

The bivalent metal hypophosphites $\text{Sr}(\text{H}_2\text{PO}_2)_2$, $\text{Pb}(\text{H}_2\text{PO}_2)_2$ and $\text{Ba}(\text{H}_2\text{PO}_2)_2$

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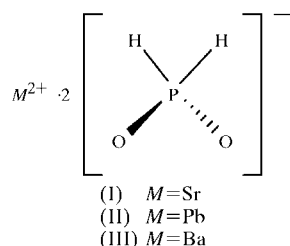
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The structures of isomorphous monoclinic strontium and lead bis(dihydrogenphosphate), $\text{Sr}(\text{H}_2\text{PO}_2)_2$ and $\text{Pb}(\text{H}_2\text{PO}_2)_2$, and orthorhombic barium bis(dihydrogenphosphate), $\text{Ba}(\text{H}_2\text{PO}_2)_2$, consist of layers of hypophosphite anions and metal cations exhibiting square antiprismatic coordination by O atoms. The Sr and Pb atoms are located on sites with point symmetry 2, and the Ba atoms are on sites with point symmetry 222. Within the layers, each anion bridges four metal cations.

Comment

Although anhydrous metal hypophosphites find numerous practical applications and have been used for studies of various aspects of solid-state reactivity, their crystal structures are not adequately known and analysed. A small number of studies of anhydrous hypophosphorous acid salts, namely $\text{NH}_4\text{H}_2\text{PO}_2$ (Zachariasen & Mooney, 1934), $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (Goedkoop & Loopstra, 1959), $\text{CaNa}(\text{H}_2\text{PO}_2)_3$ (Matsuzaki & Iitaka, 1969), $\text{Zn}(\text{H}_2\text{PO}_2)_2$ (Weakley, 1979; Tanner *et al.*, 1997), $\text{La}(\text{H}_2\text{PO}_2)_3$ (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), have been reported. The present paper continues our research on anhydrous hypophosphorous acid salts, which has included KH_2PO_2 , RbH_2PO_2 and CsH_2PO_2 (Naumova *et al.*, 2004), LiH_2PO_2 and $\text{Be}(\text{H}_2\text{PO}_2)_2$ (Naumov *et al.*, 2004), and



$\text{Cu}(\text{H}_2\text{PO}_2)_2$ (Naumov *et al.*, 2002), and the coordination function of the hypophosphite anion. All known structures of

bivalent metal hypophosphites have been shown to consist of layers.

The structures of all three title compounds, *viz.* $\text{Sr}(\text{H}_2\text{PO}_2)_2$, (I), $\text{Pb}(\text{H}_2\text{PO}_2)_2$, (II), and $\text{Ba}(\text{H}_2\text{PO}_2)_2$, (III), consist of layers formed by hypophosphite anions and metal cations. The Sr and Pb compounds are isomorphous and the Ba compound is very similar but the layers are oriented differently in the unit cell. All three structures exhibit square antiprismatic coordination of the metal cations by O atoms. The Sr and Pb atoms are located on sites with point symmetry 2 and the Ba atoms are on sites with point symmetry 222. These square antiprisms, which possess a pseudo-fourfold axis, share four edges within a layer (Fig. 1). Also within the layers, slightly distorted tetrahedral $\text{H}_2\text{PO}_2^{2-}$ anions bridge four metal cations *via* the O atoms (see Table 1 for angles). The H atoms are directed out of the layers (Fig. 2).

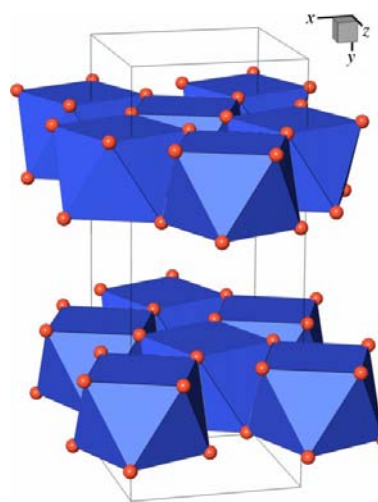


Figure 1

A representation of the BaO_8 square antiprisms of $\text{Ba}(\text{H}_2\text{PO}_2)_2$, shown stacking in layers perpendicular to [100].

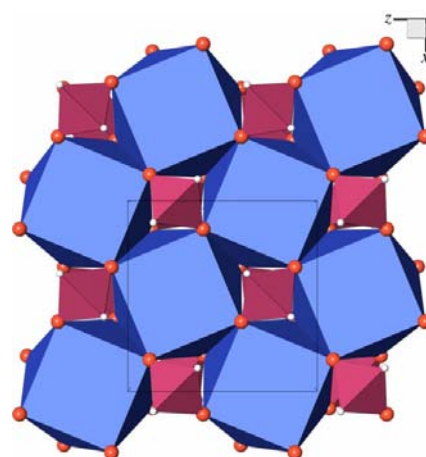


Figure 2

The linkage of square antiprisms and H_2PO_2 tetrahedra in the structure of $\text{Ba}(\text{H}_2\text{PO}_2)_2$.

This situation contrasts with $\text{Be}(\text{H}_2\text{PO}_2)_2$ (Naumov *et al.*, 2004), where the Be atom has tetrahedral coordination and the hypophosphite anion acts as a bidentate bridge, and $\text{Ca}(\text{H}_2\text{PO}_2)_2$ (Goedkoop & Loopstra, 1959), where the anion acts as a tridentate bridge in combination with the distorted octahedral coordination sphere of the Ca atom. For the larger cations (Sr, Pb and Ba) more coordination sites are needed.

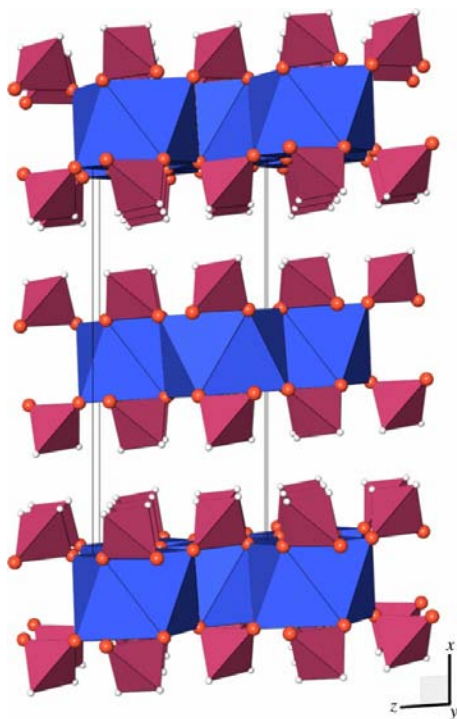


Figure 3
The packing of layers in the structure of $\text{Sr}(\text{H}_2\text{PO}_2)_2$.

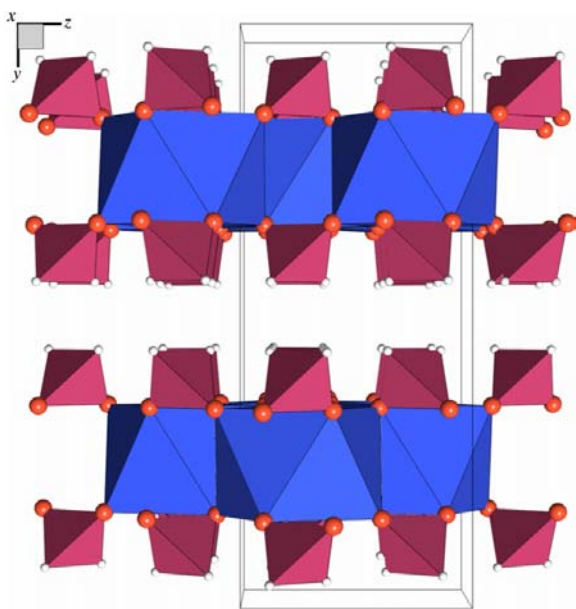


Figure 4
The packing of layers in the structure of $\text{Ba}(\text{H}_2\text{PO}_2)_2$ [shown in the same orientation as the two upper layers of the $\text{Sr}(\text{H}_2\text{PO}_2)_2$ structure presented in Fig. 3].

This requirement leads to changes in the linkage of the metal cations by the hypophosphite anions, even though the stoichiometry is the same. Thus, in the isomorphous Sr and Pb compounds, the cations have slightly distorted square antiprismatic coordination spheres and the hypophosphite anions act as tetradentate bridges. The introduction of extra symmetry and the conservation of the tetradentate bridging role of hypophosphite anions leads to the structure of $\text{Ba}(\text{H}_2\text{PO}_2)_2$. The packing of the layers in $\text{Sr}(\text{H}_2\text{PO}_2)_2$ and $\text{Pb}(\text{H}_2\text{PO}_2)_2$ (Fig. 3) differs very little from that in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ (Fig. 4). The layers in both the Sr and Pb hypophosphites are shifted along (001) by 0.533 Å in comparison with the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ structure.

The structures are layered parallel to (100) for $\text{Sr}(\text{H}_2\text{PO}_2)_2$ and $\text{Pb}(\text{H}_2\text{PO}_2)_2$ (Fig. 3), and (010) for $\text{Ba}(\text{H}_2\text{PO}_2)_2$ (Fig. 4). The unit-cell dimensions of the title compounds are similar and can be transformed from $\text{Ba}(\text{H}_2\text{PO}_2)_2$ to $\text{Sr}(\text{H}_2\text{PO}_2)_2$ and $\text{Pb}(\text{H}_2\text{PO}_2)_2$ by the matrix (010/100/001). Separate layers are linked by van der Waals interactions. The shortest H...H contacts between the layers are 2.50 (9) Å for $\text{Sr}(\text{H}_2\text{PO}_2)_2$, 2.32 Å for $\text{Pb}(\text{H}_2\text{PO}_2)_2$ and 2.49 (7) Å for $\text{Ba}(\text{H}_2\text{PO}_2)_2$.

Experimental

Crystals of the Sr, Pb and Ba hypophosphites were grown from aqueous solutions prepared by the reaction of hypophosphorous acid with the corresponding metal carbonates. Crystal growth was carried out at room temperature in a dry-box. Powder diffraction analysis shows agreement between the bulk products and single crystals. The powder patterns for $\text{Sr}(\text{H}_2\text{PO}_2)_2$, $\text{Pb}(\text{H}_2\text{PO}_2)_2$ and $\text{Ba}(\text{H}_2\text{PO}_2)_2$ are similar.

Compound (I)

Crystal data

$\text{Sr}(\text{H}_2\text{PO}_2)_2$
 $M_r = 217.59$
Monoclinic, $C2/c$
 $a = 15.6553$ (16) Å
 $b = 5.9436$ (7) Å
 $c = 5.9177$ (7) Å
 $\beta = 93.905$ (9)°
 $V = 549.36$ (11) Å³
 $Z = 4$

$D_x = 2.631$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
 $\theta = 10.4\text{--}13.9^\circ$
 $\mu = 10.31$ mm⁻¹
 $T = 293$ (2) K
Prism, colourless
0.08 × 0.08 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2 θ/θ scans
Absorption correction: empirical (CADDAT; Enraf–Nonius, 1989)
 $T_{\min} = 0.426$, $T_{\max} = 0.438$
530 measured reflections
477 independent reflections
279 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -18 \rightarrow 18$
 $k = 0 \rightarrow 7$
 $l = 0 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.072$
 $S = 0.79$
477 reflections
40 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.96$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.68$ e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0067 (8)

Compound (II)

Crystal data

Pb(H₂PO₂)₂ $D_x = 4.032 \text{ Mg m}^{-3}$
 $M_r = 337.16$ Mo $K\alpha$ radiation
 Monoclinic, $C2/c$ Cell parameters from 22 reflections
 $a = 15.516 (3) \text{ \AA}$ $\theta = 10.4\text{--}13.8^\circ$
 $b = 6.0081 (12) \text{ \AA}$ $\mu = 30.86 \text{ mm}^{-1}$
 $c = 5.9686 (12) \text{ \AA}$ $T = 293 (2) \text{ K}$
 $\beta = 93.30 (3)^\circ$ Plate, colourless
 $V = 555.49 (19) \text{ \AA}^3$ $0.10 \times 0.10 \times 0.02 \text{ mm}$
 $Z = 4$

Data collection

Enraf–Nonius CAD-4 $R_{\text{int}} = 0.024$
 diffractometer $\theta_{\text{max}} = 25.0^\circ$
 $2\theta/\theta$ scans $h = -18 \rightarrow 18$
 Absorption correction: by integration (SHELX76; Sheldrick, 1976) $k = 0 \rightarrow 7$
 $T_{\text{min}} = 0.071$, $T_{\text{max}} = 0.531$ $l = 0 \rightarrow 7$
 528 measured reflections 3 standard reflections
 483 independent reflections frequency: 60 min
 284 reflections with $I > 2\sigma(I)$ intensity decay: none

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2)]$
 $R[F^2 > 2\sigma(F^2)] = 0.033$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.058$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 0.99$ $\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$
 483 reflections $\Delta\rho_{\text{min}} = -0.90 \text{ e \AA}^{-3}$
 34 parameters Extinction correction: SHELXL97
 H-atom parameters constrained Extinction coefficient: 0.00011 (8)

Compound (III)

Crystal data

Ba(H₂PO₂)₂ Mo $K\alpha$ radiation
 $M_r = 267.30$ Cell parameters from 22 reflections
 Orthorhombic, $Ccca$ $\theta = 10\text{--}15^\circ$
 $a = 6.2390 (8) \text{ \AA}$ $\mu = 7.07 \text{ mm}^{-1}$
 $b = 15.584 (3) \text{ \AA}$ $T = 296 (2) \text{ K}$
 $c = 6.1726 (13) \text{ \AA}$ Plate, colourless
 $V = 600.15 (19) \text{ \AA}^3$ $0.27 \times 0.24 \times 0.04 \text{ mm}$
 $Z = 4$
 $D_x = 2.958 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4 $R_{\text{int}} = 0.085$
 diffractometer $\theta_{\text{max}} = 29.2^\circ$
 $2\theta/\theta$ scans $h = 0 \rightarrow 8$
 Absorption correction: empirical $k = -18 \rightarrow 21$
 (CADDAT; Enraf–Nonius, 1989) $l = 0 \rightarrow 8$
 $T_{\text{min}} = 0.168$, $T_{\text{max}} = 0.750$ 3 standard reflections
 671 measured reflections frequency: 60 min
 415 independent reflections intensity decay: none
 269 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0384P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.032$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.083$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 0.89$ $\Delta\rho_{\text{max}} = 1.68 \text{ e \AA}^{-3}$
 415 reflections $\Delta\rho_{\text{min}} = -1.34 \text{ e \AA}^{-3}$
 20 parameters Extinction correction: SHELXL97
 H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.0016 (5)

For (I), H atoms were located in a difference map and positional coordinates were refined freely; P–H distances are 1.28 (7) and

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I), (II) and (III).

	$M = \text{Sr}$	$M = \text{Pb}$	$M = \text{Ba}$
$M\text{--}O1$			2.785 (4)
$M\text{--}O1^{\text{i}}$	2.621 (5)	2.679 (10)	2.779 (4)
$M\text{--}O1^{\text{ii}}$	2.637 (5)	2.645 (12)	
$M\text{--}O2$	2.630 (5)	2.663 (10)	
$M\text{--}O2^{\text{iii}}$	2.627 (5)	2.656 (9)	
$P\text{--}O1$	1.504 (5)	1.474 (13)	1.501 (4)
$P\text{--}O2$	1.507 (5)	1.531 (12)	
$O1\text{--}P\text{--}O2$	116.8 (2)	118.1 (5)	
$O1\text{--}P\text{--}O1^{\text{ii}}$			117.4(4)

Symmetry codes: for $M = \text{Sr}$ and Pb , (i) $-x, 1 - y, -z$; (ii) $x, y, 1 - z$; (iii) $-x, 1 - y, 1 - z$; for $M = \text{Ba}$, (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, y, \frac{1}{2} - z$.

1.30 (7) \AA . For (II), H atoms were placed in calculated positions and both angles (tetrahedral) and P–H distances were constrained (P–H = 1.40 \AA). A similar approach was taken in (III), except that the P–H distances were refined [P–H = 1.27 (4) \AA]. $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}$ of the attached P atom. In (III), the highest and lowest peaks in the difference maps were 1.07 and 0.81 \AA from the Ba atom, respectively.

For all three 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: BS (Kang & Ozawa, 2002); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1468). Services for accessing these data are described at the back of the journal.

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