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FULL PAPER

Hydrothermal synthesis and structure of a zinc arsenate–oxalate, $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$, and a zinc arsenate, $[\{NH_3(CH_3)_2NH_2(CH_3)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$, with three-dimensional structures†

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Received 18th June 2002, Accepted 4th September 2002
First published as an Advance Article on the web 16th October 2002

Two new open-framework solids, a zinc arsenate–oxalate, $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$, **I**, and a zinc arsenate, $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$, **II**, have been synthesized in the presence of dipropylenetriamine (DPTA) under mild hydrothermal reaction conditions. Both **I** and **II** possess a three-dimensional architecture with channels. The structure of the zinc arsenate–oxalate, **I**, consists of anionic zinc arsenate–oxalate layers cross-linked by arsenate units giving rise to 10-membered channels. The zinc arsenate structure, **II**, on the other hand, is made from the linkages involving zinc arsenate layers and arsenate pillars. The structures of both **I** and **II** possess large number of hydrogen bond interactions involving the framework oxygen atoms and the hydrogen atoms of the amine molecule. The synthesis conditions employed and the close structural similarity between the two structures indicates that **I** could be the precursor for **II**.

Introduction

Hydrothermal crystallization, in the presence of organic amine molecules, has provided a convenient route to microporous tetrahedral framework solids, such as zeolites and aluminophosphates.[1] The versatility of the hydrothermal technique has been employed with great success in the preparation of a variety of new framework materials.[2] Of the many solids that have been synthesized and characterized, the zinc phosphate, ND-1,[3] and the nickel phosphates, VSB-1[4] and VSB-5,[5] are important for their extra-large pore channels. During the last few years, a new class of mixed anionic hybrid frameworks, containing both phosphate and oxalate moieties, have been prepared and characterized. Thus, phosphate–oxalate solids with open architectures have been reported for V,[6] Mn,[7] Fe,[8,9] Co,[10] Zn,[11] Al,[12] Ga,[13] In[14] and Sn.[15] Similar to the many open-framework phosphates, compounds based on arsenates as building units have also been prepared and characterized.[16,17] Only a very few arsenate–oxalates, on the other hand, have been synthesized.[6,18] In a continuing program of research aimed at producing new hybrid materials with novel frameworks as well as to correlate the structures and to understand the formation of these phases, we have been exploring the formation of arsenate based networks. During the course of such investigations, we have now isolated a zinc arsenate–oxalate, $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$, **I**, and a zinc arsenate, $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$, **II**, both with three-dimensional connectivity and possessing channels. Besides being the first zinc arsenate–oxalate material to be synthesized in the presence of an organic amine, **I** also appears to have some structural relationship to the zinc arsenate, **II**. In this paper, the syntheses and structures of these unusual solids are presented.

Experimental

Synthesis and initial characterization

Compounds **I** and **II** were synthesized in the presence of dipropylenetriamine (DPTA) employing mild reaction conditions. Typically, for the synthesis of **I**, 0.0904 g of ZnO was dispersed in a mixture of water and THF. To this, 0.091 ml of HCl (35 %), 2 ml of H_3AsO_4 and 0.07 g of oxalic acid were added under continuous stirring. Finally 0.16 ml of DPTA was added and the mixture was homogeneized for 30 min at room temperature. The final reaction mixture with the composition 2ZnO:2HCl:4H_3AsO_4:1$H_2C_2O_4$:1DPTA:(22THF + 200H_2O) was taken in a Teflon-lined Parr autoclave and heated at 75 °C for 72 h followed by at 150 °C for 24 h. After cooling, a few colorless needle-like crystals along with some white powder were vacuum filtered from the mother-liquor, washed with water, and dried at room temperature. The powder XRD pattern of the white powder was found to be weakly diffracting with the crystalline lines corresponds to the zinc arsenate phase, **II**. Pure single phase material **II** was prepared by employing similar heat treatment cycles but with a reaction mixture of the composition 1ZnO:2HCl:2H_3AsO_4:1$H_2C_2O_4$:2DPTA:(22THF + 200H_2O). This synthesis resulted in large quantities of rod-shaped colorless single crystals. The initial pH in both the cases was ~5 and did not show any appreciable change after the reaction. Our efforts to improve the yield or to prepare **I** as a pure phase was not successful. An EDAX analysis on the single crystals indicated a Zn/As ratio of 1.0 for **I** and 0.86 for **II**. Elemental analysis results of the bulk product, in the case of **II**, is also consistent with the stoichiometry. Anal. Found: C, 8.19; H, 2.61; N, 4.71. Calc.: C, 8.71; H, 2.72; N, 5.08%.

Infrared (IR) spectroscopic studies of **II** have been carried out in the mid-IR region as a KBr pellet. The results indicate characteristic sharp lines. The various bands are: 3541 br (ν_{as}OH), 3422 br (ν_sOH), 3019w ($\nu_s N^+–CH_2$, C–H symmetric stretching), 2866w ($\nu_s CH_2$, C–H symmetric stretching), 1627s

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† Electronic supplementary information (ESI) available: Figs. 1 and 2: ORTEP diagrams of **I** and **II** showing the asymmetric unit. See http://www.rsc.org/suppdata/dt/b2/b205874j/

DOI: 10.1039/b205874j

Table 1 Crystal data and structure refinement parameters for $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$ **I** and $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$ **II**

	I	**II**
Chemical formula	$C_8H_{22}N_3O_{16}As_3Zn_3$	$C_{12}H_{45}N_6O_{29}As_7Zn_6$
Formula mass	837.16	1654.20
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
T/K	293(2)	293(2)
a/Å	16.0857(2)	9.1724(4)
b/Å	9.1973(2)	9.2118(4)
c/Å	15.4216(3)	25.7459(11)
α/°	90.0	87.265(1)
β/°	112.033(1)	86.477(1)
γ/°	90.0	71.270(1)
V/Å^3	2114.92(7)	2055.38(15)
Z	4	2
D_c/g cm^{-3}	2.629	2.673
μ/mm^{-1}	8.118	9.140
No. of measured/observed reflections	11648/3035	14656/5838
R_1, wR_2 $[I > 2\sigma(I)]$	$R_1 = 0.0293$,[a] $wR_2 = 0.0587$[b]	$R_1 = 0.0341$,[a] $wR_2 = 0.0929$[b]

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0170$ and $b = 0.0$ for **I** and $a = 0.0388$ and $b = 0.0$ for **II**.

($\delta_s H_2O$), 1561w and 1513w ($\delta_s NH_2$), 1492w (δN^+–CH_2 assymetric drift), 1437w (δCH_2 drift), 971s and 882s (ν_sC–N), 715s ($\rho_r CH_2$).

Single crystal structure determination

A suitable colorless single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemen's SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 10 s per frame) in the 2θ range 3–46.5°. Pertinent experimental details for the structure determinations of **I** and **II** are presented in Table 1.

An absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[19] Other effects, such as absorption by the glass fiber, were simultaneously corrected. The structures were solved by direct methods and in each case, a sufficient fragment of the structure was revealed (As, Zn and O) to enable the remainder of the non-hydrogen atoms to be located from difference Fourier maps and the refinements to proceed to $R < 10\%$. All the hydrogen positions were initially located in the difference map and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXl-97[20] package of programs. Selected bond distances and angles are presented in Tables 2 and 3 for **I**, and in Tables 4 and 5 for **II**.

CCDC reference numbers 184189 and 184190.

See http://www.rsc.org/suppdata/dt/b2/b205874j/ for crystallographic data in CIF or other electronic format.

Results and discussion

The asymmetric unit of **I** consists of 33 non-hydrogen atoms, of which 24 belong to the framework and 9 atoms to the organic amine molecule. There are three crystallographically distinct Zn and As atoms. Of the three Zn atoms, Zn(1) is octahedrally coordinated and Zn(2) and Zn(3) are tetrahedrally coordinated by their O atom neighbors with Zn–O bond lengths in the range 1.927(4)–2.194(4) Å (av. Zn(1)–O = 2.112, Zn(2)–O = 1.951, Zn(3)–O = 1.952 Å). The octahedral O–Zn(1)–O bond angles are in the range 77.1(1)–174.6(2)° (av. 105.1°) and the tetrahedral O–Zn–O angles are in the range 99.6(2)–123.1(2)° (av. 109°). Whilst Zn(2) and Zn(3) makes four Zn–O–As bonds, Zn(1) makes only two such bonds and has four Zn–O–C bonds, which forms the oxalate linkage (Tables 2 and 3). The Zn–O–As bond angles are in the range 117.5(2)–139.6(2)° (av. 125°). Of the three As atoms, As(1) and As(2) make three As–O–Zn bonds with one terminal P–O bond, and As(3) makes four As–O–Zn bonds. The As–O distances are in the range 1.660(4)–1.741(4) Å (av. 1.684 Å) and the O–As–O angles are in the range 102.1(2)–118.2(2)° (av. 109.4°) (Tables 2 and 3). The two terminal As(1)–O(4) and As(2)–O(8) bonds with distances of 1.741(4) and 1.725(4) Å are formally As–OH linkages and correspond well with the proton positions located in the difference Fourier maps. The net negative charge of −3 is then balanced by the presence of one completely protonated DPTA molecule. The various geometrical parameters are in good agreement with those in the previously reported arsenate and arsenate–oxalate structures.[16–18]

The framework structure of **I** consists of a network of ZnO_6, ZnO_4, AsO_4, $AsO_3(OH)$ and C_2O_4 moieties connected through their vertices. The complex three-dimensional connectivity of **I** can be understood in terms of simpler building units. Thus, the structure can be considered to be made from one-dimensional zigzag ladders of zinc arsenates connected with one-dimensional zinc oxalate chains, forming a hybrid layer with 10-membered aperture (5 Zn, 3 As and 2 oxalate), with a honeycomb-like character, as shown in Fig. 1. The zinc oxalate chains are formed by octahedral Zn(1) atoms. These hybrid layers are superimposed one over the other and are arranged in AAAAA... fashion, in the *ab* plane, and are cross-linked by $As(1)O_3(OH)$ tetrahedra, on either side of the layer, resulting in three-dimensional connectivity with 10-membered channels. Another way to view the structure would be to consider a zinc arsenate layer with 8-membered channels, in the *ac* plane, cross-linked by the oxalate chains (Fig. 2). The amine molecule appears to be projecting into the channels and is not situated within the channels, probably due to the smaller size of the channels and larger size of the amine molecule. This is indeed a unique structure, as such an architecture has not been observed in any of the known phosphate–oxalate or arsenate–oxalate structures.[6–15,18] The structure of **I** possess a large number of hydrogen bond interactions involving the framework oxygen and hydrogen atoms of the amine

Table 2 Selected bond distances (Å) for $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$ **I**

As(1)–O(1)	1.660(4)	Zn(1)–O(2)	2.041(4)
As(1)–O(2)	1.665(4)	Zn(1)–O(13)	2.116(4)
As(1)–O(3)	1.677(4)	Zn(1)–O(15)	2.153(4)
As(1)–O(4)	1.741(4)	Zn(1)–O(14)	2.159(4)
As(2)–O(6)	1.649(4)	Zn(1)–O(16)	2.194(4)
As(2)–O(5)	1.664(4)	Zn(2)–O(12)#2	1.927(4)
As(2)–O(7)	1.702(4)	Zn(2)–O(5)#1	1.944(4)
As(2)–O(8)	1.725(4)	Zn(2)–O(1)	1.950(4)
As(3)–O(9)	1.671(4)	Zn(2)–O(10)#3	1.980(4)
As(3)–O(10)	1.689(4)	Zn(3)–O(11)#4	1.927(4)
As(3)–O(11)	1.684(4)	Zn(3)–O(9)	1.934(4)
As(3)–O(12)	1.678(4)	Zn(3)–O(7)	1.968(4)
Zn(1)–O(6)#1	2.009(4)	Zn(3)–O(3)	1.980(4)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y - 3/2, z + 1/2$; #2 $-x + 1, y - 1/2, -z - 1/2$; #3 $x, -y - 1/2, z + 1/2$; #4 $-x + 1, -y - 1, -z - 1$.

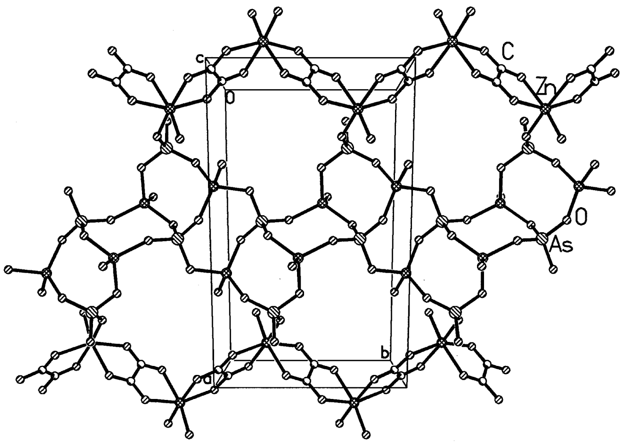

Fig. 1 The structure of **I** in the *ab* plane showing the zinc arsenate–oxalate hybrid layer with the 10-membered aperture. These layers are cross-linked by arsenate units (see text).

Table 4 Selected bond distances (Å) in **II**, $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$

As(1)–O(2)	1.661(6)	As(7)–O(26)	1.682(5)
As(1)–O(1)	1.669(5)	As(7)–O(27)	1.724(5)
As(1)–O(3)	1.674(5)	Zn(1)–O(12)	1.895(5)
As(1)–O(4)	1.692(5)	Zn(1)–O(22)	1.951(6)
As(2)–O(5)	1.674(5)	Zn(1)–O(28)#1	1.972(5)
As(2)–O(6)	1.686(5)	Zn(1)–O(19)	1.994(5)
As(2)–O(8)	1.699(5)	Zn(2)–O(21)	1.931(5)
As(2)–O(7)	1.699(5)	Zn(2)–O(2)	1.936(6)
As(3)–O(10)	1.671(4)	Zn(2)–O(17)#2	1.942(5)
As(3)–O(12)	1.675(5)	Zn(2)–O(26)	1.970(5)
As(3)–O(9)	1.675(5)	Zn(3)–O(3)	1.946(5)
As(3)–O(11)	1.683(5)	Zn(3)–O(7)#3	1.953(5)
As(4)–O(13)	1.652(5)	Zn(3)–O(8)	1.958(5)
As(4)–O(14)	1.678(5)	Zn(3)–O(23)	1.967(5)
As(4)–O(15)	1.675(5)	Zn(4)–O(13)#4	1.893(5)
As(4)–O(16)	1.711(5)	Zn(4)–O(14)	1.941(5)
As(5)–O(18)	1.653(5)	Zn(4)–O(9)	1.946(5)
As(5)–O(17)	1.666(5)	Zn(4)–O(18)	1.990(5)
As(5)–O(19)	1.679(5)	Zn(5)–O(11)#5	1.918(5)
As(5)–O(20)	1.714(5)	Zn(5)–O(10)	1.942(5)
As(6)–O(21)	1.657(5)	Zn(5)–O(15)#6	1.964(5)
As(6)–O(22)	1.666(6)	Zn(5)–O(16)#5	1.969(5)
As(6)–O(23)	1.665(5)	Zn(6)–O(4)#7	1.944(5)
As(6)–O(24)	1.735(6)	Zn(6)–O(6)#8	1.944(5)
As(7)–O(25)	1.660(5)	Zn(6)–O(5)#2	1.956(5)
As(7)–O(28)	1.678(5)	Zn(6)–O(1)	1.968(5)

Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $x - 1, y + 1, z$; #3 $-x + 1, -y + 1, -z$; #4 $-x + 2, -y, -z + 1$; #5 $-x + 1, -y + 1, -z + 1$; #6 $x, y + 1, z$; #7 $- x, -y + 2, -z$; #8 $- x, -y + 1, -z$;

molecule. Thus, strong N–H ··· O (av. N ··· O = 2.861 Å, N–H ··· O = 161°) and C–H ··· O (av. C ··· O = 3.423 Å, C–H ··· O = 161°) interactions are observed in **I**. The important hydrogen bond interactions observed in **I** are given in Table 6.

The asymmetric unit of **II** contains 60 non-hydrogen atoms, of which 41 atoms belong to the framework and the remainder to the guest molecules that comprises water and two amine molecules. There are seven crystallographically independent As and six Zn atoms all of which are tetrahedrally coordinated with their O atom neighbors. The Zn–O bond distances are in the range 1.893(5)–1.994(5) Å (av. 1.942 Å) and the O–Zn–O bond angles are in the range 97.3(2)–123.2(2)° (av. 109.3°). All the Zn atoms makes four Zn–O–As bonds with an average bond

Table 3 Selected bond angles (°) for $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$ **I**

O(1)–As(1)–O(2)	116.74(19)	O(6)#1–Zn(1)–O(16)	174.60(16)
O(1)–As(1)–O(3)	112.28(18)	O(2)–Zn(1)–O(16)	86.56(16)
O(2)–As(1)–O(3)	111.31(19)	O(13)–Zn(1)–O(16)	77.23(14)
O(1)–As(1)–O(4)	102.09(19)	O(15)–Zn(1)–O(16)	84.19(15)
O(2)–As(1)–O(4)	106.7(2)	O(14)–Zn(1)–O(16)	92.51(15)
O(3)–As(1)–O(4)	106.66(18)	O(12)#2–Zn(2)–O(5)#1	123.07(16)
O(6)–As(2)–O(5)	118.2(2)	O(12)#2–Zn(2)–O(1)	107.80(15)
O(6)–As(2)–O(7)	105.37(19)	O(5)#1–Zn(2)–O(1)	106.58(17)
O(5)–As(2)–O(7)	112.22(19)	O(12)#2–Zn(2)–O(10)#3	111.61(16)
O(6)–As(2)–O(8)	107.24(19)	O(5)#1–Zn(2)–O(10)#3	105.60(15)
O(5)–As(2)–O(8)	106.61(19)	O(1)–Zn(2)–O(10)#3	99.59(16)
O(7)–As(2)–O(8)	106.52(19)	O(11)#4–Zn(3)–O(9)	116.74(16)
O(9)–As(3)–O(12)	106.83(19)	O(11)#4–Zn(3)–O(7)	117.37(16)
O(9)–As(3)–O(11)	111.04(19)	O(9)–Zn(3)–O(7)	111.63(16)
O(12)–As(3)–O(11)	110.23(18)	O(11)#4–Zn(3)–O(3)	101.62(16)
O(9)–As(3)–O(10)	110.76(18)	O(9)–Zn(3)–O(3)	102.46(16)
O(12)–As(3)–O(10)	110.59(18)	O(7)–Zn(3)–O(3)	104.31(15)
O(11)–As(3)–O(10)	107.42(18)	As(1)–O(1)–Zn(2)	130.5(2)
O(6)#1–Zn(1)–O(13)	97.60(15)	As(1)–O(2)–Zn(1)	128.2(2)
O(2)–Zn(1)–O(13)	105.30(16)	As(1)–O(3)–Zn(3)	117.5(2)
O(6)#1–Zn(1)–O(15)	101.20(16)	As(2)–O(5)–Zn(2)#5	127.4(2)
O(2)–Zn(1)–O(15)	88.19(15)	As(2)–O(6)–Zn(1)#5	138.6(2)
O(13)–Zn(1)–O(15)	156.13(15)	As(2)–O(7)–Zn(3)	127.2(2)
O(6)#1–Zn(1)–O(14)	88.88(16)	As(3)–O(9)–Zn(3)	139.6(2)
O(2)–Zn(1)–O(14)	165.32(15)	As(3)–O(10)–Zn(2)#6	120.05(19)
O(13)–Zn(1)–O(14)	88.73(15)	As(3)–O(11)–Zn(3)#4	126.1(2)
O(15)–Zn(1)–O(14)	77.14(14)	As(3)–O(12)–Zn(2)#7	125.3(2)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y - 3/2, z + 1/2$; #2 $-x + 1, y - 1/2, -z - 1/2$; #3 $x, -y - 1/2, z + 1/2$; #4 $-x + 1, -y - 1, -z - 1$; #5 $x, -y - 3/2, z - 1/2$; #6 $x, -y - 1/2, z - 1/2$; #7 $-x + 1, y + 1/2, -z - 1/2$.

Table 5 Selected bond angles (°) for $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2]$-$[Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$ **II**

O(2)–As(1)–O(1)	106.3(3)	O(25)–As(7)–O(27)	106.4(3)
O(2)–As(1)–O(3)	115.6(3)	O(28)–As(7)–O(27)	109.3(3)
O(1)–As(1)–O(3)	109.9(2)	O(26)–As(7)–O(27)	108.2(3)
O(2)–As(1)–O(4)	104.8(3)	O(12)–Zn(1)–O(22)	115.2(3)
O(1)–As(1)–O(4)	109.3(3)	O(12)–Zn(1)–O(28)#1	119.5(2)
O(3)–As(1)–O(4)	110.7(3)	O(22)–Zn(1)–O(28)#1	105.7(2)
O(5)–As(2)–O(6)	114.5(2)	O(12)–Zn(1)–O(19)	108.9(2)
O(5)–As(2)–O(8)	108.8(3)	O(22)–Zn(1)–O(19)	106.8(2)
O(6)–As(2)–O(8)	109.5(2)	O(28)#1–Zn(1)–O(19)	99.0(2)
O(5)–As(2)–O(7)	109.9(2)	O(21)–Zn(2)–O(2)	114.3(3)
O(6)–As(2)–O(7)	105.7(2)	O(21)–Zn(2)–O(17)#2	100.7(2)
O(8)–As(2)–O(7)	108.3(2)	O(2)–Zn(2)–O(17)#2	101.7(2)
O(10)–As(3)–O(12)	110.8(3)	O(21)–Zn(2)–O(26)	119.2(2)
O(10)–As(3)–O(9)	107.5(2)	O(2)–Zn(2)–O(26)	106.8(2)
O(12)–As(3)–O(9)	111.3(3)	O(17)#2–Zn(2)–O(26)	113.0(2)
O(10)–As(3)–O(11)	112.2(3)	O(3)–Zn(3)–O(7)#3	116.9(2)
O(12)–As(3)–O(11)	102.9(3)	O(3)–Zn(3)–O(8)	105.0(2)
O(9)–As(3)–O(11)	112.1(3)	O(7)#3–Zn(3)–O(8)	111.5(2)
O(13)–As(4)–O(14)	114.5(3)	O(3)–Zn(3)–O(23)	116.9(2)
O(13)–As(4)–O(15)	108.9(3)	O(7)#3–Zn(3)–O(23)	106.2(2)
O(14)–As(4)–O(15)	108.1(2)	O(8)–Zn(3)–O(23)	99.0(2)
O(13)–As(4)–O(16)	104.8(3)	O(13)#4–Zn(4)–O(14)	112.9(2)
O(14)–As(4)–O(16)	110.0(2)	O(13)#4–Zn(4)–O(9)	115.3(2)
O(15)–As(4)–O(16)	110.6(2)	O(14)–Zn(4)–O(9)	112.0(2)
O(18)–As(5)–O(17)	107.3(3)	O(13)#4–Zn(4)–O(18)	97.3(2)
O(18)–As(5)–O(19)	111.5(3)	O(14)–Zn(4)–O(18)	108.1(2)
O(17)–As(5)–O(19)	109.8(3)	O(9)–Zn(4)–O(18)	110.2(2)
O(18)–As(5)–O(20)	110.8(3)	O(11)#5–Zn(5)–O(10)	119.2(2)
O(17)–As(5)–O(20)	112.0(2)	O(11)#5–Zn(5)–O(15)#6	99.8(2)
O(19)–As(5)–O(20)	105.5(2)	O(10)–Zn(5)–O(15)#6	109.8(2)
O(21)–As(6)–O(22)	111.0(3)	O(11)#5–Zn(5)–O(16)#5	123.2(2)
O(21)–As(6)–O(23)	113.8(3)	O(10)–Zn(5)–O(16)#5	98.0(2)
O(22)–As(6)–O(23)	112.1(3)	O(15)#6–Zn(5)–O(16)#5	106.3(2)
O(21)–As(6)–O(24)	107.7(3)	O(4)#7–Zn(6)–O(6)#8	117.7(2)
O(22)–As(6)–O(24)	106.3(3)	O(4)#7–Zn(6)–O(5)#2	113.1(2)
O(23)–As(6)–O(24)	105.4(3)	O(6)#8–Zn(6)–O(5)#2	110.5(2)
O(25)–As(7)–O(28)	112.7(3)	O(4)#7–Zn(6)–O(1)	111.9(2)
O(25)–As(7)–O(26)	111.7(3)	O(6)#8–Zn(6)–O(1)	103.3(2)
O(28)–As(7)–O(26)	108.5(3)	O(5)#2–Zn(6)–O(1)	98.0(2)

Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $x - 1, y + 1, z$; #3 $-x + 1, -y + 1, -z$; #4 $-x + 2, -y, -z + 1$; #5 $-x + 1, -y + 1, -z + 1$; #6 $x, y + 1, z$; #7 $-x, -y + 2, -z$; #8 $-x, -y + 1, -z$.

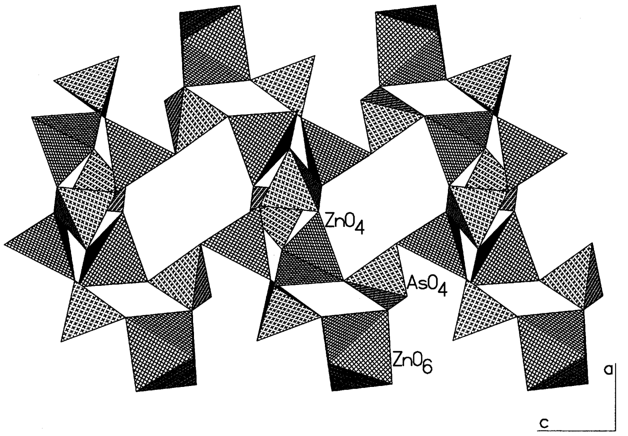

Fig. 2 Polyhedral view of the structure of **I** along the *ac* plane showing the zinc arsenate layers with 8-membered cavities.

angle of 132.2° arising from a wide spread of angles. Of the seven As atoms, As(7) makes two As–O–Zn linkages, As(5) and As(6) makes three such bonds and the remaining As atoms make four As–O–Zn connections. The As–O bond distances are in the range 1.652(5)–1.735(6) Å (av. 1.681 Å) and the O–As–O bond angles are in the range 102.9(3)–115.6(3)° (av. 109.5°). The As(5)–O(20), As(6)–O(24) and As(7)–O(27) bonds with distances of 1.714(5), 1.735(6) and 1.724(5) Å are terminal As–OH linkages which corresponds well with the proton positions located in the difference Fourier maps. The other terminal linkage, As(7)–O(25) with a distance of 1.660(5) Å is a As=O double bond. This assignment is also consistent with bond valence sum calculations.[21] The net negative charge on the framework of −6 is balanced by the presence of two completely protonated DPTA molecules. The various geometrical parameters observed are in agreement with those in the previously reported arsenate and arsenate–oxalate structures.[16–18] Selected bond distances and angles are presented in Tables 4 and 5.

Unlike **I**, the structure of **II** does not have any octahedral Zn atoms, and is formed only by ZnO_4 and AsO_4 tetrahedral units, strictly alternating, connected through their vertices. The three-dimensional structure of **II**, like **I**, can be understood in terms of simpler building units. Thus, $Zn(4)O_4$, $Zn(5)O_4$, $As(3)O_4$ and $As(4)O_4$ tetrahedra are connected together forming one-dimensional ladders which are joined through a 4-membered ring giving rise to a layer with hanging $As(5)O_4$ units (Fig. 3).

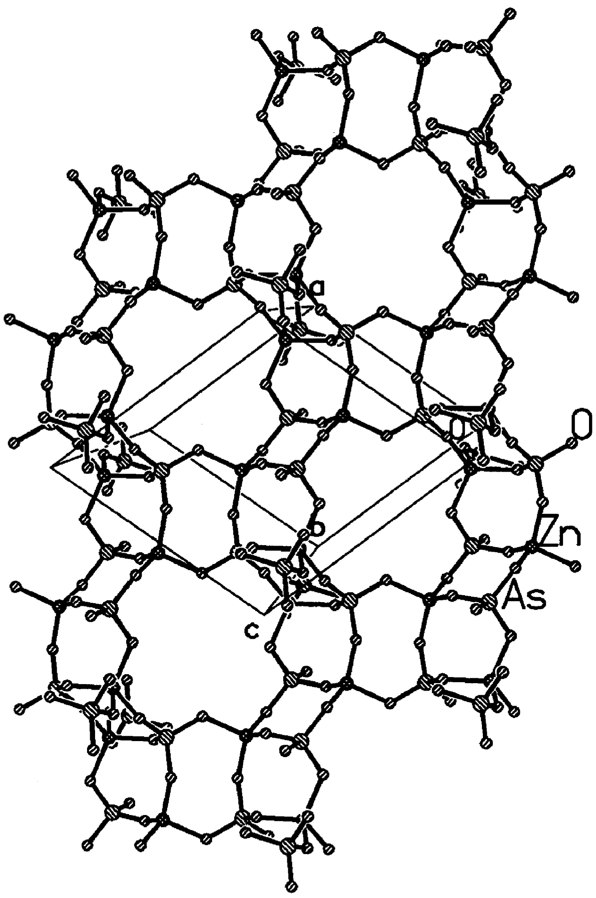

Fig. 3 The structure of **II** showing the connectivity between ZnO_4 and AsO_4 tetrahedra in the *ab* plane. Note the hanging arsenate groups. Two such layers exist in **II** (see text).

Another similar layer is formed by the linkages involving $Zn(3)O_4$, $Zn(6)O_4$, $As(1)O_4$ and $As(2)O_4$ with $As(6)O_4$ units hanging from the Zn(3) center. The two layers are connected through a one-dimensional wire, made from $Zn(1)O_4$, $Zn(2)O_4$, $As(6)O_4$ and $As(7)O_4$ units, giving rise to the three-dimensional structure with two distinct channels bound by 8-T atoms (T = Zn, As) as shown in Fig. 4. The structure of **II** also possesses a large number of hydrogen bond interactions involving the framework oxygen and hydrogen atoms of the amine molecule. Thus, strong N–H ⋯ O (av. N ⋯ O = 2.884 Å, N–H ⋯ O = 162°) and C–H ⋯ O (av. C ⋯ O = 3.389 Å, C–H ⋯ O =

Table 6 Important hydrogen bond interactions in $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3][Zn_3(AsO_4)(HAsO_4)_2(C_2O_4)]$ **I** and $[\{NH_3(CH_2)_3NH_2(CH_2)_3NH_3\}_2][Zn_6(AsO_4)_4(HAsO_4)_3]\cdot H_2O$ **II**

D–H ··· A/°	D–H/Å	H ··· A/Å	D ··· A/Å	D–H ··· A/°
I				
N(1)–H(3) ··· O(13)	0.89	1.96	2.829(5)	166
N(2)–H(10) ··· O(10)	0.90	2.01	2.870(4)	158
N(2)–H(11) ··· O(7)	0.90	1.99	2.868(2)	165
N(3)–H(18) ··· O(11)	0.89	1.97	2.837(7)	164
N(3)–H(20) ··· O(3)	0.89	2.12	2.987(1)	165
O(4)–H(30) ··· O(7)[a]	0.82	2.08	2.812(5)	149
O(8)–H(40) ··· O(2)[a]	0.82	2.05	2.822(5)	157
C(1)–H(5) ··· O(10)	0.97	2.52	3.444(3)	160
C(4)–H(12) ··· O(4)	0.97	2.40	3.355(4)	170
C(4)–H(13) ··· O(15)	0.97	2.51	3.461(1)	165
C(5)–H(15) ··· O(11)	0.97	2.57	3.432(1)	148
II				
N(1)–H(1) ··· O(11)	0.89	2.02	2.896(3)	168
N(1)–H(3) ··· O(20)	0.89	2.10	2.955(8)	161
N(2)–H(10) ··· O(16)	0.90	2.05	2.926(5)	166
N(2)–H(11) ··· O(18)	0.90	1.88	2.773(1)	173
N(3)–H(18) ··· O(9)	0.89	1.95	2.820(1)	165
N(3)–H(19) ··· O(15)	0.89	1.99	2.865(1)	167
N(3)–H(20) ··· O(25)	0.89	1.87	2.755(2)	177
N(4)–H(21) ··· O(26)	0.89	1.94	2.823(2)	172
N(4)–H(22) ··· O(1)	0.89	2.06	2.878(2)	152
N(5)–H(30) ··· O(8)	0.90	2.05	2.879(3)	153
N(5)–H(31) ··· O(4)	0.90	1.91	2.809(2)	173
N(6)–H(38) ··· O(3)	0.89	2.42	3.202(1)	147
N(6)–H(40) ··· O(100)	0.89	2.13	2.926(4)	149
O(20)–H(50) ··· O(25)[a]	0.82	1.74	2.512(1)	157
O(24)–H(60) ··· O(28)[a]	0.82	2.19	2.933(2)	150
C(3)–H(9) ··· O(21)	0.97	2.48	3.431(2)	167
C(10)–H(33) ··· O(100)	0.97	2.49	3.405(1)	156
C(12)–H(37) ··· O(4)	0.97	2.50	3.332(2)	143

[a] Intra-framework.

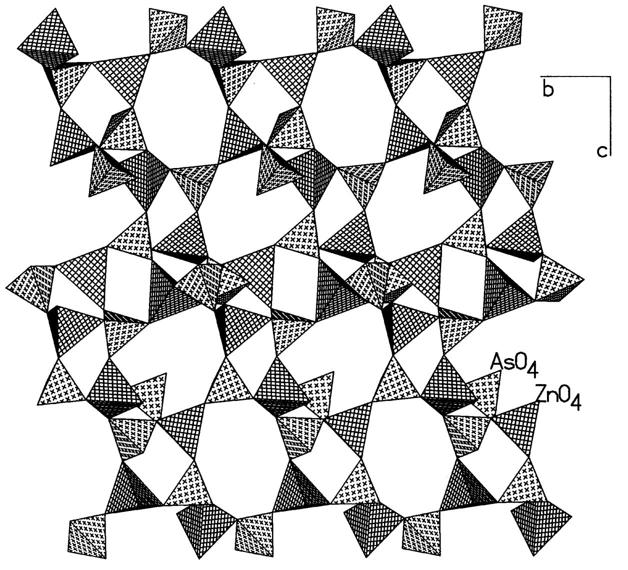

Fig. 4 Structure of **II** in the *bc* plane showing two distinct 8-membered channels.

156 Å) interactions are observed. The important hydrogen bond interactions observed in **II** are listed in Table 6.

Careful analysis of the structures of **I** and **II** reveals some relationships between them. The ladder structures in both **I** and **II** appear to be similar, though the connectivity between the two are different. In the former, it is through a zinc oxalate chain and in the latter it is through another ladder giving rise to layers. Zinc oxalate chains separated by organic amine molecules have been prepared recently, and have been proposed as an intermediate in the synthesis of open-framework zinc oxalate structures.[22] The zinc arsenate–oxalate layer in **I** and the zinc arsenate layer in **II** are further connected giving rise to the three-dimensional structures. It is likely that the lower crystal symmetry in **II** might be responsible for the observation of two distinct layers. The octahedral coordination for the Zn(1) atom in **I** might be the result of lower charges associated with the oxalate oxygens (0.5) compared to the phosphate oxygens (0.75). It is to be noted that **I** is the first example of a zinc arsenate–oxalate, possessing an ionic hybrid layer that are cross-linked through arsenate pillars. In the phosphate–oxalate structures where hybrid layers are seen,[8–10] the layers are usually connected by oxalate units giving rise to the three-dimensional structure.

The relationship between **I** and **II**, and the formation of **II** from **I** can be visualized as a simple reaction given below:

$$2[Zn_3(AsO_4)_3(C_2O_4)] \xrightarrow[+AsO_4]{-2C_2O_4} Zn_6(AsO_4)_7$$

According to the above, the oxalate units in **I** are probably replaced by the arsenate units. This suggests that the arsenate–oxalate might be reactive. The transformation sequence, then, might proceed *via* a solution mediated process, rather than a solid-state transformation. It is likely that *in-situ* experiments employing synchrotron X-ray radiation may be used to follow the reactions, as such studies have been employed with great success to elucidate similar processes.[23] Though the reactivity of the oxalate–phosphates have not been studied, it has been shown recently that lower dimensional iron arsenate–oxalates are reactive giving rise to novel iron arsenates.[18] It is likely that the arsenate–oxalates of the type described here are also reactive and undergo instant transformation to form the zinc arsenate. Further work is needed to understand the reactivity of these unusual solids.

Acknowledgements

The authors thank Prof. C. N. R. Rao, FRS for his support and encouragement. S. N. thanks the Department of Science and Technology (DST), Govt. of India, for the award of a research grant.

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