

$\beta$ -Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>

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Received 26 April 2010

Accepted 11 May 2010

Online 14 May 2010

In the title compound, trizinc(II) diarsenite or trizinc(II) bis[trioxidoarsenate(III)], the constituent polyhedra that make up the structure are very distorted ZnO<sub>4</sub> tetrahedra and AsO<sub>3</sub> trigonal pyramids. These species fuse together to generate a three-dimensional network containing unusual edge-sharing tetrahedra, with a Zn···Zn separation of 2.903 (3) Å. The structure also features eight-ring pseudo-channels occupied by the As<sup>III</sup> lone pairs of electrons. The title compound is a polymorph of the mineral reinerite, which also features edge-shared ZnO<sub>4</sub> tetrahedra.

## Comment

XO<sub>4</sub> tetrahedra rarely share edges in crystal structures. The reason given historically is the unfavourable Coulombic repulsion that occurs due to the close contact of the central cations through the shared edge (Wells, 1962). However, a few structures containing such edge-shared tetrahedra are known, including the (non-isostructural) phases K<sub>6</sub>Mn<sub>2</sub>O<sub>6</sub> and K<sub>6</sub>Fe<sub>2</sub>O<sub>6</sub>, which contain isolated [M<sub>2</sub>O<sub>6</sub>]<sup>6-</sup> (M = Mn<sup>III</sup> or Fe<sup>III</sup>) tetrahedral pairs (Brachtel & Hoppe, 1978). For the first of these, the complete edge-shared tetrahedral pair is generated by 2/m crystallographic site symmetry and the Mn···Mn separation is 2.780 Å (s.u. values not supplied by authors). For K<sub>6</sub>Fe<sub>2</sub>O<sub>6</sub>, the tetrahedral pair has inversion symmetry and the Fe···Fe separation is 2.713 Å.

The phases Cs<sub>2</sub>Co<sup>II</sup>SiO<sub>4</sub> and Cs<sub>5</sub>Co<sup>III</sup>SiO<sub>6</sub> (Hansing & Möller, 2001) contain the novel combination of edge-sharing CoO<sub>4</sub> and SiO<sub>4</sub> tetrahedra [Co···Si = 2.630 (8) and 2.7099 (19) Å for Cs<sub>2</sub>CoSiO<sub>4</sub> and Cs<sub>5</sub>CoSi<sub>6</sub>, respectively]. The rare earth borates α-Ln<sub>2</sub>B<sub>4</sub>O<sub>9</sub> (Ln = Eu, Gd, Tb or Dy) (Emme & Huppertz, 2003), made under very high pressure (>8 GPa), contain novel B<sub>2</sub>O<sub>6</sub> groups (*i.e.* edge-sharing BO<sub>4</sub> tetrahedra) with unprecedented short inversion-generated B···B contacts [*e.g.* 2.04 (2) Å in α-Gd<sub>2</sub>B<sub>4</sub>O<sub>9</sub>] as part of an extended boron/oxygen network also containing corner-sharing BO<sub>4</sub> groups.

The mineral epididymite, of ideal composition Na<sub>2</sub>Be<sub>2</sub>-Si<sub>6</sub>O<sub>15</sub>·H<sub>2</sub>O (Gatta *et al.*, 2008), contains edge-sharing BeO<sub>4</sub> tetrahedra [ $\bar{1}$ ; Be···Be = 2.3148 (5) Å] within an infinite BeO<sub>4</sub>/

SiO<sub>4</sub> array. Another mineral, reinerite, Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> (Ghose *et al.*, 1977), hereinafter referred to as the α modification (space group *Pbam*) of this stoichiometry, contains edge-shared ZnO<sub>4</sub> tetrahedra [Zn···Zn = 2.8974 (13) Å; a crystallographic mirror plane generates the complete edge-shared unit] as well as vertex-sharing ZnO<sub>4</sub> groups.

In this paper, we report the solution-mediated synthesis and single-crystal structure of the title compound, β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>, a polymorph of reinerite which also contains edge-shared ZnO<sub>4</sub> tetrahedra.

Selected bond distances and angles for β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> are presented in Table 1 and its structure is illustrated in Fig. 1. There are three Zn, two As and six O atoms in the asymmetric unit. Both As atoms form the centres of isolated (from each other) trigonal-pyramidal [AsO<sub>3</sub>]<sup>2-</sup> arsenite groups, with the unobserved As<sup>III</sup> [Ar]3d<sup>10</sup>4s<sup>2</sup> lone pair of electrons presumed to occupy the fourth tetrahedral vertex. The mean As—O bond length and its estimated error (Taylor & Kennard, 1983) of 1.763±0.016 Å in β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> is similar to that in reinerite (1.769 Å; Ghose *et al.*, 1977) and slightly less than that in leitite, ZnAs<sub>2</sub>O<sub>4</sub> (1.784 Å; Ghose *et al.*, 1987), which contains infinite *catena*-arsenite chains. The O—As—O bond angles in β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> are clustered in the narrow range 94.3 (5)–98.6 (4)°, all far smaller than the nominal tetrahedral bond angle of 109.5°, perhaps indicating that the sp<sup>3</sup> hybridization model that justifies the pyramidal shape of the arsenite ion is simplistic. The As atoms are displaced from the planes of their three attached O atoms by 0.876 (6) (As1) and 0.888 (6) Å (As2).

The three Zn atoms in β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub> form the centres of tetrahedral ZnO<sub>4</sub> groups. Both Zn1 and Zn2 share each of their four O-atom vertices with an As atom and a Zn atom, and unexceptional mean Zn—O distances of 1.969±0.011 and 1.965±0.027 Å arise for Zn1 and Zn2, respectively. The Zn3-centred tetrahedra form an edge-shared pair in β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>

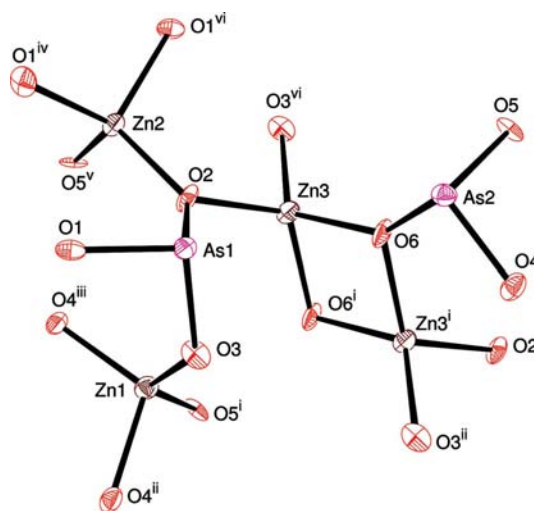
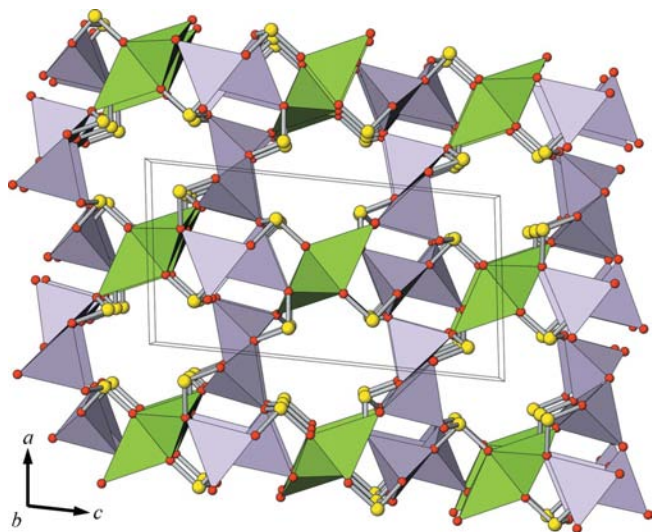


Figure 1

The asymmetric unit of β-Zn<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>, expanded to show the coordination environments of the Zn atoms and the edge-sharing Zn<sub>3</sub>O<sub>4</sub> groups. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) 1 - x, -y, 1 - z; (iii) x,  $\frac{1}{2} - y, z - \frac{1}{2}$ ; (iv) -x, y +  $\frac{1}{2}, \frac{1}{2} - z$ ; (v) x,  $\frac{3}{2} - y, z - \frac{1}{2}$ ; (vi) x, y + 1, z.]

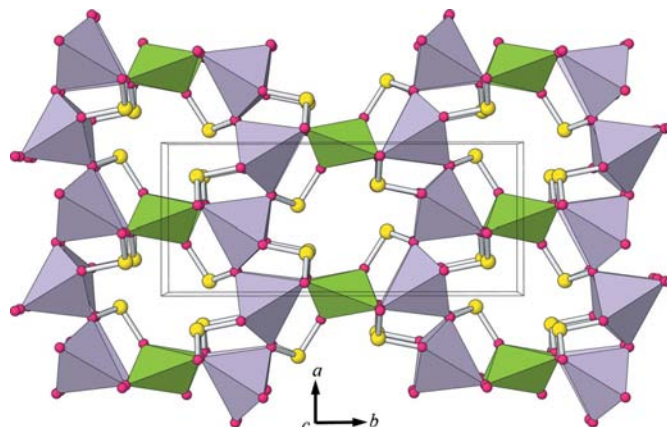


**Figure 2**  
Projection down [010] of the structure of  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$ , with the  $\text{ZnO}_4$  groups represented as polyhedra. In the electronic version of the paper, the Zn1- and Zn2-centred vertex-sharing tetrahedra are lilac, and the Zn3-centred edge-sharing groups are green.

(Fig. 1) and a similar mean Zn3—O distance of  $1.964 \pm 0.019$  Å results. In terms of the variation  $\zeta$  (Robinson *et al.*, 1971) of the O—Zn—O bond angles from their nominal ideal values of  $109.5^\circ$ , the Zn2 tetrahedron displays a moderate degree of distortion, with  $\zeta = 36.6^\circ$ , whereas the Zn1 and Zn3 polyhedra are grossly distorted ( $\zeta = 161.6$  and  $204.5^\circ$ , respectively). The displacements of the Zn atoms from the geometric centres (mean location of their four attached O atoms) are 0.19, 0.13 and 0.14 Å for Zn1, Zn2 and Zn3, respectively.

It is notable that all six asymmetric O atoms in  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  are tricoordinated to two Zn atoms plus one As atom, rather than their more common bicoordinate bridging mode. The mean Zn—O—Zn and Zn—O—As angles are  $109.7 \pm 7.2$  and  $123.6 \pm 7.5^\circ$ , respectively. For each O atom, its Zn—O—Zn angle is smaller than its two Zn—O—As angles. Atom O6 plays a key role by bridging the two Zn3 atoms in the edge-shared tetrahedra, as well as linking to As2. For nominally undistorted tetrahedra, the calculated Zn—O—Zn bond angle for an edge-shared pair is  $70.5^\circ$  and the Zn $\cdots$ Zn separation is 2.266 Å, assuming a Zn—O distance of 1.964 Å; the actual values of 94.9 (5)° and 2.903 (3) Å in  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  indicate the high degree of distortion that must occur to allow the tetrahedral edge-sharing interaction.

It seems remarkable that  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$ , as a polymorph of reinerite, also features the very unusual situation of edge-shared  $\text{ZnO}_4$  tetrahedra. Comparing  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  and reinerite indicates that the two structures share some common features but also some significant differences. When  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  is viewed in projection down [010] (Fig. 2), the edge-shared tetrahedral pairs bridge the layers, forming a three-dimensional network. The structure features distinctive [010] pseudo-channels [shortest As $\cdots$ As separation = 4.811 (2) Å], delineated by four  $\text{ZnO}_4$  and four  $\text{AsO}_3$  polyhedra; it seems that these channels could provide the required space for the As<sup>III</sup> lone pairs. In  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$ , the Zn $\cdots$ Zn axis of the



**Figure 3**  
Projection down [001] of the structure of reinerite [redrawn from the data of Ghose *et al.* (1977)], with the  $\text{ZnO}_4$  groups represented as polyhedra. The colour key is the same as that used for Fig. 2.

tetrahedral pair lies roughly perpendicular to the channels. The spatial requirement of lone pairs of electrons in oxoanions has also been noted in tellurites (Brown, 1974) and selenites (Johnston & Harrison, 2001).

The structure of reinerite, when viewed down [001] (Fig. 3), shows similar eight-ring lone-pair channels, but the role of the edge-sharing tetrahedral pair is different; in this structure, the Zn $\cdots$ Zn axes lie parallel to the [001] direction and hence serve to line the lone-pair channel. A comparison of the densities of  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  [ $4.383 \text{ Mg m}^{-3}$ ] and reinerite [ $4.283 \text{ Mg m}^{-3}$ ] suggests that  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  may be more stable than reinerite at low temperatures, in terms of the ‘density rule’ of Burger & Ramberger (1979).

## Experimental

ZnO (0.156 g) and NaAsO<sub>2</sub> (0.500 g) were placed in a 23 ml Teflon-lined autoclave with water (10 ml). The sealed vessel was heated to 423 K for 3 d and then cooled slowly to room temperature. Upon opening the autoclave, tiny rhombs and blocks of  $\beta$ - $\text{Zn}_3(\text{AsO}_3)_2$  were recovered, accompanied by significant amounts of unreacted ZnO.

### Crystal data

$\text{Zn}_3(\text{AsO}_3)_2$	$V = 669.71$ (11) Å <sup>3</sup>
$M_r = 441.95$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.2438$ (8) Å	$\mu = 20.44 \text{ mm}^{-1}$
$b = 5.1781$ (4) Å	$T = 120 \text{ K}$
$c = 15.8222$ (16) Å	$0.02 \times 0.01 \times 0.01 \text{ mm}$
$\beta = 97.445$ (5)°	

### Data collection

Nonius KappaCCD area-detector diffractometer	7371 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	1547 independent reflections
$T_{\min} = 0.685$ , $T_{\max} = 0.905$	921 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.154$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	101 parameters
$wR(F^2) = 0.152$	$\Delta\rho_{\max} = 1.59 \text{ e Å}^{-3}$
$S = 1.04$	$\Delta\rho_{\min} = -1.92 \text{ e Å}^{-3}$
1547 reflections	

**Table 1**

Selected geometric parameters (Å, °).

Zn3—O3 <sup>i</sup>	1.937 (10)	Zn3—O6	1.973 (10)
Zn3—O6 <sup>ii</sup>	1.968 (10)	Zn3—O2	1.977 (9)
O3 <sup>i</sup> —Zn3—O6 <sup>ii</sup>	116.4 (4)	O3 <sup>i</sup> —Zn3—O2	103.1 (4)
O3 <sup>i</sup> —Zn3—O6	125.3 (4)	O6 <sup>ii</sup> —Zn3—O2	118.8 (4)
O6 <sup>ii</sup> —Zn3—O6	85.1 (5)	O6—Zn3—O2	108.6 (4)

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

The crystal used for data collection was very small and a rather weak diffraction pattern arose. This probably correlates with the rather high  $R_{\text{int}}$  value and a degree of noise in the final difference map; the deepest hole and highest peak are 0.93 and 0.74 Å, respectively, from As2.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The author thanks the EPSRC National Crystallography Service (University of Southampton) for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3222). Services for accessing these data are described at the back of the journal.

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