K$_2$Bi(PO$_4$)(WO$_4$) with a layered anionic substructure

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Dipotassium bismuth phosphate tungstate has been synthesized using the flux technique. It crystallizes in the space group *Ibca* and is isotypic with Na$_2$Y(PO$_4$)(MoO$_4$). It exhibits a layered structure, which is built up from [Bi(PO$_4$)(WO$_4$)]$_\infty^{2-}$ layers. Each layer is composed of [BiO$_8$]$_\infty$ zigzag chains, which are connected *via* PO$_4$ and WO$_4$ tetrahedra. The parallel anionic [Bi(PO$_4$)(WO$_4$)]$_\infty^{2-}$ layers are stacked along [100] and are held together by K$^+$ counter-cations which occupy sites in the interlayer space. Bi, W and P atoms are all located on twofold axes.

Comment

Complex phosphates with mixed-anionic framework structures have been extensively studied in the past. Double phosphates containing additional XO_4 anionic tetrahedra (X = V, Si, Ge, Mo, W) are known either as solid solutions or as compounds with unique structures. The solid solutions usually are members of well known structural types, *e.g.* the phosphate silicate Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$ (Hong 1976; Goodenough *et al.* 1976) and the phosphate molybdate Na$_{1-x}$Zr$_2$(PO$_4$)$_{3-x}$(MoO$_4$)$_x$ (Pet'kov *et al.*, 2003; Sukhanov *et al.* 2006) are both isotypic with NaZr$_2$(PO$_4$)$_3$ (NZP) (Hagman & Kierkegaard, 1968), whereas the phosphate vanadates K$_3$Ln(PO$_4$)$_x$(VO$_4$)$_{2-x}$ (0.53 < x < 2.00) (Kirichenko *et al.*, 1999; Komissarova *et al.*, 2002) are isotypic with arcanite (K$_2$SO$_4$) (McGinnety, 1972). Other complex phosphates with an additional tetrahedral anion have stoichiometric formulas, *e.g.* Ln$_{11}$O$_{10}$(XO_4)(PO$_4$)$_3$ (Ln = Pr—Er; X = Si, Ge; Palkina *et al.*, 1997; Dzhurinskii & Krut'ko, 2000) and Ln$_3$O(XO_4)(PO$_4$) (Ln = La–Er; X = Si, Ge; Dzhurinskii *et al.*, 1991; Dzhurinskii & Lysanova, 1998). The phosphate tungstate Zr$_2$(PO$_4$)$_2$(WO$_4$) (Evans *et al.*, 1995), and the phosphate molybdates Na$_3$Ba(MoO$_4$)(PO$_4$) (Kolsi *et al.*, 1981) and Na$_2$Y(MoO$_4$)(PO$_4$) (Ben Amara & Dabbabi, 1987) are also known. The structure of the latter has previously been reported as monoclinic with space group *C2/c* (Ben Amara & Dabbabi, 1987), but was later revised to be orthorhombic with space group *Ibca* (Marsh, 1987). We report here the flux-growth synthesis and structural characterization of K$_2$Bi(PO$_4$)(WO$_4$), (I), which is isotypic with Na$_2$Y(MoO$_4$)(PO$_4$).

The Bi atom is situated on a position with .2. symmetry and is surrounded by eight O atoms with a distorted dodecahedral environment. The BiO$_8$ polyhedron exhibits four pairs of Bi—O distances within the range 2.358 (6) to 2.562 (6) Å (Table 1). By edge-sharing, the BiO$_8$ polyhedra form infinite zigzag chains extending parallel to [001], with a Bi—Bi distance of 4.058 (1) Å. The PO$_4$ tetrahedron is joined to four BiO$_8$ polyhedra, each of which in turn is linked to four phosphate tetrahedra, which results in the formation of four-membered
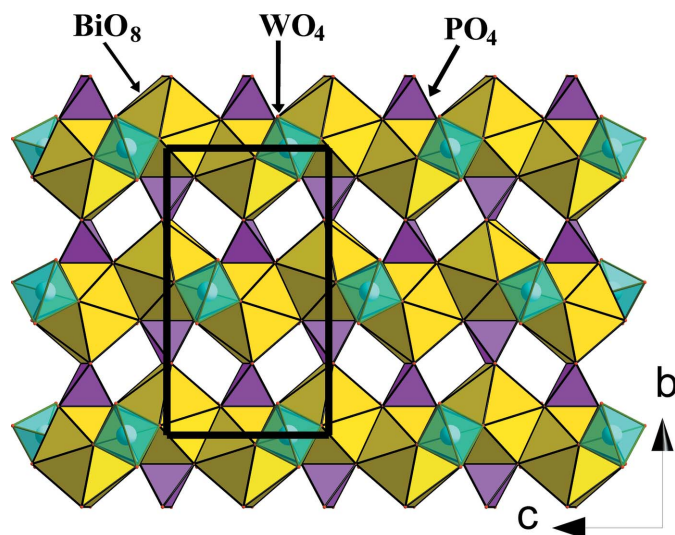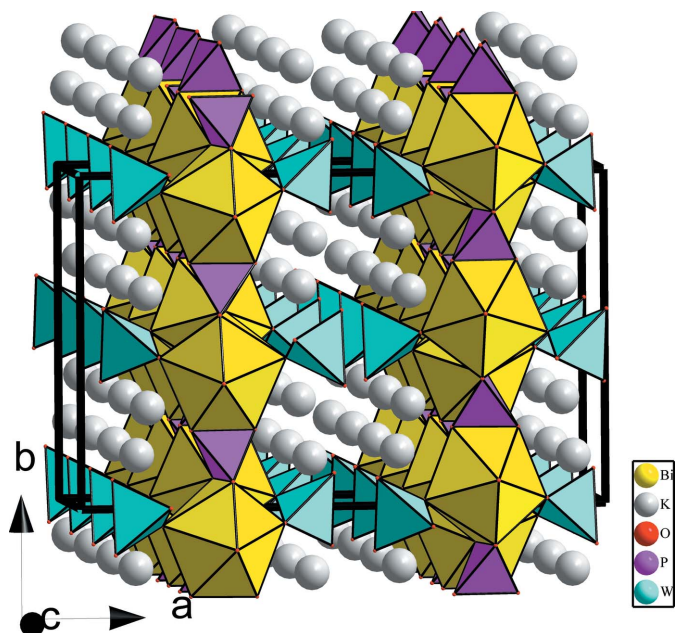
Figure 1
Projection of the anionic layer $[Bi(PO_4)(WO_4)]^{2-}_\infty$ on to the *bc* plane.
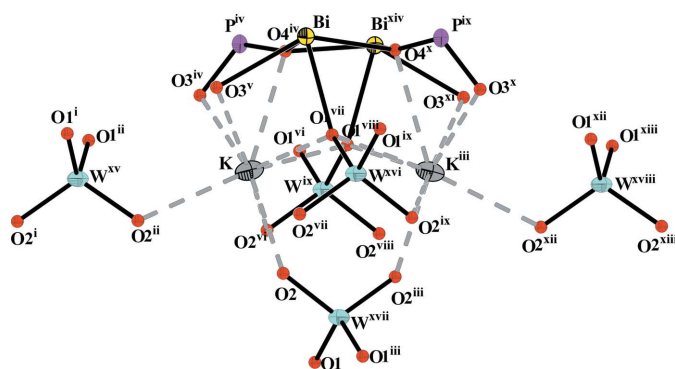
Figure 2
A view of the cage where the potassium atoms are located, displayed with anisotropic displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $1 - x, y, -\frac{1}{2} - z$; (ii) $1 - x, \frac{1}{2} - y, z$; (iii) $x, -y, -\frac{1}{2} - z$; (iv) $x, y, -\frac{1}{2} - z$; (v) $x, \frac{1}{2} - y, -z$; (vi) $1 - x, y, -\frac{1}{2} + z$; (vii) $1 - x, y, \frac{1}{2} + z$; (viii) $1 - x, -y, -1 - z$; (ix) $1 - x, -y, -z$; (x) $x, -y, z$; (xi) $x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (xii) $1 + x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (xiii) $1 - x, -\frac{1}{2} - y, z$; (xiv) $-x, -y, -\frac{1}{2} + z$; (xv) $-x, -y, -1 + z$; (xvi) $1 - x, -y, 1 - z$; (xvii) $x, y, -1 + z$; (xviii) $1 - x, -y, -1 + z$].

planar rings with a composition $BiO_2PO_2BiO_2$. The arrangement of corner-sharing BiO_8 dodecahedra and phosphate tetrahedra is remarkably similar to that in $BiPO_4$ (Romero *et al.*, 1994). Two BiO_8 polyhedra of individual chains are linked together *via* WO_4 tetrahedra. Both tetrahedral WO_4 and PO_4 units have local C_{2v} symmetry (Table 1). As a result of connection of the BiO_8, PO_4 and WO_4 polyhedra, the layered anion $[Bi(PO_4)(WO_4)]^{2-}_\infty$ is formed parallel to the *bc* plane (Fig. 1). The distance between two neighbouring layers is $a/2$ [9.8627 (12) Å].

All potassium cations are located in the vacancies that are formed by stacking of the anionic layers. K^+ is eight-coordinated by O atoms with K—O distances ranging from 2.658 (7) to 3.230 (7) Å (Table 1). Each WO_4 tetrahedron of the anionic layer coordinates to two potassium cations, which occupy sites in the cavities of the next layer (Fig. 2). As a result, the potassium cations contribute to the stability of the structure

Figure 3
The structure of $K_2Bi(PO_4)(WO_4)$ in a view approximately along [001].

and consolidate the structure into a three-dimensional framework (Fig. 3).

The ionic radii of the trivalent rare-earth elements (Ce–Gd) lie between those of Y and Bi (Shannon, 1976). Consequently, it is worthy of note that a large family of compounds of general formula $M_2Ln(PO_4)(AO_4)$ (M = Na, K; Ln = Ce—Gd; A = Mo, W) is expected to be synthesized.

Experimental

All reagents used were of analytical grade (Merck, p.A.). Single crystals of (I) were grown by spontaneous crystallization of a flux in the system K_2O–Bi_2O_3–P_2O_5–WO_3. Bi_2O_3 (1.280 g, 2.75 mmol), KPO_3 (0.865 g, 7.32 mmol), $K_4P_2O_7$ (1.209 g, 3.66 mmol), K_2WO_4 (3.882 g, 11.91 mmol) and WO_3 (2.763 g, 11.91 mmol) were mixed in an agate mortar, placed in a platinum crucible and heated to 1223 K in air. The homogenous flux was cooled at a rate of 30 K h^{-1} in the temperature range 1223–873 K. After cooling to room temperature, colorless crystals of (I) with mostly plate-like habit were washed with hot deionized water. Elemental analysis indicated the presence of K, Bi, W and P in an atomic ratio close to 2:1:1:1.

Crystal data

$K_2[Bi(PO_4)(WO_4)]$	$Z = 8$
$M_r = 630$	$D_x = 4.838$ Mg m^{-3}
Orthorhombic, $Ibca$	Mo $K\alpha$ radiation
$a = 19.7253$ (12) Å	$\mu = 34.77$ mm^{-1}
$b = 12.4764$ (8) Å	$T = 293$ (2) K
$c = 7.0284$ (2) Å	Prism, colorless
$V = 1729.69$ (16) Å^3	$0.08 \times 0.07 \times 0.03$ mm

Data collection

Oxford XCalibur-3 CCD area-detector diffractometer	16151 measured reflections
φ and ω scans	1265 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	1098 reflections with $I > 2\sigma(I)$
$T_{min} = 0.075$, $T_{max} = 0.351$	$R_{int} = 0.064$
	$\theta_{max} = 30°$

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2$	
$R[F^2 > 2\sigma(F^2)] = 0.035$		$+ 34.3351P]$	
$wR(F^2) = 0.094$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.18$		$(\Delta/\sigma)_{max} < 0.001$	
1265 reflections		$\Delta\rho_{max} = 4.87$ e Å^{-3}	
62 parameters		$\Delta\rho_{min} = -2.37$ e Å^{-3}	
		Extinction correction: *SHELXL97*	
		Extinction coefficient: 0.00034 (5)	

Table 1
Selected geometric parameters (Å, °).

Bi—O1^i	2.358 (6)	K—O1^{vi}	3.001 (7)
Bi—O2	2.435 (6)	K—O4^{vi}	3.078 (9)
Bi—O3	2.441 (6)	K—O4^{vii}	3.179 (9)
Bi—O1^{ii}	2.562 (6)	K—O3^{vii}	3.230 (7)
K—O4^{iii}	2.658 (7)	W—O4	1.767 (7)
K—O2^{iv}	2.715 (6)	W—O3	1.780 (7)
K—O2^i	2.768 (6)	P—O1	1.536 (6)
K—O3^v	2.982 (7)	P—O2	1.541 (6)
O4^{vi}—W—O4	111.0 (5)	O1—P—O1^{iv}	102.9 (5)
O4^{vi}—W—O3	109.9 (4)	O1—P—O2^{iv}	110.3 (3)
O4—W—O3	106.7 (3)	O1^{iv}—P—O2^{iv}	113.4 (3)
O4^{vi}—W—O3^{vi}	106.7 (3)	O1—P—O2	113.4 (3)
O4—W—O3^{vi}	109.9 (4)	O1^{iv}—P—O2	110.3 (3)
O3—W—O3^{vi}	112.7 (4)	O2^{iv}—P—O2	106.6 (4)

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

The highest peak and the deepest hole in the final difference map are located 0.76 and 1.24 Å from Bi, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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