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FULL PAPER

Solution mediated synthesis and structure of a three-dimensional zinc arsenate, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, with intersecting helical channels

Sandip Chakrabarti and Srinivasan Natarajan *

Framework Solids Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore, 560 064, India. E-mail: raj@jncasr.ac.in

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The synthesis and single crystal structure of a zinc arsenate, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, **I**, is presented. The structure of **I** is built from a network of ZnO_4, AsO_4 and $HAsO_4$ tetrahedral units, connected through their vertices. The connectivity gives rise to 3-, 4- and 5-membered rings, which are joined together forming a one-dimensional column. The columns are connected forming the inter-connected helical channels bound by 8-T atoms (T = Zn and As) in the *bc* plane.

Introduction

Framework solids of aluminosilicates and phosphates have been studied extensively because of their utility in commercial processes such as catalysis, sorption and separation processes.[1] Intense research during the last two decades have resulted in the preparation of a variety of frameworks incorporating both tetrahedral as well as non-tetrahedral elements.[2] Though there are many new materials with novel frameworks, there have been few reports on the synthesis of chiral frameworks. Chiral frameworks are of potential importance for enantioselective separations and the synthesis of optically pure samples.[3] Zeolitic frameworks showing chirality have been readily generated by computational techniques, but the preparation of such materials has proved difficult. Of the reported chiral frameworks, goosecreekite,[4] the zinc phosphate, $NaZnPO_4\cdot H_2O$,[5] the chiral polymorphs of zeolite-β,[6–8] the titanosilicate (ETS-10),[9] and the recently discovered zinc carbonate, $[(CN_3H_6)_2][(Zn(CO_3)_2]$,[10] are important. Both zeolite-β and ETS-10 generally form as heavily intergrown materials, and only one of the polymorphs present in the intergrowth is chiral. The use of chiral amine molecules in the preparation of open-framework materials with chiral structures has met with limited success.[11–14] A chiral tin(II) phosphate has been prepared, recently, using an achiral template and both enantiomers of this material have been isolated and characterized.[15] Metal borophosphates,[16] zinc and beryllium arsenates,[17] and a zinc phosphate[18] with chiral structures and helical channels have also been prepared and characterized. We have been exploring the use of an asymmetric amine molecule, *N*-(2-aminoethyl)-1,3-diaminopropane (AE-DAP), in the synthesis of novel frameworks, under mild hydrothermal conditions. During the course of such investigations, we have been able to isolate a chiral zinc arsenate, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, **I**, possessing intersecting helical channels. In this paper, we report the synthesis and structure of **I**.

Experimental

Synthesis of $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, I

The zinc arsenate, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, **I**, was synthesized under mild hydrothermal conditions starting from a mixture containing *N*-(2-aminoethyl-1,3-diaminopropane, (AE-DAP). In a typical synthesis, 0.045 g of ZnO was dispersed in a mixture of 2 ml of water and 1 ml of THF. To this, 0.09 ml of HCl (35%), 0.156 g of H_3AsO_4 and 0.07 g of oxalic acid were added under continuous stirring. Finally 0.15 ml of AE-DAP was added and the mixture was homogenized for 30 min at room temperature. The final mixture with the composition, ZnO : 2HCl : $2H_3AsO_4$: $H_2C_2O_4$: ($200H_2O$ + 22THF), was sealed in a 23 ml PTFE-lined acid digestion bomb and heated at 75 °C for 72 h followed by heating at 150 °C for 24 h under autogeneous pressure. The resulting product contained a large quantity of rod-like crystals, which were filtered under vacuum and dried at ambient temperature. The initial pH of the mixture was ~6 and did not show appreciable change after the reaction. **I** can also be prepared by starting with zinc acetate, $Zn(OAc)_2\cdot 2H_2O$, instead of ZnO. Thus, a reaction mixture of the composition, $Zn(OAc)_2\cdot 2H_2O$: $4H_3AsO_4$: 2AE-DAP : ($200H_2O$ + 75THF), at 150 °C for 72 h gave rise to **I**. The initial pH in this preparation was ~4. In both the preparations single phasic materials resulted with a yield of about 50%.

The powder XRD pattern indicated that the product was a new material; the patterns were entirely consistent with the structures determined using single-crystal X-ray diffraction. A least-squares fit of the powder XRD (Cu-Kα) lines, using the *hkl* indices generated from single-crystal X-ray data, gave the following unit cell dimensions: $a = 10.423(2)$, $b = 8.619(2)$, $c = 12.334(1)$ Å, $\beta = 104.523(1)°$, in agreement with that determined using the single-crystal XRD. A typical powder X-ray data of **I** is given along with the simulated pattern in Fig. 1. EDAX analysis gave a Zn : As ratio of 1 : 1, which agrees with the composition obtained from the single-crystal X-ray study.

Thermogravimetric analysis (TGA) has been carried out on **I** in an oxygen atmosphere in the temperature range 25 to 700 °C with a heating rate of 5 °C min^{-1} (Mettler-Toledo, TG850). The studies show three weight losses. The weight loss of 3% in the range 80–120 °C corresponds to the loss of adsorbed and extra-framework water (calc. 1.88%) and the second weight loss of 13.9% in the range 300–450 °C corresponds to the loss of the amine and condensation of the terminal –OH group (calc. 14.1%) and the final weight loss of 34% in the range 400–600 °C corresponds to the loss of arsenate from the solid (calc. 41%). The calcined sample is poorly

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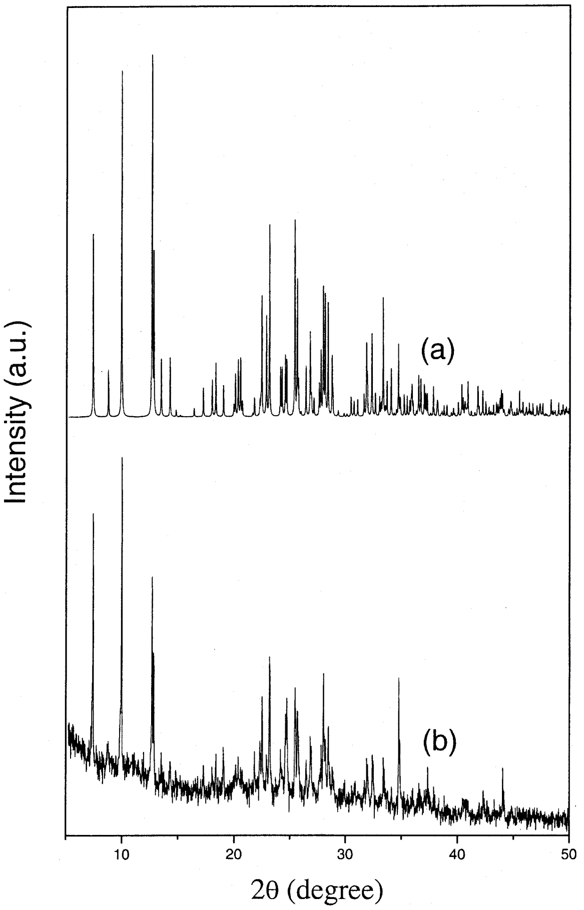


Fig. 1 Simulated (a) and observed (b) powder X-ray (Cu-Kα) diffraction (XRD) pattern for **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$.

Table 1 Crystal data and structure refinement parameters for **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$

Empirical formula	$Zn_4As_4O_{17}N_3C_5H_{21}$
Formula mass	956.41
Crystal system	Monoclinic
Space group	$P2_1$ (no. 4)
a/Å	10.4536(2)
b/Å	8.6462(1)
c/Å	12.3684(2)
β/°	104.534(1)
V/Å^3	1082.13(3)
Z	2
T/K	293
ρ_{calc}/g cm^{-3}	2.935
μ/mm^{-1}	10.535
Reflections total, observed	8213, 3049
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0362$,[a] $wR_2 = 0.0816$[b]

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$; $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$; $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0355$ and $b = 0.0$ for **I**.

Table 2 Selected bond distances (Å) for **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$

As(1)–O(1)	1.662(8)	Zn(1)–O(5)#2	1.905(7)
As(1)–O(2)	1.662(8)	Zn(1)–O(3)	1.960(6)
As(1)–O(4)	1.684(8)	Zn(1)–O(9)#3	1.964(7)
As(1)–O(3)	1.682(6)	Zn(1)–O(10)	1.971(8)
As(2)–O(5)	1.673(7)	Zn(2)–O(1)#4	1.926(8)
As(2)–O(6)	1.674(7)	Zn(2)–O(7)#5	1.934(7)
As(2)–O(7)	1.690(7)	Zn(2)–O(14)	1.950(8)
As(2)–O(8)	1.691(7)	Zn(2)–O(16)	1.991(7)
As(3)–O(9)	1.655(7)	Zn(3)–O(4)#4	1.893(8)
As(3)–O(10)	1.666(7)	Zn(3)–O(13)#1	1.947(8)
As(3)–O(11)	1.687(7)	Zn(3)–O(8)	1.948(7)
As(3)–O(12)	1.749(7)	Zn(3)–O(16)#1	1.994(7)
As(4)–O(13)	1.659(7)	Zn(4)–O(2)	1.914(8)
As(4)–O(14)	1.663(7)	Zn(4)–O(6)	1.924(7)
As(4)–O(15)	1.681(7)	Zn(4)–O(15)	1.973(7)
As(4)–O(16)#1	1.717(7)	Zn(4)–O(11)#6	1.991(7)

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

crystalline with very few characteristic XRD lines that correspond to the mineral zincite, ZnO.

Infra-red (IR) spectroscopic studies have been carried out in the mid-IR region as a KBr pellet (Bruker IFD-66/V). The results indicate characteristic sharp lines. The various bands are: 3466br (ν_{as} OH), 3376br (ν_s OH), 2986w (ν_s N^+–CH_2, C–H symmetric stretching), 2827w (ν_s CH_2, C–H symmetric stretching), 1608s (δ_s H_2O), 1561w and 1522w (δ_s NH_2), 1479w (δ N^+–CH_2 asymmetric drift), 1459w (δCH_2 drift), 913s and 882s (ν_sC–N), 742s ($\rho_r CH_2$) cm^{-1}.

X-Ray crystallography

A suitable single crystal of compound **I** (0.20 × 0.12 × 0.12 mm) was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemens 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 40 kV and 40 mA. Pertinent details for the structure determinations are presented in Table 1. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[19] Other effects, such as absorption by the glass fiber *etc.* were simultaneously corrected. The systematic absences in the reduced data ($0k0$, $k \neq 2n$) indicated space groups $P2_1$ or $P2_1/m$. The structure was solved and refined using the SHELXTL-PLUS suite of programs.[20] The direct methods solution readily established all the heavy atom positions (As and Zn) and facilitated the identification of most of the other fragments (O, C, N and H) from the difference Fourier maps and the refinements to proceed to $R < 10\%$. All the hydrogen atoms were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The Flack polarity parameter[21] was optimized to establish the absolute structure for **I**. A refined value of −0.01(2) indicated that the absolute structure is as given in the Results section. Final R values of $R_1 = 0.0364$ and $wR_2 = 0.0954$ were obtained for refinements varying atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. By setting the Flack parameter to 1.00 (opposite absolute structure) and repeating the refinement resulted in R values of $R_1 = 0.044$ and $wR_2 = 0.114$. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[20] suite of programs. Details of the final refinements are given in Table 1. The selected bond distances and angles for **I** are listed in Tables 2 and 3.

CCDC reference number 185817.

See http://www.rsc.org/suppdata/dt/b2/b204669p/ for crystallographic data in CIF or other electronic format.

Results and discussion

The asymmetric unit of **I** contains 33 non-hydrogen atoms as shown in Fig. 2, of which 24 atoms belong to the framework and 9 atoms to the organic amine and water guest molecules. There are four crystallographically distinct Zn and As atoms. The zinc atoms are tetrahedrally coordinated by their O atom neighbors with Zn–O bond lengths in the range 1.895(8)–1.999(7) Å [av. Zn(1)–O = 1.951, Zn(2)–O = 1.9485, Zn(3)–O =

Table 3 Selected bond angles (°) for **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$

O(1)–As(1)–O(2)	111.5(5)	O(1)#4–Zn(2)–O(16)	116.1(4)
O(1)–As(1)–O(4)	109.8(4)	O(7)#5–Zn(2)–O(16)	115.8(3)
O(2)–As(1)–O(4)	113.5(5)	O(14)–Zn(2)–O(16)	104.3(3)
O(1)–As(1)–O(3)	110.5(4)	O(4)#4–Zn(3)–O(13)#1	102.3(3)
O(2)–As(1)–O(3)	103.8(3)	O(4)#4–Zn(3)–O(8)	106.8(3)
O(4)–As(1)–O(3)	107.6(4)	O(13)#1–Zn(3)–O(8)	108.2(3)
O(5)–As(2)–O(6)	114.9(4)	O(4)#4–Zn(3)–O(16)#1	129.2(4)
O(5)–As(2)–O(7)	105.1(4)	O(13)#1–Zn(3)–O(16)#1	107.9(3)
O(6)–As(2)–O(7)	108.3(4)	O(8)–Zn(3)–O(16)#1	101.4(3)
O(5)–As(2)–O(8)	107.1(4)	O(2)–Zn(4)–O(6)	107.4(4)
O(6)–As(2)–O(8)	110.8(4)	O(2)–Zn(4)–O(15)	118.4(4)
O(7)–As(2)–O(8)	110.4(4)	O(6)–Zn(4)–O(15)	116.3(3)
O(9)–As(3)–O(10)	109.0(4)	O(2)–Zn(4)–O(11)#6	106.6(3)
O(9)–As(3)–O(11)	113.4(4)	O(6)–Zn(4)–O(11)#6	111.7(3)
O(10)–As(3)–O(11)	113.2(4)	O(15)–Zn(4)–O(11)#6	95.4(3)
O(9)–As(3)–O(12)	106.8(4)	As(1)–O(1)–Zn(2)#1	132.2(5)
O(10)–As(3)–O(12)	106.3(4)	As(1)–O(2)–Zn(4)	133.1(5)
O(11)–As(3)–O(12)	107.8(4)	As(1)–O(3)–Zn(1)	130.4(4)
O(13)–As(4)–O(14)	116.0(4)	As(1)–O(4)–Zn(3)#1	143.4(5)
O(13)–As(4)–O(15)	106.4(4)	As(2)–O(5)–Zn(1)#6	137.0(5)
O(14)–As(4)–O(15)	110.2(4)	As(2)–O(6)–Zn(4)	127.7(4)
O(13)–As(4)–O(16)#1	109.3(4)	As(2)–O(7)–Zn(2)#7	128.1(4)
O(14)–As(4)–O(16)#1	106.0(4)	As(2)–O(8)–Zn(3)	130.1(4)
O(15)–As(4)–O(16)#1	108.8(4)	As(3)–O(9)–Zn(1)#8	127.9(4)
O(5)#2–Zn(1)–O(3)	111.8(3)	As(3)–O(10)–Zn(1)	130.6(4)
O(5)#2–Zn(1)–O(9)#3	111.4(3)	As(3)–O(11)–Zn(4)#2	127.7(4)
O(3)–Zn(1)–O(9)#3	109.6(3)	As(4)–O(13)–Zn(3)#4	127.2(4)
O(5)#2–Zn(1)–O(10)	108.4(3)	As(4)–O(14)–Zn(2)	132.0(4)
O(3)–Zn(1)–O(10)	102.0(3)	As(4)–O(15)–Zn(4)	130.2(4)
O(9)#3–Zn(1)–O(10)	113.3(3)	As(4)#4–O(16)–Zn(3)#4	114.3(4)
O(1)#4–Zn(2)–O(7)#5	100.6(3)	As(4)#4–O(16)–Zn(2)	120.6(4)
O(1)#4–Zn(2)–O(14)	108.3(4)	Zn(3)#4–O(16)–Zn(2)	125.1(4)
O(7)#5–Zn(2)–O(14)	111.9(3)		

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

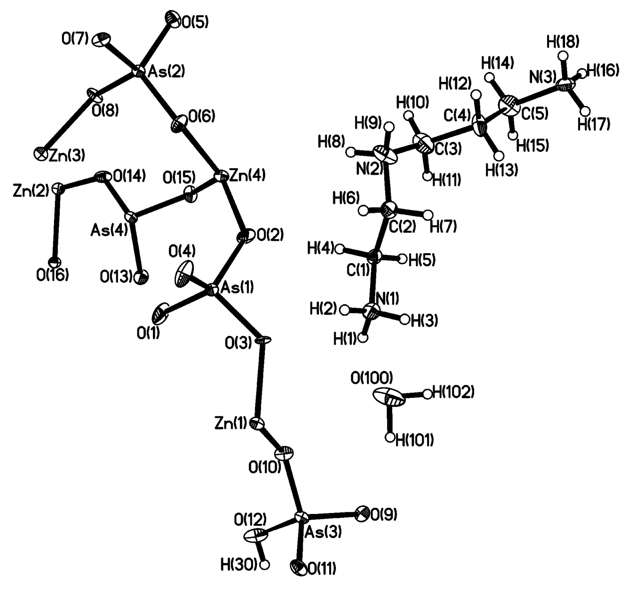
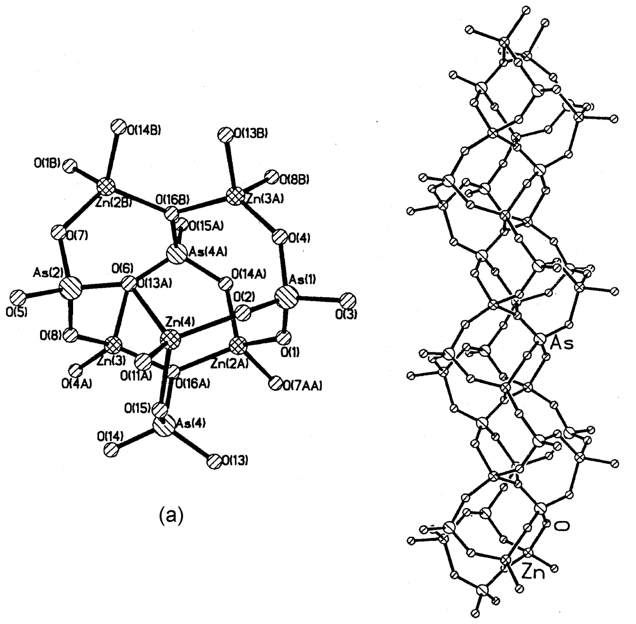


Fig. 2 ORTEP[27] plot showing the asymmetric unit in **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$. Thermal ellipsoids are given at 50% probability.

1.942, Zn(4)–O = 1.951 Å, see Table 2] and O–Zn–O bond angles are in the range 95.4(3)–129.3(4)° [av. O–Zn(1)–O = 109.4, O–Zn(2)–O = 109.5, O–Zn(3)–O = 109.3, O–Zn(4)–O = 109.3°, see Table 3]. One oxygen atom is three-coordinated connecting two zinc atoms, Zn(2) and Zn(3), and one As(4) atom. All the Zn atoms make four Zn–O–As bonds with an average Zn–O–As bond angle of 126.3° arising from a fairly wide spread of angles. Of the four arsenic atoms, As(3) makes three and possesses one terminal linkage whilst the remaining As atoms make four As–O–Zn bonds. The P–O distances are in the range 1.660(8)–1.741(5) Å [av. As(1)–O = 1.676, As(2)–O = 1.682, As(3)–O = 1.687 and As(4)–O = 1.685 Å] and the O–As–O bond angles have an average value of 109.5°. The terminal As(3)–O(12) linkage with a distance of 1.741(7) is a –OH group. The total negative charge on the framework of −3 is balanced by the presence of one fully protonated AE-DAP molecule. Bond valence sum calculations[22] on the framework agree with the above results.

The framework structure of **I** is built from the vertex linkages of ZnO_4, AsO_4 and $HAsO_4$ tetrahedral units. The three-dimensional structure of **I** can be understood from simpler building units. Thus, the connectivity between $Zn(2)O_4$, $Zn(3)O_4$, $Zn(4)O_4$ and $As(1)O_4$, $As(2)O_4$ and $As(4)O_4$ tetrahedral units forms 3- and 5-membered rings, which are joined through 4-membered rings forming the fundamental building unit as shown in Fig. 3a. These building units are further connected forming a hollow column (Fig. 3b), which sits on the two-fold screw axis thereby giving helicity to the structure. Two such columns are linked through $Zn(1)O_4$and $As(3)O_3(OH)$ tetrahedra forming the helical channels bound by 8-T atoms (T = Zn and As) in the *bc* plane (Fig. 4). The 8-membered channels are also connected to another 8-membered channel in the *ac* plane giving rise to interconnected helical one-dimensional channels, within which the amine and water molecules are situated. The channel along the *b* axis is shown in Fig. 5.

Multipoint hydrogen bond interactions are an integral part of the open-framework structures and help in the formation and stability of such architectures. In the present case also, we find strong hydrogen bond interactions involving the hydrogen atoms attached to the amine and water molecule with framework oxygen atoms. Thus, a large number of strong N–H ··· O and C–H ··· O hydrogen bond interactions exist in **I**. The majority of the interactions are quite strong as indicated by the short donor–acceptor distances (~2.8 Å) and donor–hydrogen–acceptor anlges of >150°. The important hydrogen bond interactions for **I** are listed in Table 4.



(a)

(b)

Fig. 3 (a) The basic building unit in **I**. Note that the 3- and 5-membered rings are connected through 4-membered rings. (b) The one-dimensional helical column formed by the connectivity between the basic building unit.

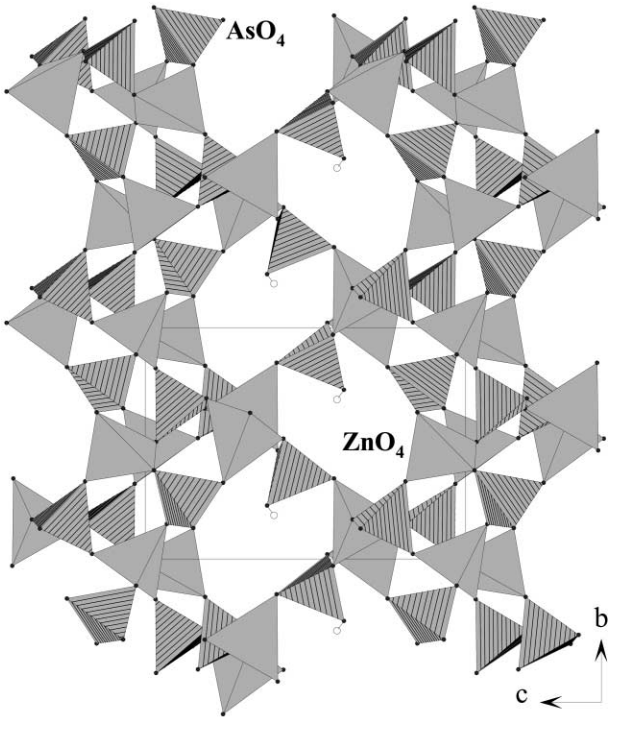


Fig. 4 The structure of **I** showing the polyhedral connectivity and the 8-membered helical channels along the [100] direction. Amine and water molecules are omitted for clarity.

The framework density,[23] defined as the number of tetrahedral atoms per 1000 Å^3, for **I** is 16.7. This indicates a fair degree of openness in the structure and is comparable to aluminophosphate molecular sieves such as AlPO-12 and AlPO-16.[23] Compound **I** has a Zn : As ratio of 1 : 1, which is rather unusual as most of the zinc arsenates and phosphates have a Zn : As/P ratio >1.0. The difficulty in obtaining a zinc arsenate or phosphate structure with a Zn : As ratio of 1 : 1, is in packing enough bulky organic cations into the extra-framework pores to achieve the charge balance. In **I**, the presence of a fully protonated amine molecule along with the presence of the terminal As–OH linkages helps in the charge neutrality.

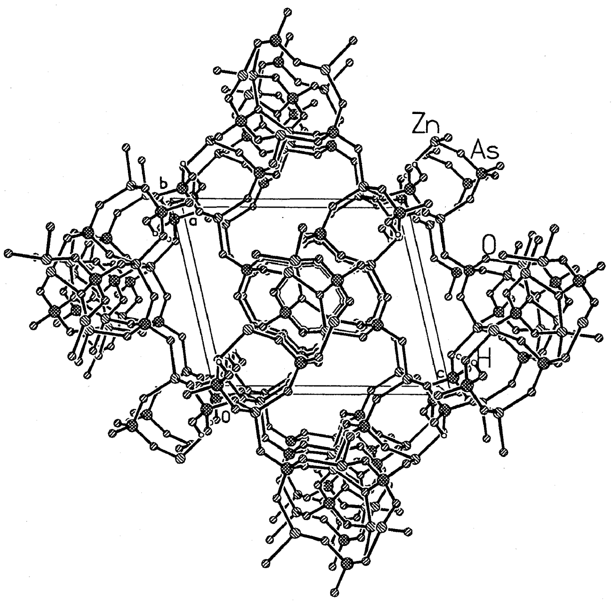


Fig. 5 The structure of **I** along the [010] direction. Amine and water molecules are not shown.

The initial synthesis of **I** has been carried out by the addition of oxalic acid in the medium, in addition to hydrochloric acid. It is likely that the Cl^- ions might just be acting as a mineralizer similar to the F^- ions in some of the syntheses of the phosphates of Al and Ga.[24] The role of oxalic acid in the formation of **I** is not clear. It is likely that the oxalate ions, present in the mixture during the synthesis, might act as a base and favor deprotonation of the H_3AsO_4. The fact that **I** predominantly contains AsO_4 units (completely deprotonated H_3AsO_4) lends credence to this argument. This suggestion is also validated by the formation of **I** employing zinc acetate in place of ZnO in the starting mixture, acetate anions might have played a similar role to the oxalate ions in solution. The use of organic mono- and di-acids as additives in the synthesis of zinc phosphates invariably resulted in the formation of zinc phosphates possessing completely deprotonated PO_4 units.[25,26] It appears that by deprotonating the arsenic acid, the mono- and di-carboxylic acids help in maintaining the pH of the reaction mixture, which might be crucial in the synthesis of new open architectures. The framework structure of **I** is similar to the zinc phosphate structure described earlier.[18] The zinc phosphate structure was prepared in the presence of diethylenetriamine (DETA), a symmetrical amine compared to the present case where an asymmetrical amine has been used. Though it is difficult to comment on the role of the amine molecule in directing the formation of a particular framework, it is becoming clear that the use of diamines and polyamines appears to favor the formation of newer architectures.

In summary, the solution mediated synthesis and structure of a new three-dimensional zinc arsenate, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$, **I**, possessing intersecting helical channels has been accomplished. The use of asymmetric amine molecules appears to hold much promise and we are currently pursuing this theme to prepare many novel hybrid solids.

Acknowledgements

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Table 4 Important hydrogen bond interactions in **I**, $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]\cdot H_2O$

D–H ··· A	D–H/Å	H ··· A/Å	D ··· A/Å	D–H ··· A/°
N(1)–H(1) ··· O(100)	0.89	1.92	2.710(4)	146
N(1)–H(2) ··· O(15)	0.89	2.09	2.970(6)	171
N(1)–H(3) ··· O(3)	0.89	2.06	2.804(8)	140
N(2)–H(8) ··· O(11)	0.90	1.89	2.781(5)	170
N(2)–H(9) ··· O(10)	0.90	2.03	2.907(7)	164
N(3)–H(17) ··· O(8)	0.89	1.91	2.751(2)	158
N(3)–H(18) ··· O(7)	0.89	1.95	2.802(1)	161
O(12)–H(30) ··· N(1)	0.82	2.50	3.276(2)	159
O(100)–H(101) ··· O(9)	0.97	2.06	2.947(6)	150
C(1)–H(4) ··· O(4)	0.97	2.56	3.517(8)	169

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