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$ZnHg(AsO_4)(OH)$ with a descloizite-type structure

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Single crystals of zinc mercury(II) arsenate(V) hydroxide, $ZnHg(AsO_4)(OH)$, were obtained under hydrothermal conditions and structurally characterized using X-ray diffraction. $ZnHg(AsO_4)(OH)$ crystallizes isotypically with the mineral descloizite, $ZnPb(VO_4)(OH)$. The structure is composed of linear chains of edge-sharing $[Zn(OH)_2O_4]$ octahedra which are linked by vertices of AsO_4 tetrahedra to form an open framework structure. In the channels of this arrangement, Hg atoms are situated, having two short bonds to one O atom of the AsO_4 group and to the OH group. Additional stabilization of the structure is accomplished by weak hydrogen bonding.

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(Zn–O) = 0.003 Å
R factor = 0.018
wR factor = 0.041
Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Crystals of the title compound were obtained during a recent project on phase formation experiments in the systems Hg—M—X—O—H [M = Zn, Cd; X = S, Se (Weil, 2004), and X = As].

The present study revealed that the synthetic compound $ZnHg(AsO_4)(OH)$ crystallizes isotypically with the mineral descloizite, $ZnPb(VO_4)(OH)$ (Hawthorne & Faggiani, 1979), and other lead oxysalt minerals of the descloizite family with the general formula $M\text{Pb}(XO_4)(\text{OH})$, where M = Cu^{II}, Fe^{II}, Mn^{II} or Zn^{II}, and X = As^{V} or V^{V}. This is remarkable since mercury oxo compounds usually show a quite unique crystal chemistry. However, the common preference for a $[2 + x]$ or $[x + 2]$ coordination (x can range from 2 to 6) for the Hg^{II}

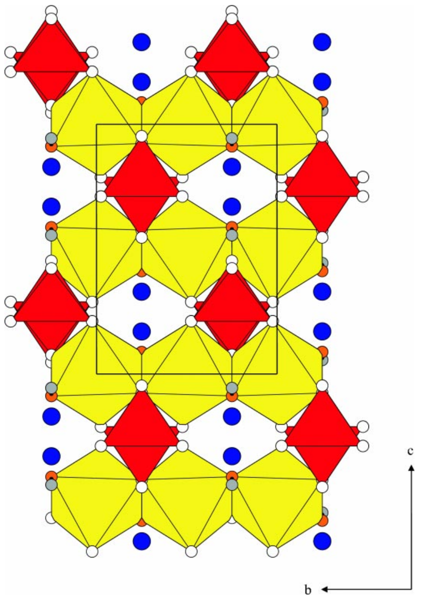

Figure 1
Projection of the title structure along [100]. $[Zn(OH)_2O_4]$ octahedra are yellow, AsO_4 tetrahedra are red, Hg atoms are blue, O atoms (except for the OH group, which is orange) are white and H atoms are grey.

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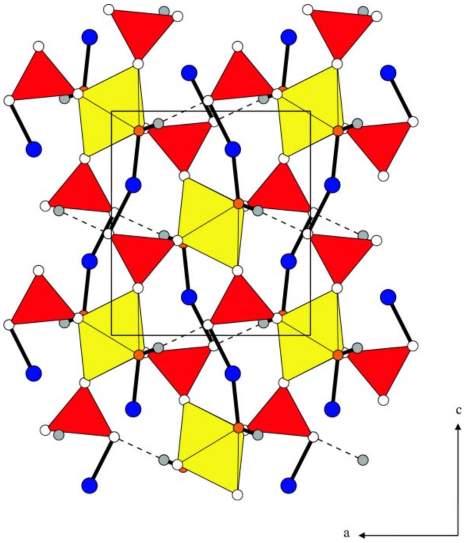

Figure 2
Projection of the structure along [010], including the two short Hg—O bonds and hydrogen bonding (dashed lines). Colour key as in Fig. 1.

atom with a more or less linear O—Hg—O angle is also realised in the title compound.

The structure is composed of edge-sharing $[Zn(OH)_2O_4]$ octahedra, building infinite chains parallel to [010], and AsO_4 tetrahedra which link the chains *via* common vertices to form an open framework structure (Fig. 1). The corresponding coordination figures are slightly distorted and show $\overline{1}$ symmetry and $.m.$ symmetry, respectively. The average distances of $\overline{d}(Zn—O) = 2.093$ Å and $\overline{d}(As—O) = 1.693$ Å are both in the typical range for $[ZnO_6]$ and AsO_4 groups. The Hg atoms are situated in the channels of this framework and are bonded to the OH group and an O atom of the AsO_4 group at short distances $[\overline{d}(Hg—O)_{short} = 2.109$ Å] (Fig. 2). The [2 + 5] coordination figure is augmented by additional O atoms at considerably longer distances, $2.64 < \overline{d}(Hg—O)_{long} < 2.74$ Å. The H atom is bonded to O4 and exhibits a weak hydrogen-bonding interaction to O2, with an HO4···O2 distance of 2.90 Å. Fig. 3 shows a part of the structure represented by anisotropic displacement ellipsoids.

Results from the bond-valence sum calculations (v.u.), taking into account that the contributions from hydrogen bonds are neglected and using the parameters of Brese & O'Keeffe (1991), are in agreement with the expected values for the cations and reflect the weak hydrogen bonding between O4 and O2: Zn 2.11, Hg 1.97, As 4.89, O1 1.89, O2 1.84, O3 1.97, O4 1.50.

Experimental

Stoichiometric amounts of $Zn(NO_3)\cdot 4H_2O$ (Merck, p.A.), $Hg(NO_3)_2\cdot H_2O$ (Fluka, >99%) and Na_2HAsO_4 (Merck, p.A.) were charged in a Teflon inlay with 10 ml capacity which was two-thirds filled with demineralized water and then sealed in a steel autoclave. This device was heated up to 493 K, kept at that temperature for 5 d and cooled down to room temperature within 1 d. After filtering off the remaining solution, a few colourless crystals of the title compound were obtained. The main product consisted of graphtonite-type $Hg_3(AsO_4)_2$ crystals (Larsson *et al.*, 1993).

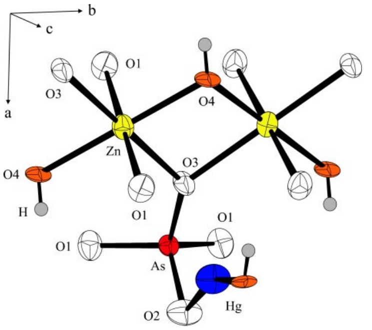

Figure 3
Part of the structure, with anisotropic displacement ellipsoids drawn at the 90% probability level. H atoms are represented as small grey spheres of arbitrary radii.

Crystal data

$HgZn(AsO_4)(OH)$
$M_r = 421.89$
Orthorhombic, *Pnma*
$a = 7.6826\ (7)$ Å
$b = 6.2459\ (6)$ Å
$c = 8.6691\ (8)$ Å
$V = 415.98\ (7)$ Å^3
$Z = 4$
$D_x = 6.736$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2675 reflections
$\theta = 3.5–30.3°$
$\mu = 50.43$ mm^{-1}
$T = 295\ (2)$ K
Parallelepiped, colourless
0.08 × 0.08 × 0.05 mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993–1997)
$T_{min} = 0.088$, $T_{max} = 0.209$
4303 measured reflections
677 independent reflections
617 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 30.5°$
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 8$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 1.12$
677 reflections
50 parameters
H atoms treated by a mixture of independent and restrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 0.725P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.80$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0111 (5)

Table 1
Selected geometric parameters (Å, °).

Hg—O4	2.108 (4)	As—O3	1.694 (4)
Hg—O2^{i}	2.109 (5)	As—O2^{viii}	1.713 (4)
Hg—O1^{ii}	2.638 (3)	Zn—O4^{ix}	2.039 (2)
Hg—O1^{iii}	2.638 (3)	Zn—O4^{x}	2.039 (2)
Hg—O1^{iv}	2.736 (3)	Zn—O1^{ix}	2.105 (3)
Hg—O1^{v}	2.736 (3)	Zn—O1^{x}	2.105 (3)
Hg—O3^{vi}	2.740 (4)	Zn—O3	2.133 (3)
As—O1^{vii}	1.682 (3)	Zn—O3^{xi}	2.133 (3)
As—O1	1.682 (3)		
O4—Hg—O2^{i}	159.35 (16)	O1^{vii}—As—O2^{viii}	109.34 (13)
O1^{vii}—As—O1	113.7 (2)	O1—As—O2^{viii}	109.34 (13)
O1^{vii}—As—O3	110.33 (12)	O3—As—O2^{viii}	103.2 (2)
O1—As—O3	110.33 (12)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H···O2	0.80 (5)	2.12 (5)	2.910 (6)	175 (10)

The H atom was found by difference Fourier analysis. Its position was refined with a restrained D—H distance of 0.80 (5) Å. The $U_{\rm iso}$ value of the H atom was refine freely. The highest peak is located at a distance of 0.72 Å from Hg, and the deepest hole at a distance of 1.02 Å from O4. After the last refinement cycle, the structural data were standardized using the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97.

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