>2</sub>-bridging bidentate mode. The bridging bidentate mode results in the formation of discretely linked chain of {LiO<sub>4</sub>} tetrahedra unlike the interlinked chains of face-sharing {KO<sub>7</sub>} polyhedra in KHP (Fig. 7). The hydrogen phthalates of Li exhibit dimensionalities ranging from one to three and it is interesting to note that both the denticity and bridging nature of the hydrogen phthalate in the 2D (μ<sub>3</sub>-tridentate) or 3D (μ<sub>4</sub>-tetradentate) compounds are enhanced as compared to the μ<sub>2</sub>-bidentate mode in the 1D compound. Normally many ammonium salts are isotypic with the corresponding potassium compounds. However, in the case of hydrogen phthalate this behavior is not observed since the ammonium hydrogen phthalate<sup>29</sup> crystallizes in the

centrosymmetric *Pbca* space group. In this series, the title K<sup>+</sup> salt is isostructural with the hydrogen phthalates of Rb<sup>+</sup>, Cs<sup>+</sup> and Tl<sup>+</sup>. All four compounds are anhydrous and their structures have been refined in the non-centrosymmetric orthorhombic *Pca2*<sub>1</sub> space group (no. 29). It is interesting to note that Rb<sup>+</sup> exhibits seven coordination like K<sup>+</sup> while the coordination numbers of Cs<sup>+</sup> and Tl<sup>+</sup> are eight and six, respectively. The binding mode of the hydrogen phthalate is identical in K<sup>+</sup> and Rb<sup>+</sup> both of which contain a μ<sub>3</sub>-oxygen in the ionized carboxylate group. In Cs<sup>+</sup> (entry no. 8) the carboxylate oxygen binds to four symmetry related Cs<sup>+</sup> and is a μ<sub>4</sub>-oxygen which can explain the additional link while in Tl<sup>+</sup> (entry no. 9) the binding mode of the anionic carboxylate is same as in K<sup>+</sup> and Rb<sup>+</sup> but the unionized carboxylic acid exhibits a monodentate binding (η<sup>1</sup>) which can account for the hexa coordination (Supplementary Data, Fig. S7). In all the four compounds the bridging binding of the hydrogen phthalate ligand results in three different M···M (M=K or Rb or Cs or Tl)

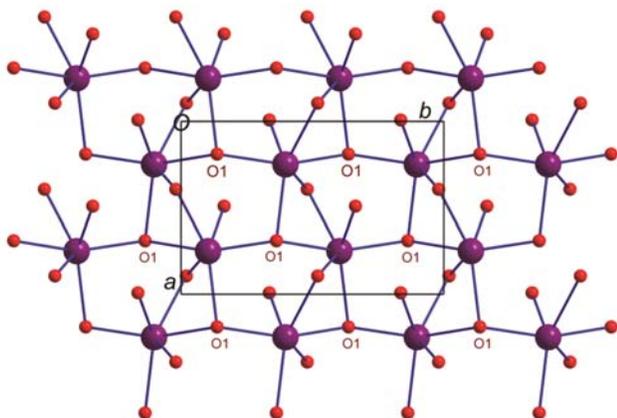


Fig. 8 — A portion of the 2D layer in  $\text{Tl}(\text{C}_8\text{H}_5\text{O}_4)$  showing hexacoordination around the central metal. O1 is a  $\mu_3$ -oxygen which binds to three  $\text{Tl}^+$  ions. For the interlinked  $\{\text{TlO}_6\}$  polyhedra see Fig. S11 in Supplementary Data

distances resulting in two-dimensional connectivity of the metals (Supplementary Data, Figs S8 and S9). Hence all the four isostructural compounds adopt a two dimensional structure consisting of interlinked parallel chains of  $\{\text{MO}_x\}$  ( $x = 6$  to  $8$ ) polyhedra. Due to a different coordination number of the central metal, the polyhedra in Cs and Tl are  $\{\text{CsO}_8\}$  and  $\{\text{TlO}_6\}$ , respectively (Fig. 8). Due to the presence of a  $\mu_4$ -oxygen in Cs, this vertex is shared by four polyhedra (Supplementary Data, Fig. S10) when the parallel chains are interlinked.

### Conclusions

In this work we have investigated the crystal structure of potassium hydrogen phthalate (KHP) and compared this with the structures of other alkali metal hydrogen phthalates. Our studies reveal a rich and variable structural chemistry of alkali metal hydrogen phthalates. An interesting observation of this study is the identification of interlinked chains of face-sharing  $\{\text{KO}_7\}$  polyhedra in KHP resulting in a two-dimensional (2D) architecture. The isostructural hydrogen phthalates of Tl and Cs exhibit the same 2D architecture but the interlinked chains are made up of  $\{\text{TlO}_6\}$  and  $\{\text{CsO}_8\}$  polyhedra. It is of interest to incorporate either Cs or Tl in the crystal structure of K or Rb to prepare bi or trimetallic hydrogen phthalates and efforts in this direction are currently underway in our laboratory.

### Supplementary Data

Deposition Number CCDC 1976019 contains the supplementary crystallographic data for the structure

of (1) described in this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures). Supplementary Data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA\\_59A\(12\)1785-1792\\_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(12)1785-1792_SupplData.pdf).

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