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A three-dimensional open-framework zinc arsenate, (C4H12N2)2-[Zn7(AsO4)6(H2O)2]

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The title compound, dipiperazinium heptazinc hexakis(arsenate) dihydrate, is built from vertex-sharing AsO_4 tetrahedra, ZnO_4 tetrahedra and ZnO_5 trigonal bipyramids. The connectivity between these polyhedra give rise to an open framework with eight-ring channels along the crystallographic [001] and [011] directions. The piperazinium cations are located within these channels.

Comment

Compared to silicate and phosphate open-framework structures, rather little is known about similar arsenate structures. Open-framework arsenate structures incorporating organic cations in channels and cavities include two aluminoarsenates (Yang *et al.*, 1989; Li *et al.*, 1991), one galloarsenate (Chen *et al.*, 1989), one molybdenum arsenate (Wang *et al.*, 1994), two iron arsenates (Ekambaram & Sevov, 2000) and two zinc arsenates (Gier *et al.*, 1998; Bu *et al.*, 1998). The present paper describes the synthesis and crystal structure of a new zinc arsenate, (C4H12N2)2[Zn7(AsO4)6(H2O)2], refined from single-crystal data. Its crystal structure is isostructural with a zinc phosphate denoted UiO-17 (Kongshaug *et al.*, 1999). The three-dimensional anionic framework is made up of vertex-sharing AsO_4 tetrahedra, ZnO_4 tetrahedra and ZnO_5 trigonal bipyramids. It can be described in terms of sheets parallel to (100) that consist of edge-sharing three-, four- and six-rings. These sheets are connected *via* As_2O_4 and Zn_4O_4 tetrahedra to form an open framework with a two-dimensional eight-ring channel system along [001] and [011]. The piperazinium cations are located within these channels. The framework is interrupted with a terminal $Zn3-OH_2$ bond, and two out of twelve framework O atoms (O3 and O9) are three-coordinated (1 As + 2 Zn). A bond-valence analysis (Brown & Altermatt, 1985) confirms the expected oxidation states of Zn and As as +2 and +5 for all the relevant atoms. This analysis further revealed that atoms O1, O4, O5, O7 and O12 all have bond-valence sums significantly lower than the expected value of 2. Their valences are, however, fulfilled by mean of hydrogen-bonding contributions from the piperazinium cations and water molecules [$d(H1\cdots O4^i) = 2.09$, $d(H2\cdots O7^{ii}) = 1.93$, $d(H3\cdots O5^{iii}) = 2.02$, $d(H4\cdots O12^{iv}) = 1.78$, $d(H13\cdots O12^v) = 1.89$ and $d(H14\cdots O1^i) = 1.97$ Å; symmetry codes: (i) $x, 1 - y, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $1 - x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

Experimental

The title compound was prepared hydrothermally from a mixture of zinc acetate, arsenic acid, piperazine and water in the molar ratio 2:2:1.5:50. The resulting mixture was heated at 453 K for 48 h in a teflon-lined steel autoclave, then filtered, washed and dried at room temperature. Powder X-ray analysis indicated the product to be a mixture of adamite, $Zn_2(OH)PO_4$ (Hawthorne, 1976) and the title compound. Examination under an optical microscope showed two different crystal morphologies, *i.e.* plate and cube-shaped crystals. Isolation of suitable crystals of each type and subsequent X-ray diffraction analyses showed the crystalline plates to be the title compound and the cubes to be adamite.

Crystal data

(C4H12N2)2[Zn7(AsO4)6(H2O)2]	$D_x = 3.179$ Mg m^{-3}
$M_r = 1503.455$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3669
$a = 16.5880 (14)$ Å	reflections
$b = 8.3559 (7)$ Å	$\theta = 3.0-27.5°$
$c = 23.4129 (18)$ Å	$\mu = 11.636$ mm^{-1}
$\beta = 104.564 (4)°$	$T = 150 (2)$ K
$V = 3140.9 (4)$ Å^3	Plate, colourless
$Z = 4$	$0.40 \times 0.10 \times 0.05$ mm

Data collection

Siemens SMART CCD diffract-ometer	3602 independent reflections
Sets of exposures each taken over $0.6°$ ω rotation scans	2639 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.079$
	$\theta_{max} = 27.52°$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$h = -21 \rightarrow 21$
$T_{min} = 0.26$, $T_{max} = 0.55$	$k = -10 \rightarrow 10$
17 378 measured reflections	$l = -30 \rightarrow 30$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.947$	$(\Delta/\sigma)_{max} = 0.001$
3602 reflections	$\Delta\rho_{max} = 0.87$ e Å^{-3}
273 parameters	$\Delta\rho_{min} = -0.92$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn3—O10^i	1.940 (4)	Zn3—O12	2.090 (4)
Zn3—O8	1.942 (4)	Zn3—O3^{ii}	2.282 (4)
Zn3—OW	1.995 (4)		
O10^i—Zn3—O8	134.22 (17)	OW—Zn3—O12	97.00 (16)
O10^i—Zn3—OW	108.83 (17)	O10^i—Zn3—O3^{ii}	89.12 (15)
O8—Zn3—OW	116.77 (17)	O8—Zn3—O3^{ii}	88.56 (14)
O10^i—Zn3—O12	84.50 (15)	OW—Zn3—O3^{ii}	87.97 (15)
O8—Zn3—O12	93.67 (15)	O12—Zn3—O3^{ii}	172.91 (15)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x, 1 - y, z - \frac{1}{2}$.

The positions of the H atoms were refined with a common constant isotropic displacement parameter of 0.02 Å^2 [C—H 0.85 (7)–0.96 (7) Å and N—H 0.79 (7)–0.93 (7) Å].

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Bu, X. H., Feng, P. Y., Gier, T. E. & Stucky, G. D. (1998). *J. Solid State Chem.* **136**, 210–215.
Chen, J. S., Li, L., Yang, G. D. & Xu, R. R. (1989). *Chem. Commun.* pp. 1217–1218.
Ekambaram, S. & Sevov, S. C. (2000). *Inorg. Chem.* **39**, 2405–2410.
Gier, T. E., Bu, X. H., Feng, P. Y. & Stucky, G. D. (1998). *Nature*, **395**, 154–157.
Hawthorne, F. C. (1976). *Can. Mineral.* **14**, 143–149.
Kongshaug, K. O., Fjellvåg, H. & Lillerud, K. P. (1999). *J. Mater. Chem.* **9**, 3119–3123.
Li, L., Wu, L. X., Chen, J. S. & Xu, R. R. (1991). *Acta Cryst.* C**47**, 246–249.
Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Gottingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wang, S. L., Hsu, K. F. & Nieh, Y. P. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1681–1684.
Yang, G. D., Li, L., Chen, J. S. & Xu, R. R. (1989). *Chem. Commun.* pp. 810–811.