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Layered zincoarsenate templated by *N,N,N′,N′*-tetramethylethylenediamine molecules

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The title compound, *N,N,N′,N′*-tetramethylethylenediammonium diaqua(arsenate)(hydrogen arsenate)dizinc(II), $(C_6H_{18}N_2)_{0.5}[Zn_2(AsO_4)(HAsO_4)(H_2O)_2]$, is a new zincoarsenate obtained by hydrothermal synthesis. The structure consists of infinite two-dimensional anionic layers alternating with planes containing centrosymmetric organic diprotonated template *N,N,N′,N′*-tetramethylethylenediammonium cations, $[H_3NC_6H_{12}NH_3]^{2+}$. The latter are interconnected to the framework through hydrogen bonds.

Comment

Microporous compounds with an anionic framework are of particular interest because of their catalytic properties (Thomas, 1988) and their use as molecular sieves. Over the last decade, many aluminophosphates (Chippindale *et al.*, 1992; Yao *et al.*, 1999), gallophosphates (Jones *et al.*, 1991; Chippindale *et al.*, 1998) and zincophosphates (Harrison *et al.*, 1992; Chavez *et al.*, 1999) with open frameworks have been synthesized hydrothermally. Replacement of phosphate by arsenate in the framework leads to a variety of phases (Bu *et al.*, 1998; Harrison *et al.*, 1999), some of which are analogous to zincophosphates (Harrison *et al.*, 1999). In our search for novel framework structures containing zinc in combination with P or As atoms, we have discovered two new zincophosphate materials, namely $Zn_2(HPO_4)_2Cl_2 \cdot 2C_6H_{14}N$ (Trojette *et al.*, 1998) and $[H_3NC_6H_{12}NH_3]_{0.5}[Zn_2(PO_4)(HPO_4)(H_2O)] \cdot H_2O$ (Hajem *et al.*, 1999). As part of these studies, we have examined the structure of $[H_3NC_6H_{12}NH_3]_{0.5}[Zn_2(AsO_4)(HAsO_4)(H_2O)_2]$, (I), and report here its synthesis and structural characterization.

The title compound contains a layered structure (Fig. 1) consisting of organic sheets corresponding to *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) molecules and inorganic layers alternating along [010].

In the framework structure, the Zn atoms exhibit two types of coordination. The polyhedron around Zn1 is a distorted trigonal bipyramid formed by four O atoms and one terminal water molecule (O*W*2). The Zn2 atom is surrounded by five O atoms and one terminal water molecule (O*W*1), resulting in an octahedral coordination. The two As atoms are tetrahedrally coordinated by O atoms. The As1 atom has two As—O bonds bridging to Zn atoms. The remaining As—O bonds consist of an As1—O4H group and an As1═O1 double bond. For the As2 atom, three of the coordinating O atoms are bonded to Zn atoms, while the fourth O atom is terminal (As2═O5).

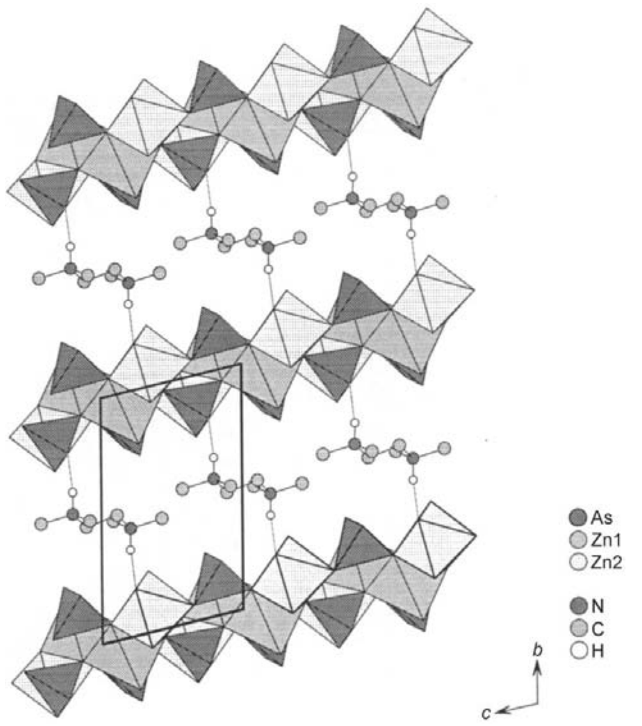

Figure 1
View of the structure of (I) down the *a* axis showing the location of the TMEDA molecules.

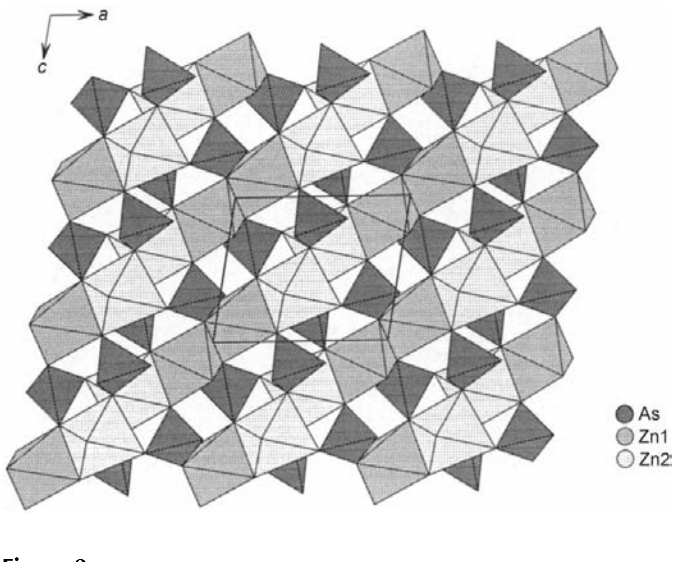

Figure 2
A polyhedral representation of the anion sheet viewed down the *b* direction.

The two-dimensional framework can be considered as a parallel arrangement (along the [101] direction) of chains built up from ZnO_6 and ZnO_5 polyhedra interconnected by AsO_4 tetrahedra (Fig. 2). Each chain makes –Zn1—Zn1—Zn2—Zn2– linkages (oxygen designation omitted) and every zinc polyhedron shares two edges with its nearest-neighbour zinc polyhedron through four trigonally coordinated O atoms. These O atoms have a trigonal coordination because they contain not only Zn—O—Zn linkages, but also Zn—O—As linkages.

The TMEDA molecules are inserted between the inorganic layers and give rise to hydrogen bonds between H atoms of the protonated diamine and O atoms of the framework (N—HN···O8; Fig. 1). Finally, the terminal –OH and H_2O groups participate in in-sheet hydrogen bonds, *i.e.* O4—HO4···O8, O*W*1—H1*W*1···O1, O*W*1—H2*W*1···O5, O*W*2—H1*W*2···O5 and O*W*2—H2*W*2···O1.

Experimental

The title compound was synthesized hydrothermally from a 1:2:2:3:100 mixture of ZnO (0.12 g), HCl (38%, 0.29 g), H_3AsO_4 (80%, 0.51 g), $C_6H_{16}N_2$ (0.50 g) and H_2O (2.58 g). A thick gel formed which was then heated at 373 K for 7 d. The crystalline product obtained was filtered off, washed with distilled water and dried in air at room temperature.

Crystal data

$(C_6H_{18}N_2)_{0.5}[Zn_2(AsO_4)(HAsO_4)(H_2O)_2]$
$M_r = 504.73$
Triclinic, $P\bar{1}$
$a = 8.087$ (1) Å
$b = 11.354$ (2) Å
$c = 6.622$ (2) Å
$\alpha = 101.15$ (2)°
$\beta = 96.64$ (2)°
$\gamma = 102.79$ (1)°
$V = 573.7$ (2) Å^3
$Z = 2$
$D_x = 2.922$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.24$–13.93°
$\mu = 9.952$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.45 × 0.25 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.063$, $T_{\max} = 0.248$
2630 measured reflections
2499 independent reflections
2284 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 26.97°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 0$
$l = -8 \rightarrow 8$
2 standard reflections
frequency: 120 min
intensity decay: 0.7%

Table 1
Selected geometric parameters (Å).

As1—O1	1.656 (2)	Zn1—O3	2.048 (2)
As1—O2	1.669 (2)	Zn1—O6$^{\rm i}$	2.056 (2)
As1—O3	1.683 (2)	Zn1—O7$^{\rm ii}$	2.086 (2)
As1—O4	1.725 (2)	Zn2—O2$^{\rm iii}$	2.061 (2)
As2—O5	1.669 (2)	Zn2—O3	2.071 (2)
As2—O6	1.692 (2)	Zn2—O*W*1	2.074 (3)
As2—O7	1.693 (2)	Zn2—O2$^{\rm iv}$	2.078 (2)
As2—O8	1.707 (2)	Zn2—O6$^{\rm i}$	2.116 (2)
Zn1—O*W*2	2.032 (3)	Zn2—O8$^{\rm v}$	2.182 (2)
Zn1—O7	2.036 (2)		

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.077$
$S = 1.120$
2499 reflections
196 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.7750P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.45$ e Å^{-3} (0.76 Å from As2)
$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0095 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—HN···O8$^{\rm i}$	0.90 (1)	1.87 (1)	2.760 (4)	168 (4)
O4—HO4···O8$^{\rm ii}$	0.82	1.80	2.619 (4)	174
O*W*1—H1*W*1···O1$^{\rm iii}$	0.90 (1)	1.81 (1)	2.700 (4)	173 (5)
O*W*1—H2*W*1···O5	0.90 (1)	1.84 (3)	2.682 (3)	156 (7)
O*W*2—H1*W*2···O5$^{\rm iv}$	0.90 (1)	1.77 (1)	2.659 (4)	170 (5)

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

H atoms other than those of the aqua ligands or NH groups were treated as riding, with O—H = 0.82 Å and C—H = 0.96–0.97 Å. The H atoms of the NH groups were refined freely and aqua H atoms were refined with *DFIX* constraints and O—H = 0.90 Å.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1075). Services for accessing these data are described at the back of the journal.

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