inorganic papers

Tripotassium dibismuth(III) tris[arsenate(V)], $K_3Bi_2(AsO_4)_3$

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The title compound was prepared by a solid-state reaction at 1123 K. Its structure is closely related to that of alluaudite. The main structural feature is the presence of infinite chains of edge-sharing Bi_2O_{10} dimers, which are linked by AsO_4 tetrahedra to form a framework enclosing two types of channels where K^+ cations reside. The $X1$ site of the alluaudite structure is occupied by K^+, whereas the $X2$ site is empty.

Comment

Phosphates such as $M_3^IM_2^{III}(PO_4)_3$ (M^I = Li, Na, M^{III} = Cr, Fe, Sc) have been extensively investigated. They are known to be fairly good ionic conductors, structurally related to Nasicon, $Na_3Zr_2Si_2PO_{12}$. In contrast, arsenates exhibit other structure types: $Li_3Cr_2(AsO_4)_3$ has a garnet structure, $Na_3Sc_2(AsO_4)_3$ is structurally related to γ-$Na_3Sc_2(PO_4)_3$ (hexagonal Nasicon-like structure), whereas the three compounds $Li_3(Fe,In,Sc)_2$-$(AsO_4)_3$ are structurally related to the monoclinic $Fe_2(SO_4)_3$. The investigation of Bi compounds has the added interest that structural modifications occur in the coordination polyhedra due to the non-bonding lone pair, leading to new structures. However, the effect of lone pairs has been studied by few authors. For these reasons, we have investigated the A–Bi–P–
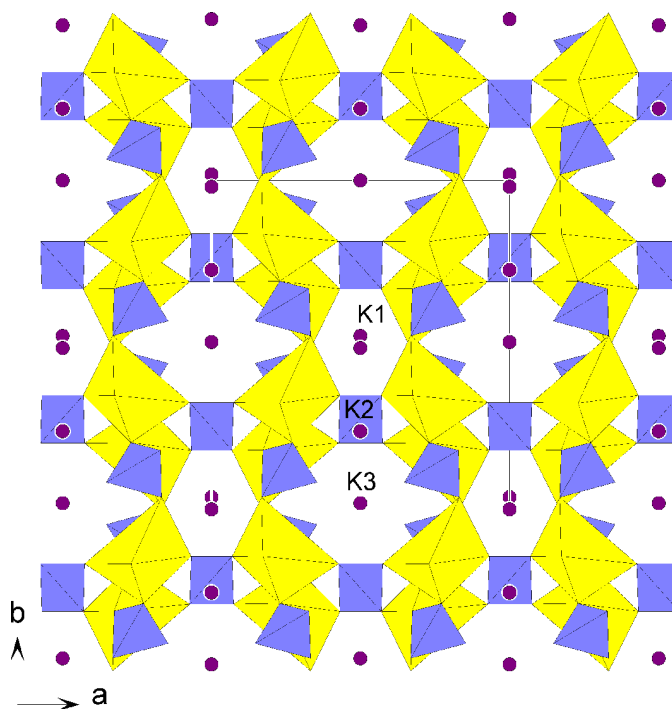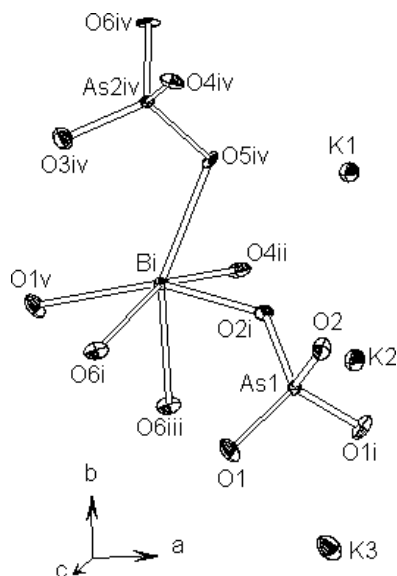

Figure 1
A projection of the structure of $K_3Bi_2(AsO_4)_3$, viewed along the c axis. Colour key: BiO_6 polyhedra yellow and AsO_6 polyhedra blue.

Figure 2
A view of a portion of the structure of $K_3Bi_2(AsO_4)_3$, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

O system (A = monovalent cation) and have previously reported the syntheses and crystal structures of $Na_5Bi(P_2O_7)_2$ (Boughzala & Jouini, 1999), $K_3Bi_2(PO_4)_3$ (Falah et al., 2001) and $Rb_6Bi_4(PO_4)_2(P_2O_7)_4$ (Falah et al., 2003). In further investigations, we replaced P by As in order to find new alkali bismuth arsenate compounds in the A–Bi–As–O system (A being a monovalent cation). In this paper, we report the synthesis and X-ray structure determination of a new arsenate, viz. $K_3Bi_2(AsO_4)_3$.

The title compound has an alluaudite-like structure (Moore, 1971; Lii & Ye, 1997). In fact, there is a second known arsenate mineral with the alluaudite structure. The structure of the title compound is built up from BiO_6 octahedra and AsO_4 tetrahedra sharing corners to form a three-dimensional framework enclosing two types of channels where K^+ ions reside (Fig. 1). The BiO_6 octahedra appear to be more distorted than is usual for MO_6 in the alluaudite structure, which is characteristic of the lone-pair effect. Bi is coordinated by three O atoms with short bonds [2.199 (6) < Bi—O < 2.296 (7) Å] on one side and by three long bonds [2.505 (6) < Bi—O < 2.579 (7) Å] on the other side (Fig. 2). This geometry is compatible with the stereoactivity of the bismuth lone pair, which points its orbital lobe between the longest Bi—O bonds. The Bi—O6 distance is characteristic of the triply bridging O atom O6, shared by $As2O_4$ tetrahedra and two BiO_6 octahedra. The bond-valence sum using Brown's method (Brown & Altermatt, 1985), which gives 2.99, is in good agreement with the oxidation state of Bi. Comparison with the crystal structure of a natural alluaudite from the Buranga pegmatite of Central Africa (Moore, 1971; Yakubovich et al., 1977) indicates that the $X1$ site at $(\frac{1}{2},0,0)$ is partly filled with Na^+, Ca^{2+} and Mn^{2+}, whereas, in the title compound, the $X1$ site is fully occupied by K3. A new site shifted from the $X1$ site by $\frac{1}{4}$ or $-\frac{1}{4}$ in z at a general position near $\frac{1}{2},0,z$ is fully occupied by K1. The $X2$ site is empty in

natural alluaudite and partly filled by cations smaller than K^+ in other alluaudite-like structures, viz. $Na_3In_2(AsO_4)_3$ (Khorari et al., 1997) and $NaCo_3(AsO_4)(HAsO_4)_2$ (Lii & Shih, 1994). In the title compound, K^+ cannot be accommodated in this site and the $X2$ site remains empty. This is the reason why K^+ has moved to the $X1$ site. The $M1$ site is occupied by K2 and the $M2$ site is filled by Bi, as observed in $K_3Bi_2(PO_4)_3$ (Falah et al., 2001). There are the two examples of the full occupancy of the $X1$ and $M1$ sites by K^+ cations. K1, K2 and K3 ions are coordinated by ten, eight and six O atoms, respectively, with distances ranging from 2.681 (6) to 3.319 (7) Å, forming irregular coordination polyhedra. The bond-valence sums of the K—O bonds using the formula of Brown & Altermatt (1985) are 1.25, 1.28 and 1.11 for K1, K2 and K3, respectively. Thus, the high valence bond sums appear to compensate for the shortfall in the sums, 4.90 and 4.86, for As1 and As2.

Experimental

The title compound can be prepared by solid-state reaction techniques. The synthesis procedure is as follows. Stoichiometric quantities of the appropriate reagents (K_2CO_3, Bi_2O_3 and $NH_4H_2PO_4$) were intimately mixed and calcined in air at 623 K for 12 h in an alumina crucible. These ingredients were then heated to 1123 K for 40 d and finally cooled to room temperature in the furnace. The product was washed with boiling water. This led to the formation of parallelepiped-shaped colourless crystals of $K_3Bi_2(AsO_4)_3$.

Crystal data

$K_3Bi_2(AsO_4)_3$	$D_x = 5.140$ Mg m^{-3}
$M_r = 952.02$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 14.030 (2)$ Å	reflections
$b = 13.773 (2)$ Å	$\theta = 9.6–14.9°$
$c = 7.009 (2)$ Å	$\mu = 37.65$ mm^{-1}
$\beta = 114.71 (2)°$	$T = 293 (2)$ K
$V = 1230.4 (3)$ Å^3	Parallelepiped, colourless
$Z = 4$	$0.11 \times 0.04 \times 0.04$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.021$
diffractometer	$\theta_{max} = 26.0°$
ω–2θ scans	$h = -17 \rightarrow 15$
Absorption correction: ψ scan	$k = 0 \rightarrow 16$
(North et al., 1968)	$l = 0 \rightarrow 8$
$T_{min} = 0.164$, $T_{max} = 0.255$	2 standard reflections
1387 measured reflections	frequency: 120 min
1203 independent reflections	intensity decay: 2%
1006 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.051$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 1.09$ e Å^{-3}
1203 reflections	$\Delta\rho_{min} = -1.22$ e Å^{-3}
95 parameters	Extinction correction: SHELXL97
	Extinction coefficient: 0.00050 (2)

Table 1
Selected geometric parameters (Å, °).

Bi—O2^{i}	2.199 (6)	K1—O2^{vi}	2.860 (7)
Bi—O4^{ii}	2.231 (6)	K1—O5	2.919 (6)
Bi—O6^{iii}	2.296 (7)	K1—O4	2.984 (7)
Bi—O5^{iv}	2.457 (7)	K1—O2^{vii}	3.319 (6)
Bi—O1^{v}	2.505 (6)	K2—O4	2.684 (6)
Bi—O6^{i}	2.579 (7)	K2—O1^{vii}	2.735 (7)
As2—O3	1.663 (6)	K2—O3^{iii}	2.865 (7)
As2—O5	1.694 (6)	K2—O2^{vii}	3.067 (7)
As2—O4	1.709 (6)	K3—O3^{viii}	2.681 (7)
As2—O6	1.717 (6)	K3—O3^{iii}	2.681 (7)
As1—O1	1.668 (7)	K3—O3^{ix}	2.757 (7)
As1—O2	1.716 (6)	K3—O1^{x}	2.854 (7)
K1—O5^{vi}	2.681 (6)		
O2^{i}—Bi—O4^{ii}	82.1 (2)	O1^{v}—Bi—O6^{i}	77.2 (2)
O2^{i}—Bi—O6^{iii}	80.7 (2)	O3—As2—O5	112.5 (3)
O4^{ii}—Bi—O6^{iii}	82.8 (2)	O3—As2—O4	108.4 (3)
O2^{i}—Bi—O5^{iv}	79.8 (2)	O5—As2—O4	108.3 (3)
O4^{ii}—Bi—O5^{iv}	79.9 (2)	O3—As2—O6	110.9 (3)
O6^{iii}—Bi—O5^{iv}	155.5 (2)	O5—As2—O6	107.0 (3)
O2^{i}—Bi—O1^{v}	155.3 (2)	O4—As2—O6	109.7 (3)
O4^{ii}—Bi—O1^{v}	108.1 (2)	O1^{i}—As1—O1	109.5 (5)
O6^{iii}—Bi—O1^{v}	78.5 (2)	O1^{i}—As1—O2	114.8 (3)
O5^{iv}—Bi—O1^{v}	123.5 (2)	O1—As1—O2	107.7 (3)
O2^{i}—Bi—O6^{i}	85.1 (2)	O1^{i}—As1—O2^{i}	107.7 (3)
O4^{ii}—Bi—O6^{i}	156.6 (2)	O1—As1—O2^{i}	114.8 (3)
O6^{iii}—Bi—O6^{i}	75.9 (2)	O2—As1—O2^{i}	102.3 (4)
O5^{iv}—Bi—O6^{i}	116.9 (2)		

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

The maximum and minimum electron-density peaks are located 1.98 and 1.76 Å from K1 and O2, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); 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*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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