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The alkali hypophosphites KH₂PO₂, RbH₂PO₂ and CsH₂PO₂

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The structures of the hypophosphites KH_2PO_2 (potassium hypophosphite), RbH_2PO_2 (rubidium hypophosphite) and CsH_2PO_2 (caesium hypophosphite) have been determined by single-crystal X-ray diffraction. The structures consist of layers of alkali cations and hypophosphite anions, with the latter bridging four cations within the same layer. The Rb and Cs hypophosphites are isomorphous.

Comment

The hypophosphite $H_2PO_2^-$ anion is a distorted tetrahedron, with the P atom at the centre and two O and two H atoms at the vertices. This anion may coordinate a metal cation *via* the O atoms in different ways, *viz*. as a mono- or bidentate ligand, or as a bridging ligand between two cations. The goal of the present work was to investigate further the functional role of the hypophosphite anion in the crystals of the title compounds.



Figure 1

The (010) layer in KH_2PO_2 . Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

Previous crystal-structure investigations of anhydrous hypophosphites include $Ca(H_2PO_2)_2$ (Goedkoop & Loopstra, 1959), $CaNa(H_2PO_2)_3$ (Matsuzaki & Iitaka, 1969), $Cu(H_2-PO_2)_2$ (Naumov *et al.*, 2002), $Zn(H_2PO_2)_2$ (Weakley, 1979; Tanner *et al.*, 1997), $GeCl(H_2PO_2)$ (Catti, 1979) and SnCl- (H_2PO_2) (Weakley & Watt, 1979), $La(H_2PO_2)_3$ (Tanner *et al.*, 1999), $Er(H_2PO_2)_3$ (Aslanov *et al.*, 1975), and $U(H_2PO_2)_4$ (Tanner *et al.*, 1992). The limited number of studies is probably due to the difficulty of preparation of these compounds, resulting from their highly hygroscopic nature and their low stability. The title compounds are rather easy to synthesize but crystals are difficult to grow.

The present crystal structure determinations show that the unit cell of KH_2PO_2 differs in size and symmetry from those of the isomorphous Rb and Cs analogues. The monoclinic unit cell of KH_2PO_2 is related to the orthorhombic unit cell of the Rb and Cs hypophosphites by the matrix $(\frac{1}{2} \ 1 \ 0 / \frac{1}{2} \ 1 \ 0 / 0 \ 0 \ 1)$.



Figure 2

The (001) layer in RbH_2PO_2 . Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.



Figure 3

The coordination environment of the K⁺ cation in KH₂PO₂ [symmetry codes: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (ii) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (iii) 1 + x, y, z].



Figure 4

The coordination environment of the Rb⁺ cation in RbH₂PO₂ [symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (iii) $x, \frac{3}{2} - y z$].

All three compounds adopt layer structures, in which the metal cations are coordinated by hypophosphite anions (Figs. 1 and 2). The packing of the cations and P atoms is identical in all three compounds, and the cations and P-atom positions are nearly coplanar, forming a layer similar to a (100) NaCl layer.

The full coordination environments of the K⁺ and Rb⁺ cations are shown in Figs. 3 and 4, respectively. The Rb and Cs environments are identical to those found in KF₂PO₂, RbF₂PO₂ and CsF₂PO₂ (Harrison et al., 1966; Granier et al., 1975; Trotter & Withlow, 1967). The H-atom positions in the present hypophosphites correspond to the F-atom positions in the difluorophosphates.

Experimental

It was established during crystal-growth experiments that the preparation of anhydrous hypophosphites of K, Rb and Cs from aqueous solutions depends on the precursor and on the presence of impurities in that precursor at levels of less than 3-5%. Crystals of the title K, Rb and Cs hypophosphites were grown from aqueous solutions prepared by the reaction of hypophosphorous acid with the corresponding alkali carbonates. Crystal growth was carried out at 313 K in a dry-box under dry nitrogen. Crystal growth is not possible at room temperature in air because of the strong hygroscopic nature of the hypophosphites and the tendency of the crystals to dissolve as a result of the fast absorption of water vapour from the atmosphere (increasing in the order $K \rightarrow Rb \rightarrow Cs$). The crystals were protected from moisture by coating them with epoxy resin. Powder diffraction analysis shows agreement between the bulk products and the single crystals. However, in the case of the rubidium hypophosphite, the presence of additional peaks in the powder pattern shows the presence of an additional phase similar to potassium hypophosphite.

Table 1

Selected geometric parameters (Å, °) for (I).

$\overline{\begin{matrix} K-O\\K-O^i\\K-O^{ii}\end{matrix}}$	2.7747 (14) 2.7368 (13) 2.9220 (15)	Р-О Р-Н	1.4914 (12) 1.28 (3)
К=О О-Р-О ^{ііі} О-Р-Н	118.04 (11) 108.3 (10)	O ⁱⁱⁱ –P–H H–P–H ⁱⁱⁱ	109.8 (11) 101 (2)
Symmetry codes: (i)	$\frac{1}{2} - x, \frac{1}{2} - y, -z;$ (ii) $\frac{1}{2} +$	$-x, y - \frac{1}{2}, z;$ (iii) $-x, y, \frac{1}{2}$	- <i>z</i> .

Compound (I)

Crystal data

KH_2PO_2
$M_r = 104.09$
Monoclinic, C2/c
$a = 7.3131 (10) \text{\AA}$
b = 7.2952 (8) Å
c = 7.1814 (10) Å
$\beta = 116.205 \ (10)^{\circ}$
V = 343.75 (8) Å ³
Z = 4
$D_x = 2.011 \text{ Mg m}^{-3}$
-

Data collection

Enraf-Nonius CAD-4 diffractometer $2\theta/\theta$ scans Absorption correction: empirical (CADDAT; Enraf-Nonius, 1989) $T_{\rm min} = 0.421, \ T_{\rm max} = 0.903$ 606 measured reflections 500 independent reflections 458 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.031$ $wR(F^2) = 0.079$ S = 1.14500 reflections 25 parameters All H-atom parameters refined

Compound (II)

Crystal data

RbH₂PO₂ Mo $K\alpha$ radiation $M_r = 150.46$ Orthorhombic, Pnma a = 7.9835(9) Å $\theta = 9.9 - 14.2^{\circ}$ b = 6.3678(7) Å c = 7.5755 (11) Å V = 385.12 (8) Å³ Z = 4 $D_x = 2.595 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4 diffractometer $2\theta/\theta$ scans Absorption correction: empirical (CADDAT; Enraf-Nonius, 1989) $T_{\min} = 0.095, \ T_{\max} = 0.593$ 732 measured reflections 366 independent reflections 289 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.023$ $wR(F^2) = 0.057$ S = 0.96366 reflections 27 parameters

Mo Ka radiation Cell parameters from 22 reflections $\theta = 9.0 - 14.7^{\circ}$ $\mu = 1.78~\mathrm{mm}^{-1}$ T = 296 (2) KPlate, colourless $0.59 \times 0.46 \times 0.06 \ \mathrm{mm}$

 $R_{\rm int} = 0.020$ $\theta_{\rm max} = 29.9^{\circ}$ $h=0\rightarrow 10$ $k = -1 \rightarrow 10$ $l=-10\rightarrow9$ 3 standard reflections frequency: 60 min intensity decay: none

 $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\rm max} < 0.001$ $\Delta \rho_{\rm max} = 0.50 \ {\rm e} \ {\rm \AA}^{-3}$ $\Delta \rho_{\rm min} = -0.59 \ {\rm e} \ {\rm \AA}^{-3}$ Extinction correction: SHELXL97 (Sheldrick, 1997) Extinction coefficient: 0.075 (8)

Cell parameters from 24 reflections $\mu = 13.06 \text{ mm}^{-1}$ T = 298 (2) KPlate, colourless $0.32 \times 0.16 \times 0.04 \text{ mm}$

 $R_{\rm int} = 0.032$ $\theta_{\rm max} = 24.9^{\circ}$ $h = -9 \rightarrow 9$ $k=0\to7$ $l = 0 \rightarrow 9$ 3 standard reflections frequency: 60 min intensity decay: none

All H-atom parameters refined $w = 1/[\sigma^2(F_o^2) + (0.026P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\rm max} < 0.001$ $\Delta \rho_{\rm max} = 0.58 \text{ e } \text{\AA}^{-3}$ $\Delta \rho_{\rm min} = -0.58 \ {\rm e} \ {\rm \AA}^{-3}$

Table 2Selected geometric parameters (Å, °) for (II).				
Rb-O	2.859 (3)	P-O	1.478 (3)	
Rb-O ⁱ	2.932 (3)	P-H1	1.18(7)	
Rb-O ⁱⁱ	3.063 (3)	P-H2	1.33 (7)	
O–P–O ⁱⁱⁱ O–P–H1	118.7 (3) 111.9 (13)	O-P-H2 H1-P-H2	107.4 (13) 97 (4)	

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, -z$; (iii) $x, \frac{3}{2} - y, z$.

Compound (III)

Crystal data

CsH ₂ PO ₂	Mo $K\alpha$ radiation
$M_r = 197.90$	Cell parameters from 24
Orthorhombic, Pnma	reflections
a = 8.3776 (9) Å	$\theta = 9.5 - 13.7^{\circ}$
b = 6.6271 (6) Å	$\mu = 8.61 \text{ mm}^{-1}$
c = 7.9165 (10) Å	T = 298 (2) K
V = 439.52 (8) Å ³	Plate, colourless
Z = 4	$0.45 \times 0.30 \times 0.11 \text{ mm}$
$D_x = 2.991 \text{ Mg m}^{-3}$	
Data collection	
Enraf-Nonius CAD-4	$R_{\rm int} = 0.058$
diffractometer	$\theta_{\rm max} = 29.9^{\circ}$
$2\theta/\theta$ scans	$h = -1 \rightarrow 11$
Absorption correction: empirical	$k = 0 \rightarrow 9$
(CADDAT: Enraf-Nonius, 1989)	$l = 0 \rightarrow 11$

(*CADDAT*; Enraf-Nonius, 1989) $T_{min} = 0.056$, $T_{max} = 0.388$ 769 measured reflections 687 independent reflections 554 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.114$	$(\Delta/\sigma)_{\rm max} < 0.001$
S = 1.04	$\Delta \rho_{\rm max} = 1.41 \text{ e } \text{\AA}^{-3}$
687 reflections	$\Delta \rho_{\rm min} = -1.06 \text{ e } \text{\AA}^{-3}$
27 parameters	Extinction correction: SHELXL97
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.050 (4)

3 standard reflections

frequency: 60 min

intensity decay: none

The H atoms were located from difference electron-density maps and their positions were refined without any constraint.

For all compounds, data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

Table	3		
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Selected geometric parameters (Å, °) for (III).

Cs-O	3.026 (5)	P-O	1.487 (6)
Cs-O ⁱ	3.094 (5)	P-H1	1.37 (11)
Cs-O ⁱⁱ	3.221 (7)	P-H2	1.48 (12)
O-P-O ⁱⁱⁱ	118.1 (5)	O-P-H2	108 (2)
O-P-H1	107 (2)	H1-P-H2	108 (7)

Symmetry codes: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$; (ii) 1 - x, $y - \frac{1}{2}$, -z; (iii) x, $\frac{3}{2} - y$, z.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1035). Services for accessing these data are described at the back of the journal.

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