

The alkali hypophosphites KH_2PO_2 , RbH_2PO_2 and CsH_2PO_2

Marina I. Naumova, Natalia V. Kuratieva, Nina V. Podberezskaya and Dmitry Yu. Naumov*

Institute of Inorganic Chemistry, SB Russian Academy of Sciences, Academician Lavrentiev Avenue 3, Novosibirsk 90, 630090 Russia
Correspondence e-mail: d.y.naumov@ngs.ru

Received 5 January 2004

Accepted 29 January 2004

Online 9 April 2004

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.

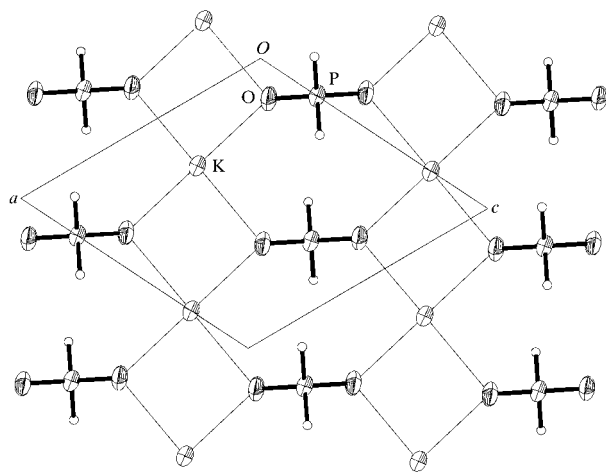


Figure 1

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 $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (Goedkoop & Loopstra, 1959), $\text{CaNa}(\text{H}_2\text{PO}_2)_3$ (Matsuzaki & Itaka, 1969), $\text{Cu}(\text{H}_2\text{PO}_2)_2$ (Naumov *et al.*, 2002), $\text{Zn}(\text{H}_2\text{PO}_2)_2$ (Weakley, 1979; Tanner *et al.*, 1997), $\text{GeCl}(\text{H}_2\text{PO}_2)$ (Catti, 1979) and $\text{SnCl}(\text{H}_2\text{PO}_2)$ (Weakley & Watt, 1979), $\text{La}(\text{H}_2\text{PO}_2)_3$ (Tanner *et al.*, 1999), $\text{Er}(\text{H}_2\text{PO}_2)_3$ (Aslanov *et al.*, 1975), and $\text{U}(\text{H}_2\text{PO}_2)_4$ (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 $(\frac{1}{2} \bar{1} 0 / \frac{1}{2} 1 0 / 0 0 1)$.

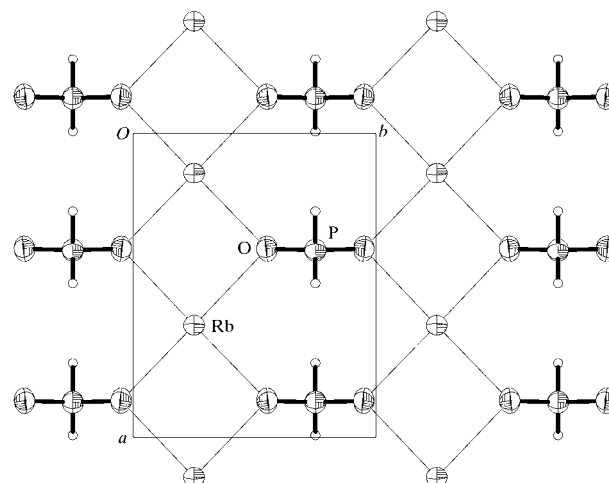


Figure 2

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.

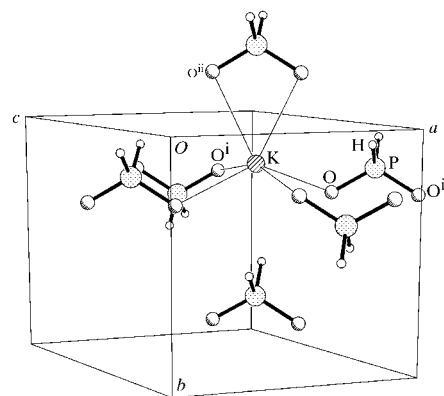


Figure 3

The coordination environment of the K^+ cation in KH_2PO_2 [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) $1 + x, y, z$].

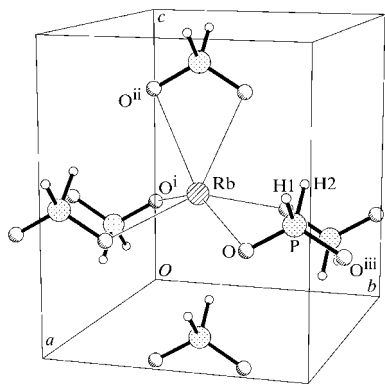


Figure 4
The coordination environment of the Rb^+ cation in RbH_2PO_2 [symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (iii) $x, \frac{3}{2} - y, z$].

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 KF_2PO_2 , RbF_2PO_2 and CsF_2PO_2 (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 $\text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$). 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 (\AA , $^\circ$) for (I).

K–O	2.7747 (14)	P–O	1.4914 (12)
K–O ⁱ	2.7368 (13)	P–H	1.28 (3)
K–O ⁱⁱ	2.9220 (15)		
O–P–O ⁱⁱⁱ	118.04 (11)	O ⁱⁱⁱ –P–H	109.8 (11)
O–P–H	108.3 (10)	H–P–H ⁱⁱⁱ	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) $-x, y, \frac{1}{2} - z$.

Compound (I)

Crystal data

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

Data collection

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.079$
 $S = 1.14$
500 reflections
25 parameters
All H-atom parameters refined

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

$R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 29.9^\circ$
 $h = 0 \rightarrow 10$
 $k = -1 \rightarrow 10$
 $l = -10 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

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

Compound (II)

Crystal data

RbH_2PO_2
 $M_r = 150.46$
Orthorhombic, $Pnma$
 $a = 7.9835 (9) \text{\AA}$
 $b = 6.3678 (7) \text{\AA}$
 $c = 7.5755 (11) \text{\AA}$
 $V = 385.12 (8) \text{\AA}^3$
 $Z = 4$
 $D_x = 2.595 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4
diffractometer
2 θ / θ 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
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.057$
 $S = 0.96$
366 reflections
27 parameters

Mo $K\alpha$ radiation
Cell parameters from 24
reflections
 $\theta = 9.9\text{--}14.2^\circ$
 $\mu = 13.06 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
Plate, colourless
 $0.32 \times 0.16 \times 0.04 \text{ mm}$

$R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 24.9^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 7$
 $l = 0 \rightarrow 9$
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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$

Table 2

Selected 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	118.7 (3)	O—P—H2	107.4 (13)
O—P—H1	111.9 (13)	H1—P—H2	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*

CsH₂PO₂
M_r = 197.90
 Orthorhombic, *Pnma*
a = 8.3776 (9) Å
b = 6.6271 (6) Å
c = 7.9165 (10) Å
V = 439.52 (8) Å³
Z = 4
D_x = 2.991 Mg m⁻³

Data collection

Enraf–Nonius CAD-4
 diffractometer
 2θ/θ scans
 Absorption correction: empirical
 (CADDAT; Enraf–Nonius, 1989)
T_{min} = 0.056, *T_{max}* = 0.388
 769 measured reflections
 687 independent reflections
 554 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.037
wR(*F*²) = 0.114
S = 1.04
 687 reflections
 27 parameters
 All H-atom parameters refined

Mo *Kα* radiation
 Cell parameters from 24
 reflections
 θ = 9.5–13.7°
 μ = 8.61 mm⁻¹
T = 298 (2) K
 Plate, colourless
 0.45 × 0.30 × 0.11 mm

R_{int} = 0.058
θ_{max} = 29.9°
h = -1 → 11
k = 0 → 9
l = 0 → 11
 3 standard reflections
 frequency: 60 min
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.41 e Å⁻³
 Δρ_{min} = -1.06 e Å⁻³
 Extinction correction: SHELXL97
 (Sheldrick, 1997)
 Extinction coefficient: 0.050 (4)

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

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) $x, \frac{3}{2} - y, z$.

The authors are grateful to Dr A. V. Virovets for helpful comments. An initial report (Naumova *et al.*, 2004) on the synthesis, growth conditions and crystal chemistry analysis of the three title compounds was presented at the National Conference on Crystal Growth (NCCG-2002, Moscow).

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.

References

- Aslanov, L. A., Ionov, V. M., Poray-Koshits, M. A., Lebedev, V. G., Kulikovskij, B. N., Gilyarov, O. N. & Novoderzhkina, T. L. (1975). *Neorg. Mater.* **11**, 117–119. (In Russian.)
 Burnett, M. N. & Johnson, C. K. (1996). ORTEPIII. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
 Catti, M. (1979). *Acta Cryst.* **B35**, 1041–1046.
 Enraf–Nonius (1989). CD4CA0 (Version 5.0) and CADDAT (Version 5.1). Enraf–Nonius, Delft, The Netherlands.
 Goedkoop, J. A. & Loopstra, L. H. (1959). *Ned. Tijdschr. Natuurkd.* **25**, 29–41.
 Granier, W., Durand, J., le Cot, L. & Galigne, J. L. (1975). *Acta Cryst.* **B31**, 2506–2507.
 Harrison, R. W., Thompson, R. C. & Trotter, J. (1966). *J. Chem. Soc. A*, pp. 1775–1780.
 Matsuzaki, T. & Iitaka, Y. (1969). *Acta Cryst.* **B25**, 1932–1938.
 Naumov, D. Y., Naumova, M. I., Kuratieva, N. V., Boldyreva, E. V. & Howard, J. A. K. (2002). *Acta Cryst.* **C58**, i55–i60.
 Naumova, M. I., Kuratieva, N. V., Naumov, D. Yu. & Podberezskaya, N. V. (2004). *Crystallogr. Rep.* **46**, 282–287.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Tanner, P. A., Faucher, M. D. & Mak, T. C. W. (1999). *Inorg. Chem.* **38**, 6008–6023.
 Tanner, P. A., Sze, T. H., Mak, T. C. W. & Yip, W. H. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 25–30.
 Tanner, P. A., Yu-Long, L. & Mak, T. C. W. (1997). *Polyhedron*, **16**, 495–505.
 Trotter, J. & Withlow, S. H. (1967). *J. Chem. Soc. A*, pp. 1383–1386.
 Weakley, T. J. R. (1979). *Acta Cryst.* **B35**, 42–45.
 Weakley, T. J. R. & Watt, W. W. L. (1979). *Acta Cryst.* **B35**, 3023–3024.