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A Synthetic Hydrated Zinc Arsenate Constructed from Tetrahedral, Trigonal Bipyramidal and Octahedral Zinc Polyhedra: [Zn₃(AsO₄)₂]₃.4H₂O

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Abstract

The synthesis and crystal structure of the first synthetic hydrated zinc arsenate, tris(zinc arsenate) tetrahydrate, are described.

Comment

There has been an increased interest in the divalent metal phosphates and arsenates since the discovery of zeolite structural analogs and other open-framework structures (Gier & Stucky, 1991; Feng, Bu & Stucky, 1995). In our search for novel framework structures based on divalent metal phosphates and arsenates (Bu, Feng & Stucky, 1996; Bu, Gier & Stucky, 1996; Feng, Bu & Stucky, 1997*a,b*; Feng, Bu, Tolbert & Stucky, 1997) we discovered a new hydrated zinc arsenate. The synthesis, structure and thermal properties of this first synthetic hydrated zinc arsenate are reported here.

The examination of the local coordination environment (Fig. 1) is helpful to the understanding of the three-dimensional connectivity of this rather dense framework structure. There are five unique zinc sites. Zn1 and Zn2 are tetrahedral and trigonal bipyramidal, respectively, with all corner O atoms bonded to one As cation and, with the exception of O2, to another Zn cation. Zn3, Zn4 and Zn5 are all octahedrally bonded. Zn5 has a pendant water molecule (O14) whereas another water molecule (O12) bridges Zn3 and Zn4. O9 and O11 on Zn3 are bicoordinated between one Zn cation and one As cation while the remaining O-atom corners are trigonally coordinated between two Zn cations and one As cation.
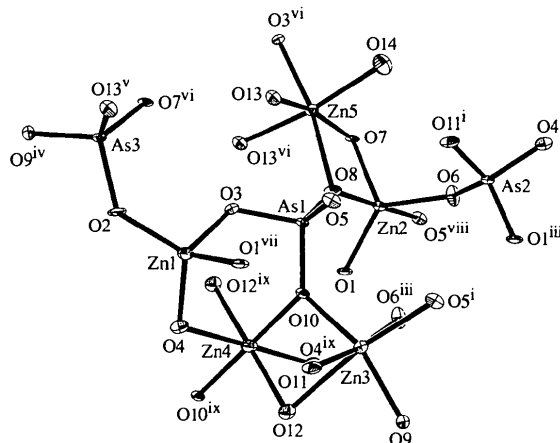

Fig. 1. An *ORTEP* (Johnson, 1976) drawing showing the local coordination environment. Ellipsoids are drawn at the 50% probability level. O12 and O14 are water molecules. O2, O9 and O11 are bicoordinated between Zn and As. Other O atoms are trigonally coordinated between two Zn atoms and one As atom. Only Zn4 is located on the inversion center. See Table 2 for symmetry codes.

The framework can be broken down into two structural units: a cluster of eight tetrahedra and an infinite chain of edge-sharing polyhedra (Fig. 2). The cluster consists of eight tetrahedra and is located at the center of inversion. All four crystallographically unique tetrahedral sites are part of this cluster. Three unique zinc octahedra and one unique zinc trigonal bipyramid form an infinite zigzag edge-sharing chain along the crystallographic [1̄11] direction. One of the unique zinc sites in the chain is located at the unit-cell body center. As a result the chain also has the symmetry of inversion. The framework can be regarded as rows of one-dimensional chains interconnected by clusters of tetrahedra.

Two other hydrated zinc arsenates, both of which are minerals, are known. The most hydrated form, koettigite (Hill, 1979), with the formula Zn₃(AsO₄)₂.8H₂O (also contains of a small amount of Co and Ni), possesses a monoclinic structure which is adopted by a variety of divalent metal phosphates and arsenates including *M*₃(PO₄)₂.8H₂O (*M* = Mg, Fe, Co) (Takagi, Mathew & Brown, 1986; Fejdi, Poullen & Gasperin, 1980; Riou, Cudennec & Gerault, 1989) and Fe₃(AsO₄)₂.8H₂O
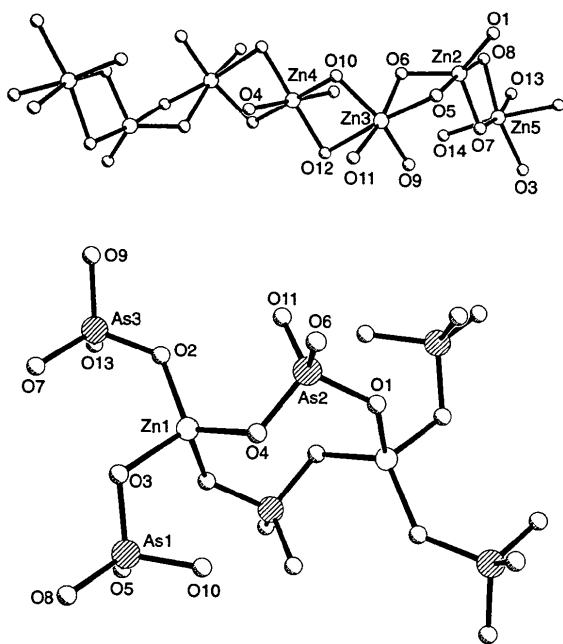
Fig. 2. A chain of edge-sharing zinc polyhedra (above) and a cluster of eight tetrahedra (below). Both units have the symmetry of the inversion center.

(Mori & Ito, 1950). The other less hydrated form, warikahnite, with the formula $Zn_3(AsO_4)_2.2H_2O$ (Riffel, Keller & Hess, 1980), like the title compound, does not have a structural counterpart in other divalent metal phosphates or arsenates. The title compound, which can be represented as $Zn_3(AsO_4)_2.1.33H_2O$, is the least hydrated of the three forms and has the densest structure (4.43 g cm^{-3} for the 1.33-hydrate *versus* 4.29 g cm^{-3} for the dihydrate and 3.24 g cm^{-3} for the octahydrate). Of the three hydrated forms the title compound is the only phase with tetrahedrally coordinated zinc sites (one tetrahedral, one five-coordinate, three octahedral). The two unique zinc sites in the octahydrate are both fairly regular octahedra while in the dihydrate three of the six zinc sites are octahedral and the other three sites are penta-coordinate.

The three hydrated zinc arsenates discovered so far match the number of hydrated zinc phosphates. Like zinc arsenates, two forms of hydrated zinc phosphates are also minerals, hopeite (Hill & Jones, 1976) and para-hopeite (Kumbasar & Finney, 1968). However, the degree of hydration in zinc phosphates is totally different from zinc arsenates. Thus, both hopeite and parahopeite are tetrahydrates while the third form is a monohydrate (Riou, Cudennec & Gerault, 1986). The various degrees of hydration in both zinc phosphates and zinc arsenates are intimately related to the flexible coordination geometry of zinc sites and the fact that different combinations of zinc coordination polyhedra can occur in the same compound. Both hopeite and parahopeite have one

tetrahedral zinc site and one octahedral site whereas the zinc phosphate monohydrate has two tetrahedral sites and one octahedral site. Thus, the title compound, which contains Zn atoms in three distinctly different coordination geometries, is uncommon.

There are three different polymorphs of anhydrous zinc phosphates (α, β, γ phases), all of which have been extensively studied as host lattices for luminescent materials (Calvo, 1963, 1965; Stephens & Calvo, 1967). The electronic levels of activator cations and thus the emission wavelength in these materials have been found to depend on their polyhedral environments. The above comparison between hydrated zinc phosphates and hydrated zinc arsenates shows that zinc arsenates can be very different from zinc phosphates in terms of zinc coordinations and thus can serve as different host lattices for luminescent materials. However, so far no anhydrous zinc arsenates are known despite its very simple formula. We have prepared the first synthetic hydrated zinc arsenate. This material might be used as a precursor for the preparation of anhydrous zinc arsenates.

Experimental

$Zn(NO_3)_2.6H_2O$ (2.19 g) was mixed with 11.19 g of distilled water. With stirring, 1.61 g of $As_2O_5.xH_2O$ and then 1.32 g of piperazine were added. The mixture was stirred for 0.5 h and then heated at 443 K for 8 d in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Translucent light-brown plate-like crystals as large as several millimeters in one dimension were obtained.

Crystal data

$[Zn_3(AsO_4)_2]_3.4H_2O$	Mo $K\alpha$ radiation
$M_r = 1493.91$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 4633
$P\bar{1}$	reflections
$a = 6.6934\,(4)$ Å	$\theta = 2.17-28.29°$
$b = 9.1833\,(5)$ Å	$\mu = 18.392$ mm^{-1}
$c = 10.1469\,(6)$ Å	$T = 293\,(2)$ K
$\alpha = 69.479\,(1)°$	Thin plate
$\beta = 77.218\,(1)°$	$0.33 \times 0.12 \times 0.017$ mm
$\gamma = 75.761\,(1)°$	Light brown
$V = 559.88\,(6)$ Å^3	
$Z = 1$	
$D_x = 4.431$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART CCD	5794 measured reflections
diffractometer	2658 independent reflections
ω scans	2195 reflections with
Absorption correction:	$I > 2\sigma(I)$
empirical, fitted by	$R_{int} = 0.0598$
spherical harmonic	$\theta_{max} = 28.29°$
functions (Blessing, 1995;	$h = -8 \rightarrow 8$
Sheldrick, 1996)	$k = -12 \rightarrow 12$
$T_{min} = 0.39$, $T_{max} = 0.79$	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$\Delta\rho_{max} = 1.79$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{min} = -1.89$ e Å^{-3}
$wR(F^2) = 0.107$	Extinction correction:
$S = 0.982$	SHELXTL-Plus (Sheldrick,
2658 reflections	1995)
197 parameters	Extinction coefficient:
H atoms not located	0.0052 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	International Tables for
$(\Delta/\sigma)_{max} = 0.001$	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}
As1	0.48181 (10)	0.10872 (8)	0.68598 (6)	0.0073 (2)
As2	1.00237 (10)	−0.29540 (8)	0.57629 (6)	0.0082 (2)
As3	−0.23425 (10)	0.21851 (8)	1.02663 (6)	0.0077 (2)
Zn1	0.06604 (12)	0.33583 (10)	0.71900 (8)	0.0116 (2)
Zn2	1.02052 (12)	−0.00683 (10)	0.69823 (8)	0.0105 (2)
Zn3	0.53535 (13)	0.24906 (10)	0.33292 (8)	0.0127 (2)
Zn4	1/2	1/2	1/2	0.0143 (3)
Zn5	0.70366 (12)	−0.11733 (10)	0.97600 (7)	0.0108 (2)
O1	1.0144 (7)	0.2228 (6)	0.6001 (4)	0.0122 (10)
O2	−0.1672 (8)	0.3423 (6)	0.8624 (5)	0.0155 (11)
O3	0.3179 (7)	0.2035 (6)	0.7990 (4)	0.0102 (10)
O4	0.1643 (7)	0.5282 (6)	0.5936 (5)	0.0140 (10)
O5	0.3663 (7)	−0.0198 (6)	0.6605 (5)	0.0134 (10)
O6	1.1171 (8)	−0.1771 (7)	0.6152 (5)	0.0173 (11)
O7	1.0156 (7)	−0.1010 (6)	0.9093 (4)	0.0089 (9)
O8	0.7026 (7)	0.0129 (6)	0.7512 (5)	0.0126 (10)
O9	0.6414 (8)	0.3339 (6)	0.1272 (5)	0.0156 (11)
O10	0.5064 (7)	0.2625 (6)	0.5329 (5)	0.0111 (10)
O11	0.2252 (7)	0.3203 (6)	0.3198 (5)	0.0147 (11)
O12	0.4729 (8)	0.5362 (6)	0.2918 (5)	0.0151 (11)
O13	0.3872 (7)	−0.1047 (6)	0.9874 (5)	0.0127 (10)
O14	0.7780 (8)	−0.3543 (7)	0.9681 (6)	0.0216 (12)

Table 2. *Selected bond lengths (Å)*

As1—O8	1.668 (4)	Zn2—O5^{viii}	2.241 (5)
As1—O5	1.676 (5)	Zn3—O9	1.986 (5)
As1—O10	1.702 (5)	Zn3—O5^i	2.027 (5)
As1—O3	1.718 (4)	Zn3—O11	2.037 (5)
As2—O6	1.665 (5)	Zn3—O10	2.040 (4)
As2—O11^i	1.666 (5)	Zn3—O6^{iii}	2.381 (5)
As2—O4^{ii}	1.688 (5)	Zn3—O12	2.463 (5)
As2—O1^{iii}	1.696 (4)	Zn4—O12^{ix}	2.062 (4)
As3—O9^{iv}	1.675 (5)	Zn4—O12	2.063 (4)
As3—O13^v	1.690 (5)	Zn4—O10	2.079 (5)
As3—O2	1.692 (5)	Zn4—O10^{ix}	2.079 (5)
As3—O7^{vi}	1.698 (4)	Zn4—O4	2.227 (5)
Zn1—O2	1.889 (5)	Zn4—O4^{ix}	2.227 (5)
Zn1—O4	1.948 (5)	Zn5—O13	2.072 (5)
Zn1—O3	1.971 (5)	Zn5—O7	2.073 (5)
Zn1—O1^{vii}	1.972 (5)	Zn5—O13^{vi}	2.118 (5)
Zn2—O6	1.938 (5)	Zn5—O3^{vi}	2.122 (4)
Zn2—O1	1.986 (5)	Zn5—O14	2.136 (6)
Zn2—O7	2.005 (4)	Zn5—O8	2.173 (4)
Zn2—O8	2.055 (5)		

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

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air with a heating rate of 5 K min^{-1} from 303 to 1273 K. Between 653 and 713 K there was an endothermic one-step weight loss of 5.0% which was in good agreement with the calculated value (4.8%). There

were three additional endothermic events occurring at about 973, 1113 and 1273 K without any weight loss.

The data collection nominally covered over a full sphere of reciprocal space, by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm. Coverage of the data set is over 89% complete to at least 28° in θ. The largest positive residual peak is 0.74 Å from O11 and 0.97 Å from As2 and the largest negative peak is 1.3 Å from Zn2. Due to the high absorption coefficient and the thin-plate shape of the crystal, the uncorrected intensities gave $R_{int} = 0.145$, which led to a similarly high value for $R(F)$. An empirical ψ-scan absorption correction using data collected on a four-circle diffractometer equipped with a point detector gave little improvement on the values of R_{int} and $R(F)$. A second set of data covering approximately the full sphere of reciprocal space was collected using a CCD detector. The program SADABS (Sheldrick, 1996) was used for this empirical absorption correction and resulted in a significant drop in R_{int} from 0.145 to 0.0575 and a similar drop in $R(F)$. It should be noted that empirical absorption correction programs can only measure relative transmission factors which also include absorption by the crystal support etc., giving a range of transmission factors which could deviate from those estimated from the crystal dimensions. This is the case for the structure described here. Such deviation could imply that non-crystal scattering is significant or that there might be unrecognized experimental problems which could require further investigation.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1995). Program(s) used to refine structure: SHELXTL-Plus. Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

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Mercury(II) Diphosphate, Hg₂P₂O₇

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Abstract

Mercury(II) diphosphate, $Hg_2P_2O_7$, belongs to the $M_2X_2O_7$ family of compounds with dichromate-type crystal structures and is isotypic with $Cd_2P_2O_7$. The structure consists of alternating layers built from P_2O_7 groups and highly distorted HgO_6 polyhedra with bond distances in the ranges $2.120\,(6) \leq d(Hg1O_6) \leq 2.793\,(7)$ Å and $2.208\,(6) \leq d(Hg2O_6) \leq 2.509\,(6)$ Å. The diphosphate anion has a P—O—P bridging angle of $133.4\,(4)°$. The average P—O bond length is 1.604 Å for bridging and 1.524 Å for terminal bonds. $[Hg1_2O_{10}]$ and $[Hg2_2O_{10}]$ form chains running along [110] through edge-sharing dimers. These chains link to form layers parallel to (1̄10) *via* common vertices.

Comment

Until now, in the system Hg–P–O only the structure of the mercury(II) orthophosphate, $Hg_3(PO_4)_2$, has been refined from single-crystal data (Aurivillius & Nilsson, 1975). For $Hg(PO_3)_2$, isotypism with the corresponding cadmium phosphate was proved (Beucher & Tordjman,

1968) by comparison of the X-ray powder diffraction patterns. Although the diphosphate $Hg_2P_2O_7$ has been known for a long time (Schwarzenberg, 1848), no crystallographic information for it has been published so far. Preliminary investigation of the X-ray powder pattern of $Hg_2P_2O_7$ showed it to be isotypic with $Cd_2P_2O_7$ (Weil, 1997), the structure of which has been refined previously (Calvo & Au, 1969). During our studies on the thermal behaviour of mercury(II) phosphates, we obtained crystals of $Hg_2P_2O_7$ suitable for X-ray investigations. Because of the particular crystal chemistry of Hg^{2+} with its d^{10} electronic configuration, refinement of the structure seemed appropriate. Additional interest in a detailed structural study arises from the relationship of dichromate-type $Hg_2P_2O_7$ (Brown & Calvo, 1970; Clark & Morley, 1976; Nord & Kierkegaard, 1980) with diphosphates of divalent 3d metals with thortveitite-type structures.

The crystal structure comprises alternating layers of HgO_6 polyhedra and diphosphate groups parallel to $(1\bar{1}0)$ (Fig. 1). The two independent Hg^{2+} ions form dimers, $[Hg1_2O_{10}]$ and $[Hg2_2O_{10}]$, by edge sharing. The common edge is O4—O4 in the case of Hg1, and O2—O2 for Hg2 (Fig. 2). The dimers are linked *via* common edges (O2 and O3) and vertices (O5) thus forming the layers. In contrast to the thortveitite-type structures, where adjacent metal–oxygen layers (*e.g.* $Mn_2P_2O_7$; Stefanidis & Nord, 1984) are joined only by diphosphate groups, additional contacts from one [Hg–O] layer to another *via* common vertices (O6) occur in $Hg_2P_2O_7$ (Fig. 1).

The diphosphate anion (Fig. 3) displays an eclipsed conformation with a dihedral angle of $7.2°$ along O4, P2, O1, P1 and O3. The P—O—P bridging angle is $133.4\,(4)°$. Both values agree with those generally observed for $[X_2O_7]$ anions in dichromate-type structures, where the eclipsed conformation is stabilized by chelate-type coordination to the two divalent cations. Bond lengths from the P atoms to the terminal and bridging O atoms are in the typical range observed for diphosphates of divalent cations $[\bar{d}_b(P—O) = 1.596\,(6)$ and $1.611\,(6)$ Å, $\bar{d}_t(P1—O) = 1.528$ Å and $\bar{d}_t(P2—O) = 1.519$ Å$]$.

Hg1 and Hg2 are coordinated by six O atoms (Fig. 2), with the nearest 'non-bonding' O atom 3.177 Å from Hg1 and 3.280 Å from Hg2. The $[Hg1O_6]$ group can be described as a highly compressed octahedron $(2 + 4$ coordination) with two short axial bonds, $\bar{d}_{ax} = 2.132$ Å, and four longer equatorial bonds, $\bar{d}_{eq} = 2.583$ Å. The coordination around Hg2 may be described as $(4 + 2)$ with $\bar{d}_{eq} = 2.28$ Å and $\bar{d}_{ax} = 2.49$ Å. The $[Hg2O_6]$ octahedron is less distorted than the $[Hg1O_6]$ octahedron. The Hg—O bond lengths found in $Hg_2P_2O_7$ are in the same range as those found in $Hg_3(PO_4)_2$ (Aurivillius & Nilsson, 1975) and $HgSO_4$ (Aurivillius & Stålhandske, 1980). The $[HgO_x]$ polyhedra in mercury(II) orthophosphate have Hg—O distances from 2.06 to 2.80 Å (five- and