

# A chiral, 16-ring channel framework and a layered caesium zincarsenate

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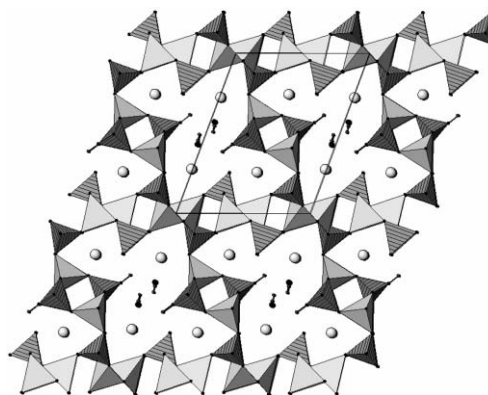
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Caesium zinc arsenate frameworks with a large, chiral pore and an expansive interlayer region have been synthesised.

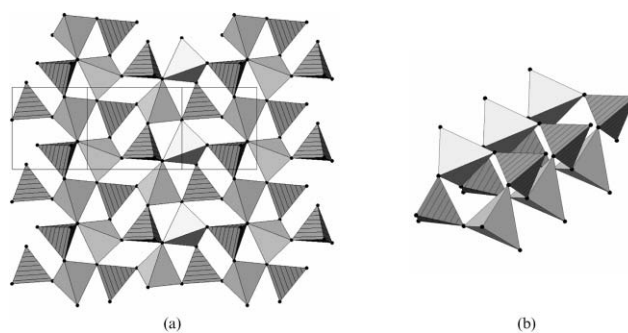
Framework materials have been extensively studied due to their important applications as, for example, cation exchangers, catalysts and non-linear optical materials. Oxotetrahedral frameworks are the most prevalent structures of this type as exemplified by the large number of zeolite, aluminophosphate and zincophosphate structures.<sup>1</sup> Major aims of synthetic framework chemistry are large pore structures, containing channels defined by more than 12 tetrahedral units, chiral porous structures to permit, potentially, asymmetric in-pore reactions and accessible layer structures with selectivity in the ion exchange of large cations, such as Cs<sup>+</sup>. At present the largest channel sizes in zeolites, 18 and 20 membered rings, are found in the high symmetry (hexagonal or cubic) frameworks with the structure codes VFI, ETR and CLO (interrupted) while zeolite BEA, with a 12-ring channel, adopting the acentric space group *P*4<sub>1</sub>22 has the largest non-centrosymmetric zeolite structure.<sup>2</sup> Structures containing ion exchangeable metal cations of toxic heavy metals or radioactive nuclides, such as <sup>134</sup>Cs and <sup>90</sup>Sr, have been sought and well characterised examples include the titanosilicates<sup>3</sup> and Cs<sub>3</sub>W<sub>4</sub>O<sub>7</sub>(PO<sub>4</sub>)·H<sub>2</sub>O.<sup>4</sup> A layered, pocketed clay-like structure would offer excellent exchange-site accessibility coupled with high site selectivity. Many structures formed from linked (hydrogen) phosphate/phosphite and zincate tetrahedra have been produced recently<sup>5–8</sup> but structures incorporating tetrahedral arsenate groups, [As(O,OH)<sub>4</sub>], have been much less well explored. However, this system offers a fertile area for generating new and useful structure types especially as the [As(O,OH)<sub>4</sub>] unit often exhibits unusual coordination environments in frameworks.<sup>9,10</sup> In this communication we report a zincarsenate framework with large chiral channels and a layered zincarsenate with a vast, pocketed interlayer region templated around Cs<sup>+</sup>.

The structure of Cs<sub>2</sub>(ZnAsO<sub>3</sub>OH)(ZnAsO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**I**) consists of alternating linked ZnO<sub>4</sub>, AsO<sub>4</sub> and As(O<sub>3</sub>OH)<sub>4</sub> tetrahedra surrounding channels containing caesium ions and water molecules, Fig. 1.† The framework can be considered as derived from dense layers of tetrahedra linked in 3 and 4 rings (Fig. 2a) that are connected together by ladders constructed from alternating As(O<sub>3</sub>OH) and ZnO<sub>4</sub> tetrahedra (Fig. 2b). The distribution of these ladders, separated by 10.7 Å, plus their significant size, separating the layers by the *c* axis dimension of 13.7 Å, leaves large voids between the layers and generates the 16-ring pores that run

through the structure along the *b* axis. The 2<sub>1</sub> screw axis, the only symmetry element in the unit cell, runs along this channel. This main channel also contains the caesium ions and water molecules. The caesium cations occupy two types of site and reside near the centre of the main channel and also in side-pockets formed by the framework tetrahedra. One caesium ion (Cs2) is solely coordinated by framework oxygen atoms (9 × Cs2–O 3–3.6 Å) while the other (Cs1) is coordinated by five framework oxygen atoms and the oxygen atoms of two of the water molecules, which are located at the centre of the channel, (total of 7 × Cs1–O 3.0–3.5 Å). The other unusual feature of this structure is the presence of a strong hydrogen bond, O–H···O 2.51 Å, between two of the As(O,OH)<sub>4</sub>



**Fig. 1** The structure of Cs<sub>2</sub>(ZnAsO<sub>3</sub>OH)(ZnAsO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**I**) viewed down *b* into the main 16-membered ring channel. AsO<sub>4</sub> tetrahedra are shown as hatched, dark grey and ZnO<sub>4</sub> as pale grey polyhedra. Oxygen and hydrogen atoms are shown in black and caesium as large pale grey spheres. The unit cell is outlined.

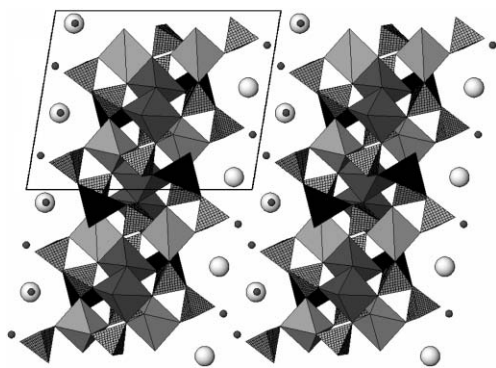


**Fig. 2** (a) The main layer in the *ab* plane of connected ZnO<sub>4</sub> and AsO<sub>4</sub> tetrahedra (shading as in Fig. 1), (b) the ladder motif that connects the layers shown in (a).

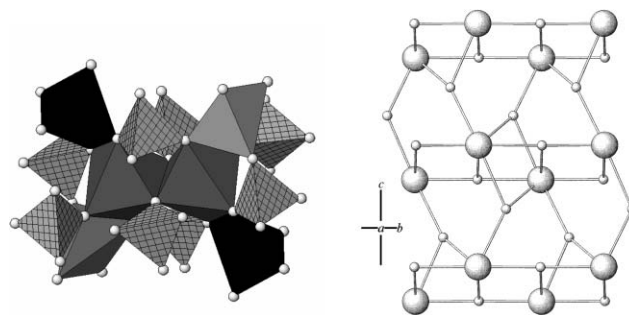
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tetrahedra, that lie at the edges of the pockets containing the caesium ions (Cs(2)). Due to their orientation and the fact the proton site is only partially occupied, the side pockets containing Cs(2) are fully accessible. Thus the structural elements present in  $\text{Cs}_2(\text{ZnAsO}_3\text{OH})(\text{ZnAsO}_4)_2 \cdot \text{H}_2\text{O}$  indicate that the material should demonstrate the properties associated with such frameworks including reversible molecular adsorption and cation exchange. Thermogravimetric analysis of the material, between room temperature and 800 °C, showed an initial, slow dehydration with an onset at around 100 °C and complete at 200 °C; the final weight loss stage, between 450 and 500 °C, is associated with the decomposition of the hydroxyl units of the  $\text{AsO}_3\text{OH}$  tetrahedra. The final product obtained following heating to 600 °C was identified, by powder X-ray diffraction, as predominantly  $\text{Cs}_2\text{As}_4\text{O}_{12}$ . Powder X-ray diffraction patterns collected between room temperature and 250 °C were analysed to determine changes in unit cell dimensions as a function of temperature associated with the loss of water from the pores to yield  $\text{Cs}_2(\text{ZnAsO}_3\text{OH})(\text{ZnAsO}_4)_2$ . This removal of water molecules from the main channel at between 100 and 200 °C results in a small expansion in unit cell volume from around 747 Å<sup>3</sup> (as measured between 25 and 100 °C) to approximately 756 Å<sup>3</sup> between 150 and 250 °C (*cf.* a cell volume of 724 Å<sup>3</sup> at 120 K). Material that had been dehydrated by heating to 250 °C was found to rapidly rehydrate on exposure to moist air to yield the parent  $\text{Cs}_2(\text{ZnAsO}_3\text{OH})(\text{ZnAsO}_4)_2 \cdot \text{H}_2\text{O}$  phase and the return of the lattice parameters to their initial values. The ion exchange potential was investigated by stirring  $\text{Cs}_2(\text{ZnAsO}_3\text{OH})(\text{ZnAsO}_4)_2 \cdot \text{H}_2\text{O}$  with various concentrations of KCl solution (0.1–2 M) for 2–12 h at between 25 and 60 °C. Powder X-ray diffraction data from the products isolated from these solutions showed that the zincocarbonate had undergone a significant contraction of the unit cell. Initial, tentative, indexing of the powder diffractogram suggested a monoclinic cell of approximate dimensions 8.1 Å × 5.2 Å × 10.5 Å,  $\beta = 108^\circ$  for the fully exchanged product obtained from 2 M KCl.

The structure of  $\text{CsAs}_3\text{Zn}_3\text{O}_{13}\text{H}_4 \cdot 2\text{H}_2\text{O}$  (**II**) consists of layers of composition  $\{\text{ZnAs}(\text{AsO}_2(\text{OH})_2)(\text{AsO}_3\text{OH})(\text{ZnO}_5)(\text{ZnO}_4\text{OH})\}^-$  separated by caesium ions and water molecules, Fig. 3.† The layers are constructed from a mixture of partially protonated  $\text{ZnO}_5$ ,  $\text{ZnO}_6$  and  $\text{AsO}_4$  polyhedra. At the centre of the layer are



**Fig. 3** The structure of **II** shown side on to the layers delineating the  $\text{ZnO}_n$  and  $\text{AsO}_4$  tetrahedra (shading as in Fig. 4). Cs ions are shown as large pale gray spheres, and oxygen atoms of the interlayer water as dark gray spheres. Proton positions are not shown for clarity.



**Fig. 4** (Left) The core unit present in compound **II** with double  $\text{ZnO}_6$  octahedra (dark grey) surrounded by  $\text{ZnO}_5$  polyhedra (mid grey and black) and  $\text{AsO}_4$  tetrahedra (hatched grey). (Right). The arrangement of the caesium ions (large grey spheres) and water oxygen atoms (small spheres) interlayer region.

two  $\text{ZnO}_6$  octahedra sharing an edge; the opposite two pairs of edges on these  $\text{ZnO}_6$  octahedra are shared with  $\text{Zn}(\text{O},\text{OH})_5$  square pyramidal units and vertices of the double octahedra are bridged by  $\text{As}(\text{O}_3\text{OH})$  groups, Fig. 4. Further  $\text{AsO}_4$  units bridge between the octahedra and the  $\text{ZnO}_5$  square-based pyramids as well as terminating the layers as  $[\text{AsO}_2(\text{OH})_2]$  tetrahedra with the protons facing out into the interlayer region. The Cs ions are 11 coordinate to the protonated layer oxygens of the  $[\text{AsO}_2(\text{OH})_2]$  groups ( $4 \times \text{Cs-O}$  3.15–3.8 Å) and to two crystallographically different interlayer water molecules ( $7 \times \text{Cs-O}$  3.23–3.67 Å). This produces an interlayer solvated network into which the Cs ions are weakly bound, Fig. 4, and thus presumably highly mobile. Preliminary ion exchange experiments show rapid replacement of the interlayer caesium, by potassium and other Group 1 and 2 metal cations, with concomitant reduction in the interlayer spacing. It is likely, based on the calculated powder X-ray diffraction pattern, that this material is an analogue of a naturally occurring magnesium arsenate (JCPDS Powder Diffraction File No 51-1473).

In summary two new framework materials have been synthesised in the zincocarbonate system. The main channels of **I** contain the only symmetry of the unit cell, a  $2_1$  screw axis, and also have pendent protons decorating their sides. The material,  $\text{Cs}_2(\text{ZnAsO}_3\text{OH})(\text{ZnAsO}_4)_2 \cdot \text{H}_2\text{O}$ , shows ion exchange and reversible adsorption properties indicating that this new type of framework may have useful applications associated with enantiomeric selectivity and selective trapping of large cations. While the material produced and studied in this work was a partial mixture of the two enantiomers (as an approximate 75 : 25 racemic twin) further investigations are ongoing with the aim of producing a single chiral form.

Compound **II** has a pocketed layer structure and initial results indicate excellent ion exchange behaviour, presumably as a result of rapid ion diffusion into the aqueous interlayer region; high selectivity for large cations should result from the pocketed nature of the interlayer region which provides large sites for ions such as caesium. Further investigations of the adsorption and ion exchange properties of these compounds, and details of other phases formed in the alkali metal–zincocarbonate system, will be reported in a full paper.

We would like to thank M. E. Light for help with the structure solutions.

## Notes and references

† The synthesis of the new zincarsenate framework compound was performed *via* a hydrothermal reaction at 453 K. A variety of reaction conditions and compositions were studied in the CsOH, H<sub>3</sub>AsO<sub>4</sub>, Zn<sup>2+</sup> system. A typical reaction involved the addition of 50 wt% caesium hydroxide solution (1.31 mL, 7.5 mmol) to a solution containing 1 M zinc chloride solution (2.5 mL, 2.5 mmol), 4 M arsenic acid solution (0.625 mL, 2.5 mmol), (Cs : Zn : As = 3 : 1 : 1 in this case) and distilled water (9 mL) in a 23 mL Teflon lined steel autoclave. The reaction was heated for 48 h. Once cool the product was filtered, washed with ethanol and dried overnight at 80 °C. Investigation of the products by powder and single crystal X-ray diffraction revealed the presence of four phases in this system; the known phases Zn<sub>9</sub>(AsO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub> and Zn<sub>2</sub>(AsO<sub>4</sub>)(OH) (adamite), and compounds **I** and **II**. Compound **I** was obtained in high yield from mixtures with Cs : Zn : As ratios in the range >3 : 1 : 1 while **II** formed typically in reactant ratios with less Cs, *e.g.* 2 : 1 : 1.

Crystal data for **I** at 120 K. Empirical formula Cs<sub>2</sub>Zn<sub>3</sub>As<sub>3</sub>O<sub>13</sub>H<sub>3</sub>, monoclinic, space group *P*2<sub>1</sub>, *a* = 10.7658(6) Å, *b* = 5.2115(3) Å and *c* = 13.7478(8) Å, β = 110.24°, *V* = 723.62(7) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 4.073 g cm<sup>-3</sup>. μ(Mo-Kα) = 16.77 mm<sup>-1</sup>. A total of 8760 reflections were collected of which 1858 were unique. There were 202 parameters with 1 restraint. SORTAV was used to perform the absorption correction, giving maximum and minimum transmission factors of 0.8502 and 0.2848 respectively. Lorentzian polarisation was corrected using Scalepack. The refined Flack parameter was 0.22(3) indicating a partially racemic twin. *R*<sub>1</sub> = 0.0488 and *wR* = 0.1243 for 2837 independent reflections (*I* > 2σ(*I*)).

Crystal data for **II** at 120 K. Empirical formula CsAs<sub>3</sub>Zn<sub>3</sub>O<sub>14</sub>H<sub>8</sub>, monoclinic space group *P*2<sub>1</sub>/*c*, *a* = 16.1047, *b* = 6.5829(4), *c* = 12.9291(7), β = 99.263(4)°, *V* = 1352.8(1) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 3.937 g cm<sup>-3</sup> μ(Mo-Kα) = 15.29 mm<sup>-1</sup>. 25027 reflections measured of which 3130 were unique (*R*<sub>1</sub> =

0.0373), *wR* 0.089. Powder X-ray diffraction data were collected on a Bruker D8 diffractometer with Anton-Parr high temperature attachment and operating with monochromated Cu-Kα<sub>1</sub> radiation.

Further details of the crystal structure solution of **I** may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number 415779. CCDC 290224 and 290225. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516293a

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