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Barium Cobalt Phosphate, $BaCo_2(PO_4)_2$

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Abstract

Barium dicobalt(II) bis(phosphate) is built up from BaO_{12} polyhedra [d_{av}(Ba—O) = 2.995 (1) Å], CoO_6 octahedra [d_{av}(Co—O) = 2.098 (2) Å] and PO_4 tetrahedra [d_{av}(P—O) = 1.544 (2) Å]. The structure has a strongly layered nature, with Ba^{2+} cations interspersing infinite sheets of edge-sharing CoO_6 groups, which are capped by phosphate tetrahedra. The title compound is isostructural with $BaNi_2(AsO_4)_2$.

Comment

Cobalt(II) phosphates built up from vertex-sharing tetrahedral CoO_4 and PO_4 units are of great current interest for their structural similarities to aluminosilicate zeolites (Feng, Bu, Tolbert & Stucky, 1997). However, other recently described cobalt(II) phosphates demonstrate the relative lack of coordinational preference of the Co^{2+} species. $NaCoPO_4$ (Feng, Bu & Stucky, 1997) contains CoO_5 trigonal bipyramids, whereas $Ba(CoPO_4)_2.H_2O$ (Bu *et al.*, 1997) contains CoO_6 octahedra. $Co_2(OH)PO_4$ (Harrison *et al.*, 1995) contains Co in both octahedral and trigonal bipyramidal coordination.

We report here the structure of $BaCo_2(PO_4)_2$ (Fig. 1) which is a layered material built up from BaO_{12} groups (Ba site symmetry $\bar{3}$), CoO_6 octahedra (Co site symmetry 3) and PO_4 tetrahedra (P site symmetry 3). $BaCo_2(PO_4)_2$ is isostructural with $BaNi_2(AsO_4)_2$ (Eymond, Durif & Martin, 1969). Based on X-ray powder data, $BaMg_2(AsO_4)_2$, $BaCo_2(AsO_4)_2$, $BaNi_2(PO_4)_2$ (Eymond, Martin & Durif, 1969) and $BaNi_2(VO_4)_2$ (Wichmann & Müller-Buschbaum, 1984) adopt the same crystal structure. We note that all these phases were prepared by high-temperature ceramic methods, compared with the hydrothermal synthesis used for $BaCo_2(PO_4)_2$.

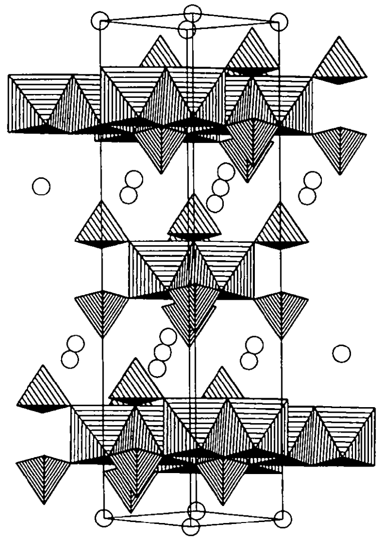

Fig. 1. Polyhedral view of the $BaCo_2(PO_4)_2$ structure. Ba^{2+} species are represented by spheres of arbitrary radii.

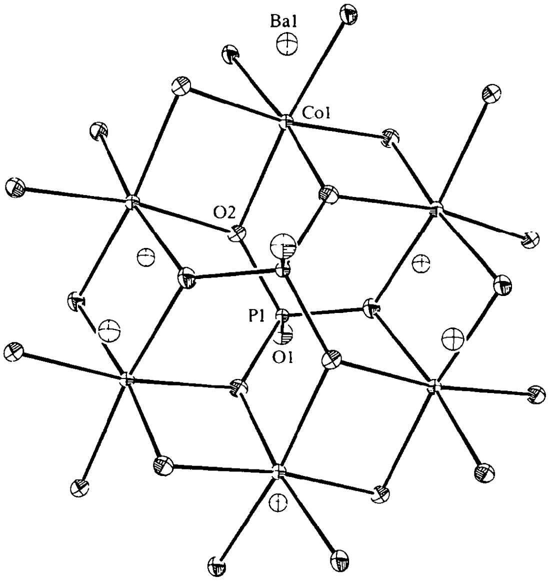

Fig. 2. Fragment of $BaCo_2(PO_4)_2$ viewed approximately down [001] (50% displacement ellipsoids).

$BaCo_2(PO_4)_2$ is built up from sheets of edge-sharing CoO_6 octahedra, arrayed normal to [001]. These layers form six-ring (six octahedra) windows. Two P1—O1 units cap both sides of each window as PO_4 tetrahedra (Fig. 2). The anionic $[Co_2(PO_4)_2]^{2-}$ sheets are stacked in an *abcabc*... sequence along [001], and are laterally displaced by $\Delta x = \frac{2}{3}a$, with $\Delta y = \frac{1}{3}b$ between layers. The interlayer separation, from Co plane to Co plane, is 7.738 (1) Å. Twelve-coordinate Ba^{2+} cations provide the charge-compensating interlayer species, forming bonds with six O1 and six O2 atoms. O2 bonds to two Co, one P and one Ba atom, whereas O1 bonds to one P and three Ba neighbours. Bond-valence-sum (BVS) calculations (Brown, 1996) are typical for the species involved: Ba1 1.86, Co1 2.01, P1 4.89, O1 2.05 and O2 1.95 (expected values: Ba 2.00, Co 2.00, P 5.00 and O 2.00).

$BaCo_2(PO_4)_2$ shows few structural similarities with $BaCo_2(PO_4)_2.H_2O$ (Bu *et al.*, 1997), even though both phases have lamellar character. The latter phase contains the unusual feature of edge-sharing $CoO_5(H_2O)$ octahedra and PO_4 tetrahedra. Its Co—O—Co connectivity results in one-dimensional corner-sharing chains of $CoO_5(H_2O)$ groups. The only other well characterized barium cobalt(II) phosphate, $BaCoP_2O_7$ (Riou *et al.*, 1988), adopts a completely different structure to $BaCo_2(PO_4)_2$ based on a three-dimensional array of vertex-sharing CoO_6 and P_2O_7 moieties. The relationship between the $AM_2(XO_4)_2$-type structure adopted by $BaCo_2(PO_4)_2$ and the rhombohedral $AMXO_4$-type structure adopted by phases such as $KNiAsO_4$ is discussed by Buckley *et al.* (1988).

Experimental

Single crystals of $BaCo_2(PO_4)_2$ were prepared from a mixture of $BaCO_3$ (1.375 g), $CoBr_2$ (1.523 g), 85% H_3PO_4 (3.33 g), guanidinium carbonate {$[C(NH_2)_3]_2CO_3$; 1.254 g} and H_2O (10 ml). These components were sealed in a 23 ml teflon-lined hydrothermal bomb and heated to 453 K for 3 d. After cooling to ambient temperature over several hours, pink crystals of the title compound were recovered by vacuum filtration and drying in air.

Crystal data

$BaCo_2(PO_4)_2$
$M_r = 445.14$
Trigonal
$R\bar{3}$
$a = 4.8554$ (6) Å
$c = 23.2156$ (17) Å
$V = 473.98$ (9) Å^3
$Z = 3$
$D_x = 4.679$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 5.0$–$13.5°$
$\mu = 11.868$ mm^{-1}
$T = 298$ (2) K
Block
0.3 × 0.2 × 0.2 mm
Pink

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.080$, $T_{max} = 0.093$
1134 measured reflections
390 independent reflections
383 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 32.44°$
$h = -1 \rightarrow 7$
$k = -7 \rightarrow 1$
$l = -34 \rightarrow 34$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.017$ (for observed reflections)
$wR(F^2) = 0.045$
$S = 1.18$
390 reflections
23 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0125P)^2 + 3.0015P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.15$ e Å^{-3} (1.42 Å from O2)
$\Delta\rho_{min} = -0.97$ e Å^{-3}
Extinction correction: *SHELX*97 (Sheldrick, 1997)
Extinction coefficient: 0.0098 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0	0	0	0.01059 (13)
Co1	0	0	0.17021 (2)	0.00725 (14)
P1	1/3	2/3	0.24129 (4)	0.00579 (18)
O1	1/3	2/3	0.30633 (13)	0.0118 (5)
O2	0.3455 (4)	0.3700 (4)	0.21959 (9)	0.0106 (3)

Table 2. *Selected geometric parameters (Å, °)*

Ba1—O1^i	2.8725 (7)	Co1—O2^{ii}	2.112 (2)
Ba1—O2^i	3.1168 (19)	P1—O1	1.510 (3)
Co1—O2	2.0837 (19)	P1—O2	1.5548 (19)
O2—Co1—O2^{iii}	92.64 (8)	O1—P1—O2^{vi}	108.90 (8)
O2—Co1—O2^{ii}	95.97 (7)	O2^{vi}—P1—O2^{vii}	110.03 (8)
O2^{iii}—Co1—O2^{ii}	86.09 (11)	P1—O2—Co1	126.15 (11)
O2^{iv}—Co1—O2^{ii}	171.34 (8)	P1—O2—Co1^{ii}	130.61 (11)
O2^{ii}—Co1—O2^{v}	85.53 (8)	Co1—O2—Co1^{ii}	84.03 (7)

Symmetry codes: (i) $x - \frac{2}{3}, y - \frac{1}{3}, z - \frac{1}{3}$; (ii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iii) $-x + y, -x, z$; (iv) $-y, x - y, z$; (v) $x - y - \frac{1}{3}, x - \frac{2}{3}, \frac{1}{3} - z$; (vi) $-x + y, 1 - x, z$; (vii) $1 - y, 1 + x - y, z$.

Data collection: *P*4 *Software* (Siemens, 1995). Cell refinement: *P*4 *Software*. Data reduction: *P*4 *Software*. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *ORTEP*3 (Farrugia, 1997). Software used to prepare material for publication: *SHELX*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1136). Services for accessing these data are described at the back of the journal.

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$K_6[As_6V_{15}O_{42}(H_2O)].6H_2O$

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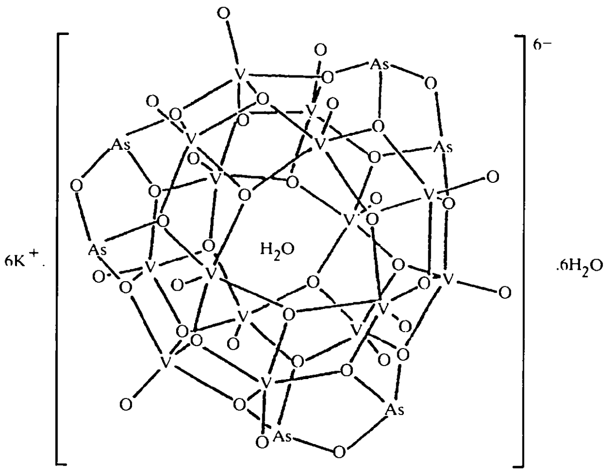
Abstract

The crystal structure of hexapotassium dotetracontaoxo(hexaarsenio)pentadecavanadate(IV) heptahydrate, $K_6[As_6V_{15}O_{42}(H_2O)].6H_2O$, is composed of an $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion, which has D_3 symmetry, and six seven-coordinate potassium ions. There is an H_2O molecule at the centre of the heteropolyanion. This anion consists of VO_5 pyramids linked by As_2O_5 units through shared O atoms. The V—O distances range from 1.604 (4) to 2.009 (4) Å, As—O from 1.772 (4) to 1.793 (3) Å, and K···O from 2.676 (6) to 3.311 (4) Å.

Comment

Iso- and heteropolyvanadates usually contain molecular anions with interesting cage structures. These polyvanadate cage anions form inclusion compounds with neutral molecules and anions, among which are $[V_{12}O_{32}(MeCN)]^{4-}$ (Day *et al.*, 1989), $[V_{18}O_{42}(H_2O)]^{12-}$ (Johnson & Schlemper, 1978), $[V_{18}O_{42}H_9(VO_4)]^{6-}$, $[V_{18}O_{42}(SO_4)]^{8-}$, $[As_6V_{15}O_{42}(H_2O)]^{6-}$, $[As_8V_{14}O_{42}(H_2O)]^{4-}$, $[As_8V_{14}O_{42}(X)]^{6-}$ (X = SO_3^{2-} or SO_4^{2-}; Müller & Döring, 1991) and $[As_8V_{14}O_{42}(H_2O)_{1/2}]^{4-}$ (Huan *et al.*, 1991). The crystal structure has been reported for an $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion with H_2O at the centre in $K_6[As_6V_{15}O_{42}(H_2O)].8H_2O$ (Müller & Döring, 1988, 1991). The present study concerns the phase $K_6[As_6V_{15}O_{42}(H_2O)].6H_2O$, (I), which contains a similar anion to that found in $K_6[As_6V_{15}O_{42}(H_2O)].8H_2O$ (Müller & Döring, 1988, 1991).



(I)

The $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion has D_3 symmetry, and consists of 15 distorted VO_5 square pyramids and six AsO_3 triangular pyramids, with a statistically disordered H_2O molecule at its centre. Two AsO_3 groups are joined to each other *via* an oxygen bridge and form an As_2O_5 unit. Every VO_5 consists of one terminal O and four bridging O atoms. The VO_5 pyramids are joined through vertices and edges to their neighbouring VO_5 pyramids, but the AsO_3 groups are connected by VO_5 pyramids only through vertices. The 15 VO_5 pyramids linked with one another through vertices and edges are connected by As_2O_5 units through shared O atoms, and form a ball-like structure.

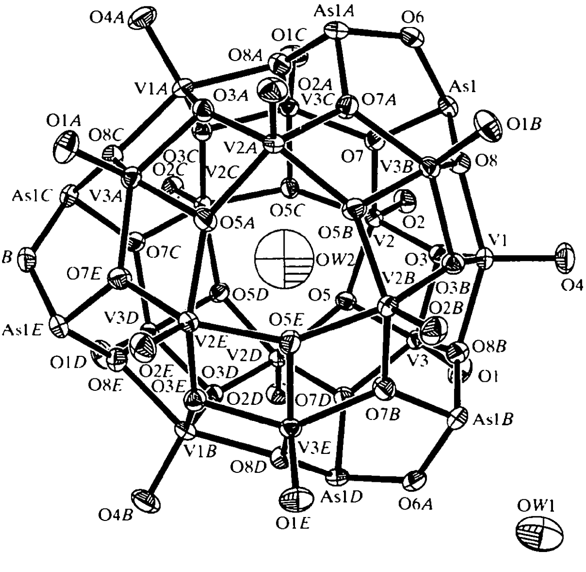


Fig. 1. View of the $[As_6V_{15}O_{42}(H_2O)]^{6-}$ anion, with displacement ellipsoids at the 50% probability level.