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Layered calcium hydrogenphosphite monohydrate at 173 K

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(P–O) = 0.0011 Å
R factor = 0.027
wR factor = 0.074
Data-to-parameter ratio = 20.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The crystal structure of the title compound, $Ca(H_2PO_3)_2 \cdot H_2O$, exhibits two-dimensional sheets formed by linked Ca and P polyhedra. The layers are held together by O—H···O hydrogen bonds.

Comment

Metal phosphites, phosphates and phosphonates are a rich class of compounds which are of current interest in many areas from fundamental research to industrial applications and medicine. The general interest in the chemistry of these compounds is mainly due to their wide range of chemical composition and structural diversity. Those with a layered structure are more important to perform chemistry such as intercalation, ion exchange and catalysis, or to function as proton conductors, chemical sensors, *etc* (Clearfield, 1998; Alberti, 1996; Mallouk *et al.*, 1996). We are interested in the chemical characteristics of phosphites and phosphonates of alkaline-earth metals, including calcium, to obtain chemically modified surfaces and thin films for the protection of different objects such as stones and metals against atmospheric influences, corrosion and decay. The study of structure–property relationships of both calcium phosphites and phosphonates would lead us to design new materials with required properties.

In general, divalent metal phosphites and phosphonates are rather soluble, especially at low pH values, which is to some extent an advantage, since one can obtain them under relatively mild conditions, or grow single crystals for diffraction studies. There are several reports on the structure of alkaline-earth metal phosphates, but there are only few structures for phosphites (Corbridge, 1956; Larbot *et al.*, 1984; Powell *et al.*, 1994). The crystal structure of calcium hydrogenphosphite monohydrate, $Ca(H_2PO_3)_2 \cdot H_2O$, has been reported by Larbot *et al.* (1984). Their choice of unit cell is different from ours. According to the rules and definitions from the International Tables of Crystallography (Vol. A, 1983, pp. 734–740), we have choosen a reduced cell, which for the data of Larbot *et al.* (1984) will be a = 6.773 (1), b = 7.007 (1), c = 8.100 (1) Å, α = 68.00 (1), β = 84.92 (1), γ = 84.28 (1)°. Compared to our data, their unit-cell volume is smaller for room temperature [354.10 (9) Å^3]. Larbot *et al.* based their cell parameters on 20 reflections in the θ range 1–25°, while our data are based on 4179 reflections with $I > 10\sigma(I)$ in the θ range 1–32.82°. Therefore, we would rather compare parameters obtained from the same crystal, same diffractometer and similar setup. Our cell parameters for room temperature are a = 6.7857 (1), b = 7.0229 (1), c = 8.1154 (1) Å, α = 68.035 (1), β = 84.997 (1), γ = 84.363 (1)° and V = 356.401 (9) Å^3. Our data are of higher

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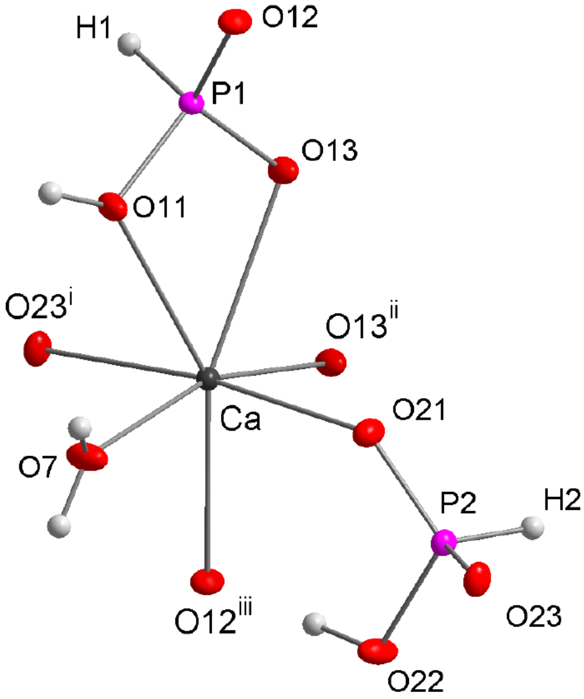


Figure 1
The geometry around the calcium ion in the crystal structure of $Ca(H_2PO_3)_2{\cdot}H_2O$ with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Symmetry codes are given in Table 1.

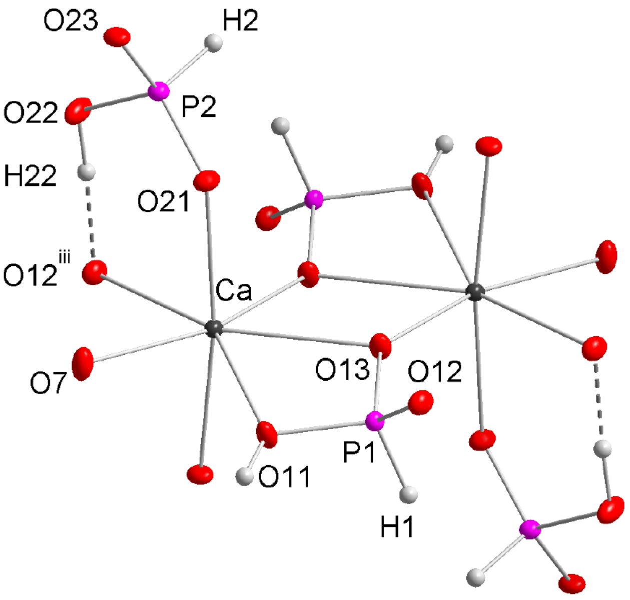
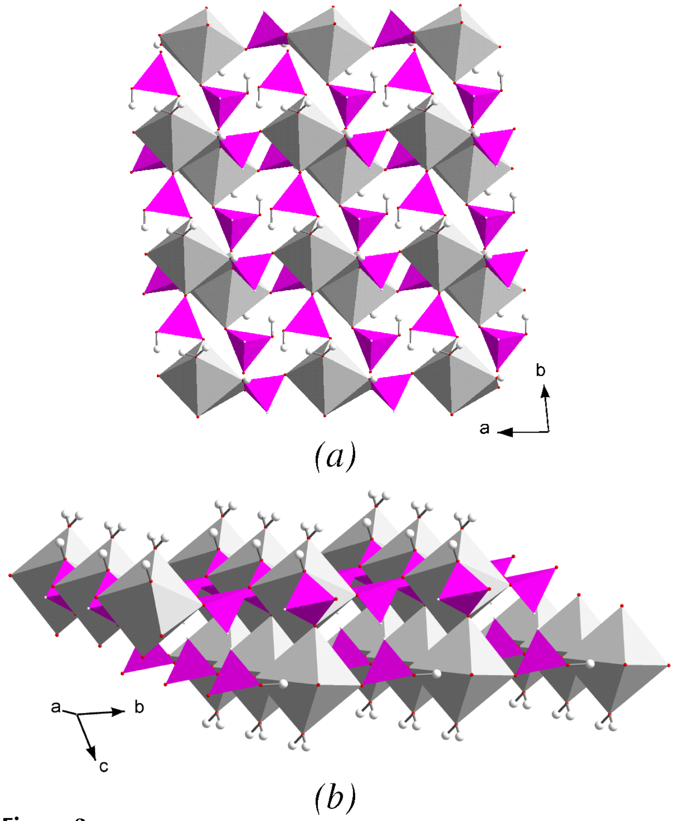


Figure 2
The geometry of a binuclear unit as a building block of the layered structure with atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level. Symmetry codes are given in Table 1.



(a)

(b)

Figure 3
Two-dimensional layer of calcium hydrogenphosphite monohydrate parallel to the *ab* plane. (*a*) Top view showing the binuclear units linking together by the P polyhera. (*b*) Side view showing the water molecules protruding from the layer.

precision by a factor of ten and show the expected temperature dependence.

Furthermore, there is no discussion about the packing features by Larbot *et al.* (1984) and, indeed, their discussion about interaction of (P—)H with O atoms in the form of hydrogen bonding is misleading and there are no hydrogen bonds of this type in the present structure. Here we present structure redetermination at 173 K using data from a Siemens SMART CCD diffractometer. The compound $Ca(H_2PO_3)_2{\cdot}H_2O$ crystallizes in the triclinic system with space group $P\overline{1}$ (No. 2). As shown in Fig. 1, the calcium ion is coordinated by seven O atoms with the Ca—O bond distances ranging from 2.3531 (10) to 2.5307 (11) Å. One of the phosphite groups is chelated to the calcium ion through O11 and O13, while the other one is just linked through O21 to the central atom. Each Ca ion is then connected to another calcium ion by a bridging O13 atom, symmetry related by ($1 - x$, $-y$, $1 - z$), to form a binuclear calcium phosphite (see Fig. 2). Each building block of this type is linked to other units through bridging O atoms of phosphite groups forming two-dimensional sheets aligned parallel to the *ab* plane. The water molecules are coordinated at axial positions of binuclear units to the Ca ions, protruding from the layers. Between the layers, water molecules are involved in hydrogen bonding with O atoms of the phosphite groups from adjacent layers. Within the layers, the O12 atom is involved in hydrogen bonding with the H22 atom, stabilizing the two-dimensional inorganic framework. The layered structure is represented by Figs. 3(*a*) (top view) and 3(*b*) (side view). Based on this study, we can understand the solubility of calcium hydrogenphosphite monohydrate in terms of the presence of regions highly accessible to water within the layers.

Experimental

Crystals suitable for X-ray diffraction analysis were obtained by very slow evaporation of the a saturated solution of calcium hydrogenphosphite monohydrate in water over a few days.

Crystal data

$Ca(H_2PO_3)_2{\cdot}H_2O$
$M_r = 220.07$
Triclinic, $P\overline{1}$
$a = 6.7777$ (2) Å
$b = 7.0282$ (1) Å
$c = 8.0970$ (2) Å
$\alpha = 67.906$ (1)°
$\beta = 84.812$ (1)°
$\gamma = 84.236$ (1)°
$V = 354.991$ (15) Å^3

$Z = 2$
$D_x = 2.059$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4179 reflections
$\theta = 1$–32°
$\mu = 1.32$ mm^{-1}
$T = 173$ (2) K
Parallelepiped, colorless
0.65 × 0.55 × 0.35 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.481$, $T_{\rm max} = 0.655$
5023 measured reflections
2416 independent reflections

2254 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 32.8°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.074$
$S = 1.05$
2416 reflections
116 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.2900P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.59$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.123 (7)

Table 1
Selected geometric parameters (Å).

Ca—O23$^{\rm i}$	2.3531 (10)	P1—O12	1.5085 (11)
Ca—O13$^{\rm ii}$	2.3531 (11)	P1—O11	1.5763 (11)
Ca—O21	2.3648 (11)	P1—H1	1.24 (2)
Ca—O7	2.3800 (12)	P2—O21	1.5075 (11)
Ca—O12$^{\rm iii}$	2.3912 (11)	P2—O23	1.5172 (11)
Ca—O13	2.5073 (11)	P2—O22	1.5831 (12)
Ca—O11	2.5307 (11)	P2—H2	1.26 (2)
P1—O13	1.5081 (11)		

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, -y, 1-z$; (iii) $1+x, y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H72$\cdots$O22$^{\rm i}$	0.83 (3)	2.03 (3)	2.8506 (16)	167 (3)
O11—H11$\cdots$O23$^{\rm ii}$	0.86 (3)	1.73 (3)	2.5756 (15)	169 (3)
O7—H71$\cdots$O21$^{\rm ii}$	0.86 (4)	2.02 (4)	2.8707 (16)	176 (3)
O22—H22$\cdots$O12$^{\rm iii}$	0.95 (3)	1.63 (4)	2.5748 (16)	176 (4)

Symmetry codes: (i) $2-x, 1-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $1+x, y, z$.

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low-temperature device at 173 K. The data were empirically corrected for absorption and other effects using *SADABS* (Sheldrick, 1996) based on the method of Blessing (1995). The structure was solved by Patterson method and refined by full-matrix least squares on all F^2 data using *SHELXTL* (Bruker, 1997). The non-H atoms were refined anisotropically. The H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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