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Lithium and beryllium hypophosphites

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The structures of monoclinic (*C*2/*m*) lithium dihydrogenphosphate, LiH_2PO_2, and tetragonal ($P4_12_12$) beryllium bis(dihydrogenphosphate), $Be(H_2PO_2)_2$, have been determined by single-crystal X-ray diffraction. The structures consist of layers of hypophosphite anions and metal cations in tetrahedral coordination by O atoms. Within the layers, the anions bridge four Li^+ and two Be^{2+} cations, respectively. In LiH_2PO_2, the Li atom lies on a twofold axis and the $H_2PO_2^-$ anion has the PO_2 atoms on a mirror plane. In $Be(H_2PO_2)_2$, the Be atom lies on a twofold axis and the $H_2PO_2^-$ anion is in a general position.

Comment

Previous studies of anhydrous hypophosphites include KH_2PO_2, RbH_2PO_2 and CsH_2PO_2 (Naumova, Kuratieva, Podberezskaya & Naumov, 2004), $NH_4H_2PO_2$ (Zachariasen & Mooney, 1934), $Ca(H_2PO_2)_2$ (Goedkoop & Loopstra, 1959), $CaNa(H_2PO_2)_3$ (Matsuzaki & Iitaka, 1969), $Cu(H_2PO_2)_2$ (Naumov *et al.*, 2002), $Zn(H_2PO_2)_2$ (Weakley, 1979; Tanner *et al.*, 1997), $GeCl(H_2PO_2)$ 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 compounds investigated is due to the difficulty of their preparation and crystal growth. This paper reports the

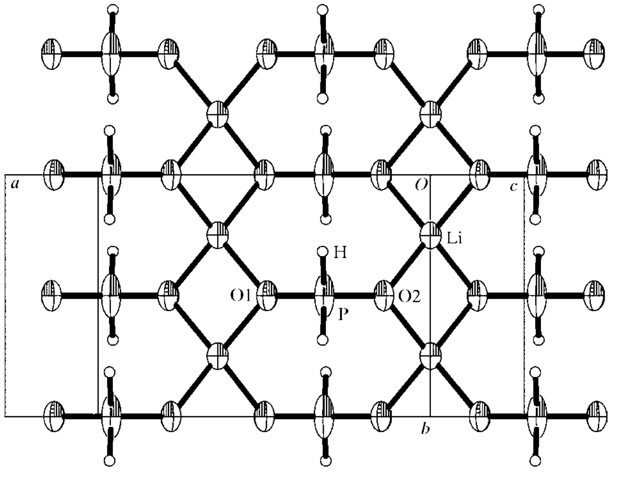

Figure 1
The (001) layer in LiH_2PO_2. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

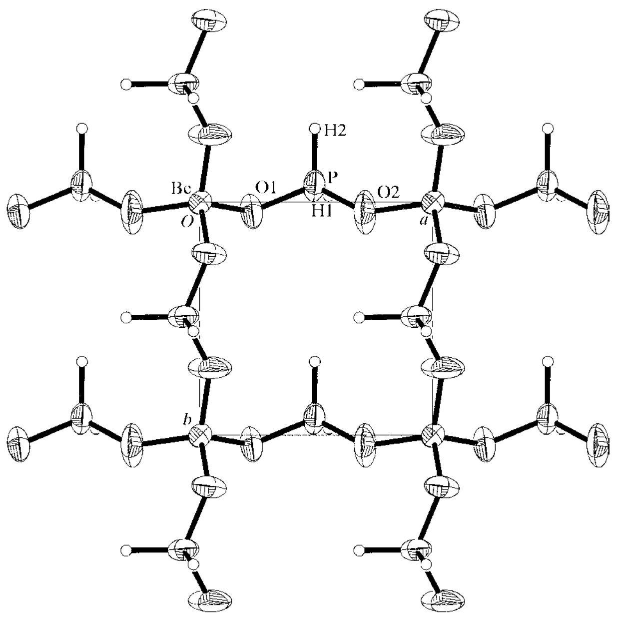

Figure 2
The (001) layer in $Be(H_2PO_2)_2$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

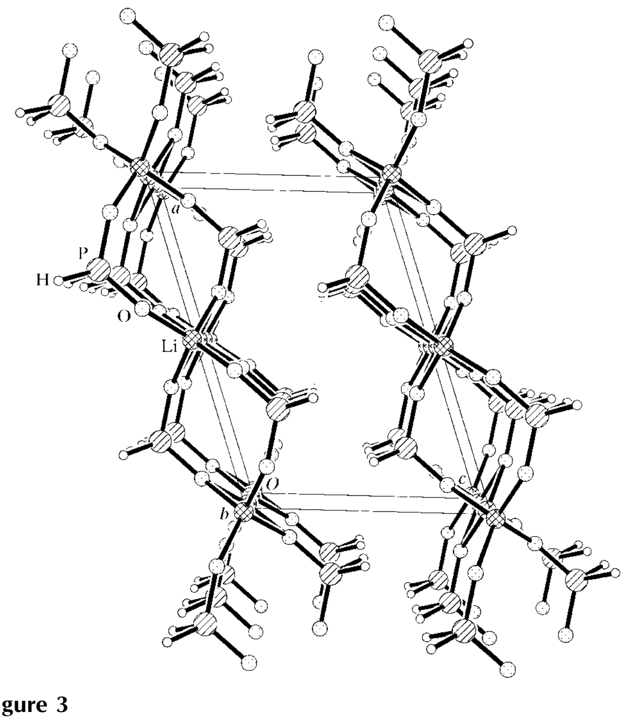

Figure 3
A packing diagram of the LiH_2PO_2 structure, viewed along [010].

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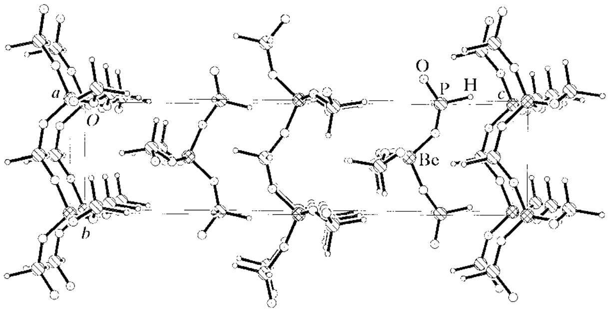

Figure 4
A packing diagram of the $Be(H_2PO_2)_2$ structure, viewed along [100].

results of our investigation of two further anhydrous hypophosphites, namely $Li(H_2PO_2)$ and $Be(H_2PO_2)_2$. The hygroscopic nature of alkali and alkaline-earth hypophosphites makes the growth of their crystals generally difficult. Nevertheless, crystals of these Li and Be hypophosphites were obtained and their structures determined by X-ray diffraction. An initial report (Naumova, Kuratieva, Naumov & Podberezskaya, 2004) on the synthesis, growth conditions and crystal chemistry analysis of $Li(H_2PO_2)$ was presented at the National Conference on Crystal Growth (NCCG-2002, Moscow).

Both title structures are layered and contain metal cations tetrahedrally coordinated by O atoms. The coordination environments of the Li^+ and Be^{2+} cations are similar in the two structures but, due to the different cation–anion ratios, the environments of the hypophosphite anions are different. The $H_2PO_2^-$ anion has the shape of a slightly distorted tetrahedron, with the P atom at the centre and two O and two H atoms as vertices. It serves as a tetradentate and bidentate bridging ligand between the Li^+ and Be^{2+} cations, respectively (Figs. 1 and 2). Separate layers are linked by van der Waals interactions (Figs. 3 and 4), with the shortest $H\cdots H$ distances between layers being 2.46 (5) and 2.70 (3) Å in $Li(H_2PO_2)$ and $Be(H_2PO_2)_2$, respectively.

Experimental

For small quantities, metal hypophosphites are usually synthesized from the corresponding sulfates and nitrates (Romanova & Demidenko, 1975), carbonates (Naumova, Kuratieva, Podberezskaya & Naumov, 2004), or hydroxides and oxides (Brun *et al.*, 1972), by reaction with hypophosphorous acid or with Na and Ba hypophosphites. All these precursors have been tried in the present work. Crystals of lithium hypophosphite were finally grown from an aqueous solution of lithium oxalate and calcium hypophosphite. Crystal growth was achieved by means of periodic cooling and heating cycles between 293 and 283 K every 12 h for 4 d in a specially constructed apparatus (Naumova, Kuratieva, Naumov & Podberezskaya, 2004). The precursors used for the preparation of lithium hypophosphite may play a role in the crystal growth. The crystals had a plate-like habit, with a maximum dimension of 0.7 mm. Crystals of beryllium hypophosphite were grown in a small quantity at room temperature from an aqueous solution of hypophosphorous acid and beryllium carbonate. The latter was prepared from $Be(NO_3)_2$ (aqueous) and Na_2CO_3 (aqueous). Carbon dioxide was removed under vacuum. The crystals had a prismatic habit, with a maximum dimension of 0.5 mm.

Compound (I)

Crystal data

LiH_2PO_2
$M_r = 71.93$
Monoclinic, $C2/m$
$a = 9.3557$ (11) Å
$b = 5.3107$ (7) Å
$c = 6.5432$ (12) Å
$\beta = 108.259$ (11)°
$V = 308.73$ (8) Å^3
$Z = 4$

$D_x = 1.547$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.2$–16.6°
$\mu = 0.62$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.47 × 0.43 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{min} = 0.741$, $T_{max} = 0.946$
430 measured reflections
329 independent reflections
306 reflections with $I > 2\sigma(I)$

$R_{int} = 0.041$
$\theta_{max} = 25.7°$
$h = -11 \rightarrow 10$
$k = -1 \rightarrow 6$
$l = 0 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.106$
$S = 1.15$
329 reflections
29 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.3682P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.16 (3)

Table 1
Selected geometric parameters (Å, °) for (I).

$Li-O1^i$	1.933 (4)	$P-O2$	1.484 (2)
$Li-O2$	1.936 (4)	$P-H$	1.35 (4)
$P-O1$	1.478 (2)		
$O1-P-O2$	120.30 (15)	$O1-P-H$	109.7 (14)
$H^{ii}-P-H$	92 (3)	$O2-P-H$	110.7 (15)

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

Compound (II)

Crystal data

$Be(H_2PO_2)_2$
$M_r = 138.98$
Tetragonal, $P4_12_12$
$a = 5.0117$ (5) Å
$c = 20.051$ (3) Å
$V = 503.62$ (10) Å^3
$Z = 4$
$D_x = 1.833$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 10.0$–12.9°
$\mu = 0.76$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.4 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{min} = 0.761$, $T_{max} = 0.796$
1372 measured reflections
699 independent reflections
599 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
$\theta_{max} = 29.9°$
$h = -6 \rightarrow 6$
$k = -4 \rightarrow 7$
$l = -27 \rightarrow 28$
3 standard reflections
frequency: 60 min
intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.098$
$S = 1.08$
699 reflections
43 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.018 (6)

Table 2
Selected geometric parameters (Å, °) for (II).

Be—O1	1.609 (3)	P—O2	1.4848 (19)
Be—O2$^{\rm iii}$	1.603 (3)	P—H1	1.38 (2)
P—O1	1.4888 (16)	P—H2	1.24 (3)
O1—P—O2	114.78 (12)	O1—P—H2	110.3 (8)
H1—P—H2	108.0 (14)	O2—P—H2	106.5 (8)

Symmetry code: (iii) $y, x-1, -z$.

In both structures, the H atoms were located from difference electron-density maps. Their positions were refined without any constraints. The refinement of the $Be(H_2PO_2)_2$ structure was carried out on a twinned crystal, with refined volume fractions of 40 (4) and 60 (4)% for the two chiral twin components.

For both compounds, data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1045). Services for accessing these data are described at the back of the journal.

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