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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1115). Services for accessing these data are described at the back of the journal.

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Refinement of CaBa₂(HPO₄)₂(H₂PO₄)₂

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Abstract

The structural model proposed previously for calcium dibarium bis(hydrogenphosphate) bis(dihydrogenphosphate) from X-ray powder data is confirmed by the present single-crystal study. The structure consists of infinite $[Ca(HPO_4)_2(H_2PO_4)_2]$ anionic chains built up from CaO_6, HPO_4 and H_2PO_4 polyhedra linked *via* Ca—O—P bonds. These chains are held together by nine-coordinate Ba^{2+} cations. A two-dimensional network of hydrogen bonds contributes to the linkage of these chains.

Comment

The alkaline earth phosphates $M_3(PO_4)_2$, $MHPO_4$ and $M(H_2PO_4)_2$ (M = Mg, Ca, Sr or Ba) have been studied extensively for their applications in different areas. Mixed alkaline earth phosphates, $M_2M'(PO_4)_2$, have also been studied. However, to our knowledge, there is very scant information on mixed alkaline earth hydrogenphosphates.

Our research efforts have focused on synthesizing new compounds of mixed alkaline earth phosphates. The title compound has recently been prepared and its structure based on X-ray powder diffraction data has been reported (Toumi *et al.*, 1997), but no attempt was made to locate the H atoms. Nevertheless, some hydrogen bonds were suggested on the basis of O···O contacts. Using hydrothermal synthesis, we have successfully obtained single crystals of this compound in order to refine the structure, including the hydrogen-bond system.

The structure of $CaBa_2(HPO_4)_2(H_2PO_4)_2$ is shown in Fig. 1. It consists of infinite chains of corner-sharing CaO_6 octahedra and H_2P1O_4 and $HP2O_4$ tetrahedra running along the *a* axis. Each CaO_6 centre is bridged to its neighbours by two pairs of P2 groups; thus, the Ca–Ca linkage is *via* Ca—O—P—O—Ca bonds. The two remaining *trans* corners of the octahedron, O4, are shared with two P1 groups. The polyhedral connectivity leads to infinite $[Ca(HPO_4)_2(H_2PO_4)_2]$ anionic chains. These chains are crosslinked by the Ba^{2+} cations. Further linkages are provided by hydrogen bonds.

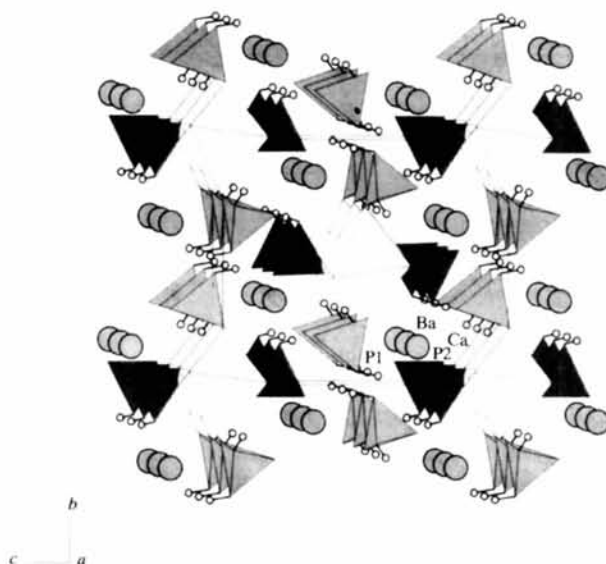Fig. 1. Polyhedral view of the structure of $CaBa_2(HPO_4)_2(H_2PO_4)_2$. Ba^{2+} ions and H atoms are represented by spheres of arbitrary radii.

The Ba^{2+} ion is coordinated to nine O atoms located within 3.1 Å. These BaO_9 polyhedra are connected *via* atoms O7 to form infinite strings running along the *a*

axis. One barium polyhedron shares two edges, O7–O8 and O5–O7^{iv} [Table 1; symmetry code: (iv) $1 + x$, y, z], with two P2 tetrahedra, an O6 corner with another P2, and the corners O1, O2, O3 and O4 with four P1 tetrahedra. The irregular geometry has d_{av} = 2.880 (3) Å for Ba—O, which is close to the distances reported for similar compounds (Toumi et al., 1997; Harrison et al., 1995). The Ca ion located on an inversion centre has a rather regular octahedral coordination, with Ca—O distances ranging from 2.285 (3) Å to 2.368 (3) Å and O—Ca—O angles varying from 84.44 (10) to 90.68 (10)°. The CaO$_6$ octahedron shares two O5–O8 edges with two adjacent BaO$_9$ polyhedra and the remaining two corners, O4, with two other BaO$_9$ polyhedra. The geometrical features of the two distinct phosphorus groups are quite regular. For P1, d_{av} = 1.544 (3) Å for P—O, with the longest distances, P1—O1 1.583 (3) and P1—O3 1.576 (3) Å, corresponding to the P—O(H) bonds and with θ_{av} = 109.3 (6)° for O—P—O. For P2, d_{av} = 1.538 (3) Å for P—O, with the longest distance, P—O 1.586 (3) Å, corresponding to the protonated oxygen O6 and with θ_{av} = 109.4 (6)° for O—P—O.

With regard to the hydrogen-bond system, all three H atoms in the title compound are involved in hydrogen bonds linking the two kinds of phosphorus tetrahedra, P1 and P2 (Fig. 2). There is a distribution of three donor (O—H) and three acceptor (O···H) functions between HPO$_4$ ($D + 2A$) and H$_2$PO$_4$ ($2D + A$). Here, we find the same connectivity as observed in K(HSO$_4$)(H$_2$SO$_4$) (Kemnitz et al., 1996): a P1 unit is linked by two strong hydrogen bonds [O3···O7^{iv} 2.507 (4) and O2···O6^{ix} 2.613 (4) Å; symmetry code: (ix) $-x$, $-y$, $1 - z$] to the two adjacent P2 units and vice versa, resulting in hydrogen-bonded tetramers (2P1 + 2P2). Eac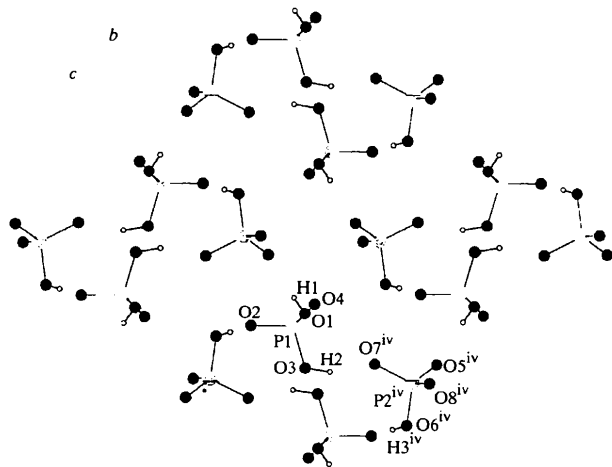h of these tetramers is located on an inversion centre, thus comprising two independent tetrahedra. Each tetramer is connected to its four neighbours by four hydrogen bonds [O1···O5^x 2.666 (4) Å; symmetry code: (x) $1 + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$], resulting in an infinite two-dimensional hydrogen-bonding network. We also note that there is no hydrogen-bond connection between two adjacent nets.

Experimental

Crystal data

CaBa$_2$(HPO$_4$)$_2$(H$_2$PO$_4$)$_2$	Mo $K\alpha$ radiation
M_r = 700.69	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
a = 5.4902 (7) Å	θ = 11–14°
b = 10.2004 (12) Å	μ = 6.685 mm^{-1}
c = 12.373 (3) Å	T = 293 (2) K
β = 100.783 (14)°	Needle
V = 680.7 (2) Å^3	0.04 × 0.02 × 0.02 mm
Z = 2	Colourless
D_x = 3.419 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.024
$\omega/2\theta$ scans	θ_{max} = 26.97°
Absorption correction:	h = 0 → 7
ψ scan (North et al., 1968)	k = 0 → 13
T_{min} = 0.851, T_{max} = 0.887	l = −15 → 15
1625 measured reflections	1 standard reflection
1473 independent reflections	frequency: 120 min
1198 reflections with	intensity decay: 0.1%
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.572 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.020	$\Delta\rho_{min}$ = −0.653 e Å^{-3}
$wR(F^2)$ = 0.043	Extinction correction:
S = 1.119	SHELXL93 (Sheldrick, 1993)
1473 reflections	Extinction coefficient:
119 parameters	0.0002 (2)
H atoms refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0101P)^2 + 0.5948P]$	International Tables for Crystallography (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} < 0.001$	

Fig. 2. The hydrogen-bonding system in CaBa$_2$(HPO$_4$)$_2$(H$_2$PO$_4$)$_2$ [symmetry code: (iv) $1 + x$, y, z].

Table 1. *Selected geometric parameters (Å, °)*

Ba—O2^i	2.679 (3)	Ca—O5^v	2.368 (3)
Ba—O6^{ii}	2.750 (3)	Ca—O5^{viii}	2.368 (3)
Ba—O3^{iii}	2.815 (3)	P1—O2	1.506 (3)
Ba—O4^{iv}	2.828 (3)	P1—O4	1.510 (3)
Ba—O7^v	2.892 (3)	P1—O3	1.576 (3)
Ba—O1	2.912 (3)	P1—O1	1.583 (3)
Ba—O7	2.948 (3)	O3—H2	0.90 (4)
Ba—O8	3.029 (3)	O1—H1	0.75 (3)
Ba—O5^v	3.065 (3)	P2—O8	1.510 (3)
Ca—O8^{vi}	2.285 (3)	P2—O7	1.525 (3)
Ca—O8	2.285 (3)	P2—O5	1.531 (3)
Ca—O4^{vii}	2.363 (3)	P2—O6	1.586 (3)
Ca—O4^i	2.363 (3)	O6—H3	0.88 (4)
O8^{vi}—Ca—O8	180.0	O2—P1—O1	109.63 (15)
O8—Ca—O4^{vii}	90.68 (10)	O4—P1—O1	110.7 (2)
O4^{vii}—Ca—O4^i	180.0	O3—P1—O1	103.0 (2)
O4^i—Ca—O5^v	84.53 (9)	O8—P2—O7	112.0 (2)
O8^{vi}—Ca—O5^{viii}	84.44 (10)	O8—P2—O5	114.1 (2)
O5^v—Ca—O5^{viii}	180.0	O7—P2—O5	108.5 (2)
O2—P1—O4	116.2 (2)	O8—P2—O6	104.8 (2)
O2—P1—O3	106.3 (2)	O7—P2—O6	108.69 (15)
O4—P1—O3	110.15 (15)	O5—P2—O6	108.6 (2)

Symmetry codes: (i) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - 1, y, z$; (v) $1 + x, y, z$; (vi) $-x, -y, -z$; (vii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $-1 - x, -y, -z$.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1995). Software used to prepare material for publication: *SHELXL*93.

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