Iron arsenate frameworks†

Seth B. Wiggin,^a Robert W. Hughes,^a Daniel J. Price^b and Mark T. Weller^{*a}

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Six new iron arsenate framework structures, $Fe_2As_2O_7 \cdot 2H_2O$, $[Fe_6As_8O_{32}H_4]^{2-}(1,4-butane-diamininium^{2+}) \cdot 2H_2O$, $[Fe_4As_6O_{22}H_2]^{2-}$ (piperazinium²⁺), $[Fe_5As_5O_{24}H_4]^{2-}$ (piperazinium²⁺) $\cdot 2H_2O$, $[Fe_6As_7O_{31}H_5]^{2-}$ (dabco²⁺) and LiFeAsO₄OH have been synthesised under hydrothermal conditions. Incorporation of the amine cation templates leads to more open framework geometries and, in contrast to iron phosphates which have topologies based on PO₄ tetrahedra, the iron arsenate structures typically contain protonated As(O,OH)₄ units. The magnetic properties of the iron arsenates studied show Curie–Weiss behaviours with maxima in the $\chi(T)$ vs. T plots in the range 10–50 K.

Introduction

Materials that adopt open-framework structures built from linked oxo-polyhedral units, MO_n , have been an area of intense research over the past few years.1 The interest in this class of compounds comes from a wide variety of potential applications, though these have mainly resulted from catalytic and adsorptive properties seen in compounds such as the zeolites (aluminosilicates) and aluminophosphates. Incorporation of transition metals into the framework often endows the materials with additional properties such as optical, electronic and magnetic effects. Transition metal containing frameworks based on phosphate groups have received most attention, although other tetrahedral moieties such as borate,² arsenate,³ sulfate⁴ and selenate⁵ have also been successfully incorporated. Hence the combination of PO43- with the late first row transition metal elements (Fe, Co, Ni) and with zinc has led to numerous framework structures, see for example the zeolite gismondine topology of ZnPO₄(H₃N(CH₂)₃NH₃)_{0.5}.⁶ With iron, several phosphate framework structures have gained importance with properties and applications associated with redox/ion (de)intercalation,⁷ e.g. LiFePO₄, molluscicides (FePO₄·2H₂O),⁸ catalysis (Fe₂(PO₃OH)P₂O₇)⁹ and magnetism (iron phosphate glass frameworks).10

Of the other oxotetrahedral units, TO_4^{n-} , T = B, As, S, Se, it is arsenate frameworks that show, perhaps, the greatest potential for forming framework structures in combination with the first row transition metals. Note that the larger size of the arsenate, AsO_4^{3-} , anion compared to phosphate, PO_4^{3-} , can lead to quite different framework topologies for a particular transition metal species and, hence, dissimilar properties. Furthermore frameworks incorporating arsenate into frameworks, using the hydrothermal conditions under which they normally form, often integrate the protonated units $As(O_3OH)$ and/or $As(O_2(OH)_2)$; this is despite the similar acidity of arsenic acid (pK_a values; 2.25 (K_1) 6.8 (K_2) 11.6 (K_3)) and of phosphoric acid (pK_a ; 2.15, 7.2, 12.7). A number of iron arsenates have been reported in the literature. $[Fe_3(AsO_4)_2(HAsO_4)_2](C_4N_2H_{12})^{11}$ and $[Fe_3(HAsO_4)_6]-(C_2N_2H_{10})\cdot NH_3\cdot NH_4^{12}$ are both examples of amine cation templated 3D structures. Fluorine can also be incorporated into the structure forming frameworks such as $Fe_2(AsO_4)F_5^{13}$ $[Fe_3F_3(AsO_4)(HAsO_4)_2](C_4N_2H_{12})_{1.5}^{11,14}$ and $[Fe_3(AsO_4)F_6](C_3N_2-H_{12})_{3/4}$,¹⁵ which contains mixed valence iron. Oxalate units have been incorporated into several hybrid oxalate–arsenate materials, for example $[Fe_4(HAsO_4)_6(C_2O_4)_2] (C_4N_2H_{12})_{2}^{16}$ and $[NH_3(CH_2)CH(NH_3)CH_3]_3 [Fe_6(AsO_4)_2(HAsO_4)_6(C_2O_4)_3]$.¹⁷

Despite these reports iron arsenate chemistry has remained relatively unexplored especially in comparison with that of iron phosphates. In this work we report the synthesis and characterisation, including preliminary magnetism data for several phases, of six new iron arsenate materials.

Experimental

Synthesis

For all materials, the reagents were sealed in a 23 ml Parr autoclave. The autoclave was heated in an oven, held at temperature and then oven cooled to room temperature. Solid products were recovered by filtration and washed with water, then ethanol before drying at 80 $^{\circ}$ C.

 $Fe_2As_2O_7.2H_2O$ (1). Iron(II) oxalate dihydrate (Aldrich, 99%, 0.4500 g, 2.5 mmol), 5 M arsenic acid solution ((synthesised from As₂O₃ (Aldrich, 99%)), 1.5 ml, 7.5 mmol), tetramethylammonium hydroxide 25 wt% soln (Aldrich, 0.9 ml, 2.5 mmol) and water (7 ml). Heated to 150 °C and held for 120 h. Product crystallised as colourless plates.

[Fe₆As₈O₃₂H₄]^{2–}(1,4-butanediamininium²⁺)·2H₂O (2). Iron(II) oxalate dihydrate (0.4500 g, 2.5 mmol), 5 M arsenic acid solution (1.5 ml, 7.5 mmol), 1 M 1,4-diaminobutane solution (Aldrich, 99%, 2.5 ml, 2.5 mmol) and water (6 ml). Heated to 150 °C and held for 120 h. Product occurred as colourless rod like crystals.

 $[Fe_4As_6O_{22}H_2]^2$ (piperazinium²⁺) (3). Iron(II) oxalate dihydrate (0.4500 g, 2.5 mmol), 5 M arsenic acid solution (1.5 ml, 7.5 mmol), 1 M piperazine solution (Aldrich, 99%, 2.5 ml, 2.5 mmol) and

^aSchool of Chemistry, University of Southampton, Southampton, UK SO17 1BJ. E-mail: mtw@soton.ac.uk

^bDepartment of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ † Electronic supplementary information (ESI) available: Table S1 - key hydrogen bond distances. See DOI: 10.1039/b702847d

water (6 ml). Heated to 160 $^{\circ}\mathrm{C}$ and held for 72 h. Product crystallised as blue needles.

 $[Fe_5As_5O_{24}H_4]^{2-}$ (piperazinium²⁺)·2H₂O (4). Iron (II) oxalate dihydrate (0.4500 g, 2.5 mmol), 5M arsenic acid solution (0.5 ml, 2.5 mmol), 1M piperazine solution (Aldrich, 99%, 2.5 ml, 2.5 mmol) and water (6 ml). Heated to 160 °C and held for 72 h. Product occurred as green fragments.

[Fe₆As₇O₃₁H₅]²⁻(dabco²⁺) (5). Iron(II) oxalate dihydrate (0.4500 g, 2.5 mmol), 5 M arsenic acid solution (1.5 mL, 7.5 mmol), 1 M 1,4-diazabicyclo[2.2.2]octane solution (Aldrich, 98%, 2.5 ml, 2.5 mmol) and water (6 ml). Heated to 150 °C and held for 120 h. Product precipitated as green plate crystals.

LiFeAsO₄**OH (6).** Iron sulfate heptahydrate (Aldrich, 99%, 0.6951 g, 2.5 mmol), ammonium dihydrogen arsenate (Alfa Aesar, 98%, 0.3975 g, 2.5 mmol), 1 M lithium hydroxide solution (Aldrich, 98%, 1.5 ml, 1.5 mmol) and water (5 ml). Heated to 220 °C and held for 24 h. Product occurred as green needle-shaped crystals.

Crystallographic determination

Suitable crystals of each material were selected for data collection on a Nonius Kappa CCD area detector diffractometer (Mo K α radiation) at 120(2) K. All calculations were carried out using the WINGX system¹⁸ (Version 1.70.01) and SHELX-97.¹⁹ Absorption corrections were applied using SADABS.²⁰ Key data collection and refinement details are given in Table 1.

CCDC reference numbers 639058-639063.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702847d

Thermal analysis

Samples of (1) and (5) were analysed using a Polymer Laboratories STA1500. In a typical experiment, 10–15 mg of compound was heated in flowing air from room temperature up to 850 °C at 10 °C min⁻¹. Mass loss and heat flow were recorded as a function of temperature.

Variable temperature powder X-ray diffraction

A sample of (1) was analysed using a Bruker D8 Advance diffractometer with Anton Parr HTK1200 furnace stage. The instrument was operated using Cu K α_1 radiation ($\lambda = 1.54056$ Å) and a SOL-X energy discriminating detector. Data were collected from 10–110° in 2 θ at 30, 150, 250, 325, 350, 375, 400, 425, 550 and 600 °C. The initial and final data sets were collected over 9 h and the intermediate sets were collected for 5 h.

Magnetic susceptibility measurements

These measurements were performed using a Quantum Design magnetic properties measuring system (MPMS) in an external magnetic field of 5 T.

Compound	1	2	6	4	S	6
Empirical formula	$\mathrm{H_4A_{S_2}Fe_2O_9}$	${ m C}_4{ m H}_{22}{ m N}_2{ m A}_{ m S_8}{ m Fe}_6{ m O}_{34}$	$C_4H_{12}N_2A_{86}Fe_4O_{22}$	$C_4 H_{18} N_2 A_{85} Fe_5 O_{24}$	$\mathrm{C}_6\mathrm{H}_{21}\mathrm{N}_2\mathrm{A}_{87}\mathrm{Fe}_6\mathrm{O}_{31}$	$HAsFeLiO_5$
Formula weight	409.56	1576.7	556.54	1168.09	1476.79	218.72
Temperature/K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Appearance	Colourless block	Colourless rod	Blue needle	Green fragment	Green plate	Green needle
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\overline{1}$	$P\overline{1}$
a/Å	6.6108(2)	10.1348(1)	6.7503(2)	6.637(2)	6.6364(1)	5.2652(3)
b/Å	14.3741(5)	10.8220(2)	7.7757(3)	22.195(6)	10.8179(4)	5.4841(3)
c/Å	7.6321(2)	14.3264(2)	11.2924(3)	17.312(6)	12.2213(5)	7.3932(4)
$a/^{\circ}$	90	06	72.396(2)	90	109.927(2)	110.669(3)
β/°	95.830(2)	90.158(3)	80.801(2)	94.14(2)	100.807(2)	105.318(3)
7 /0	06	06	79.085(2)	90	101.320(2)	98.160(4)
Volume	721.48(4)	1571.30(4)	551.40(3)	2543.7(1)	777.40(6)	185.98(2)
Z	4	7	7	4	1	1
$D_{ m c}/{ m g~cm^{-3}}$	3.771	3.332	3.352	3.050	3.154	3.906
θ range for data collection/°	3.03 - 27.485	3.10-27.53	2.91 - 27.485	2.99–27.53	3.23–27.72	3.16 - 27.70
Reflections collected	7380	34140	11548	27851	17658	3489
Independent reflections	1648	3604	2518	5819	3582	844
Data/restraints/parameters	1648/6/135	3604/3/252	2518/0/181	5819/9/397	3582/0/271	844/0/81
R_1	0.0339	0.0269	0.0345	0.0541	0.0505	0.0298
wR_2	0.0814	0.0698	0.0643	0.1318	0.1212	0.0673

 Table 1
 Crystal data for all compounds

Fe₂As₂O₇·2H₂O (1)

The formation of (1) required the presence of tetramethylammonium hydroxide in the synthesis medium, where it increases the solution pH, but the organic reagent is not incorporated into the final structure. The structure of Fe₂As₂O₇·2H₂O, which is isostructural with the reported phosphate Fe₂P₂O₇·2H₂O,²¹ has two distinct edge sharing $FeO_5(H_2O)$ octahedra that alternate to form an infinite zigzag chain. Separate chains are linked by As₂O₇ units to form a dense 3D framework with channels approximately 3×10 Å in the *a* direction. Fig. 1 shows the view down the a axis detailing the channel like structure, and a representation rotated by 90° in the *c* axis to show the packing of arsenate groups and iron chains. As can be seen from Table 1 the structure has a relatively high calculated density compared with the templated frameworks obtained in this work, vide infra, showing that other than the channels along the a axis the framework has little free space.

The hydrogen atoms were located during the refinement process and were fixed at standard O–H distances. There was no significant difference in Fe–O bond lengths between the terminal bonds to water and other bridging oxygen atoms. IR spectroscopy confirmed the presence of hydroxyl groups with a strong peak centred at 3470 cm^{-1} .

The water molecules in the structure are responsible for six intraframework hydrogen bonds of varying strength, detailed in Table S1 (see ESI).† The water molecule orientations (approximately 90° apart) presumably maximise the hydrogen bonding contacts across the channels in the structure where the water molecules are in close proximity.

Thermogravimetric analysis was carried out on an 11.420 mg sample of $Fe_2As_2O_7 \cdot 2H_2O$. The sample was heated to 850 °C at 10 °C min⁻¹. Mass was lost in two stages, from 200 to

370 °C, and then on to 600 °C at a slower rate. The mass then remained constant to maximum temperature. The total mass loss of around 8% was close to the calculated loss of 9% for complete dehydration. A further sample of Fe₂As₂O₇·2H₂O was then analysed by VTXRD in order to identify the dehydration products. The powder X-ray diffraction pattern collected, *in situ*, from a sample heated to 325 °C showed the formation of FeAsO₄ indicating that the dehydration/oxidation has proceeded *via* the reaction:

$$Fe_2As_2O_7{\cdot}2H_2O + 1/2O_2 \rightarrow 2FeAsO_4 + 2H_2O$$

This is in contrast to the known magnesium compositional analogue, $Mg_2As_2O_7$, $2H_2O$, which dehydrates to form $Mg_2As_2O_7$.²²

The material contains chains of Fe²⁺ ions, making it a d⁶ system. A $\chi(T)$ plot (Fig. 2) shows a maximum at about 13(1) K with χ_{max} at 0.160 cm³ mol⁻¹. A plot of $\chi^{-1}(T)$ shows that Curie–Weiss behaviour is followed above ~100 K and



Fig. 2 Left: Plot of magnetic susceptibility (black circles) and inverse susceptibility (white circles) *versus* temperature for $Fe_2As_2O_7 \cdot 2H_2O$.



Fig. 1 Left: Structure of $Fe_2As_2O_7$ ·2H₂O looking down the *a* direction. Right: View down the *c* axis. FeO₆ octahedra are shaded grey and AsO₄ tetrahedral units black; hydrogen positions are shown as grey shaded thermal ellipsoids.

a Curie–Weiss fit gives $C = 3.57(1) \text{ cm}^{-3} \text{ mol } \text{K}^{-1} \text{ and } \theta = -4.3(2) \text{ K}$. A plot of $\mu_{\text{eff}}(T)$ shows a decreasing moment on cooling and a room-temperature moment of 5.29 μ_{B} . The magnetic susceptibility of the isostructural cobalt sample has been investigated previously,²³ and reveals a similar behaviour. In this cobalt material the susceptibility reaches a maximum at *ca*. 10 K before a sharp drop, indicative of antiferromagnetic behaviour. A Curie–Weiss fit gave $C = 6.41 \text{ cm}^{-3} \text{ mol } \text{K}^{-1} \text{ and } \theta = 8.29 \text{ K}.$

$[Fe_6As_8O_{32}H_4]^{2-}(1,4-butanediamininium^{2+})\cdot 2H_2O(2)$

In (2) the protonated amine acts as a template and is incorporated into the final product. The structure consists of iron arsenate chains running along the *a* axis with approximate dimensions 5×8 Å. The chains (shown in Fig. 3) have three edge sharing iron octahedra separated by a layer of corner sharing arsenate tetrahedra, so that the layer iron octahedra are linked by 8-rings with neighbouring layers. The chains form into a 3D structure by linking to four other chains *via* corner sharing oxygen atoms from both the arsenate tetrahedra and iron octahedra. This corner sharing between chains leaves large channels in the structure, of similar size to the iron arsenate chains. The water and 1,4butanediamininium cations are situated in these large channels, the long dimension of the amine cation running parallel to the iron arsenate chains, as shown in Fig. 3.

Fig. 3 Upper : Structure of $Fe_6As_8O_{32}H_4(1,4\text{-diaminobutane})\cdot 2H_2O$ looking down the *a* direction. Lower: Structure of the chains which run parallel to the *a* direction. Shading of polyhedra as in Fig. 1. Water oxygen, carbon and nitrogen are medium grey spheres and hydrogen atoms are small grey spheres.

The material forms a number of hydrogen bonds between the framework and the amine cation and water molecules in the channel structure, and also intraframework linkages. As can be seen from the list of such bonds in Table S1 (see ESI),† the length, and therefore strength, of the hydrogen bonds is quite varied. The amine molecule only forms two bonds to the framework. One of these, $(O11 \cdots N1)$ is presumably quite weak due to the large bond length, 3.456(4) Å. The water molecule appears to be more strongly held with three bonds to the framework, indicating this may be harder to remove during thermal decomposition, *i.e.* requiring higher temperatures. The atoms within the structural framework of the material all have relatively small thermal displacement parameter ellipsoids. However, the oxygen atom of the water molecule, O1W, has significantly larger thermal motion consistent with a greater degree of mobility of this non-framework moiety.

This structure is the first 1,4-butanediamininium cation templated iron arsenate material reported; though *n*-alkyl diamine cations have been used for similar framework structures such as $(NH_3(CH_2)_3NH_3)_{0.5}[Fe(OH)AsO_4]$, a 2D layered iron arsenate reported by Liao *et al.*²⁴ There are two reported iron phosphate materials with a 1,4-butanediamininium cation template, though both these have a markedly different framework motif to the iron arsenate material reported herein. The hexagonal material Fe₈P₁₄O₆₂H₂₄(C₄H₁₄N₂)₃ reported by Korzenski *et al.*²⁵ has isolated FeO₆ octahedra. The iron fluorophosphate material Fe₅P₆F₃O₂₇H₆(C₄H₁₄N₂)₃·2H₂O reported by Riou-Cavellec *et al.*²⁶ adopts a 2D layered structure.

$$\label{eq:2.1} \begin{split} & [Fe_4As_6O_{22}H_2]^{2-}(piperazinium^{2+})~(3)~and \\ & [Fe_5As_5O_{24}H_4]^{2-}(piperazinium^{2+}){\cdot}2H_2O~(4) \end{split}$$

Structures (3) and (4) demonstrate the effect that varying molar ratios can have on product formation even with the same template. The same reagents and reaction conditions were used, but (3) has an As : Fe ratio of 1.5 : 1, and was isolated from an arsenic rich solution with an As : Fe molar ratio of 3 : 1, while (4) has As : Fe of 1 : 1 and is derived from a solution with an equimolar As : Fe ratio.

The structure of (3) has two crystallographically distinct iron (III) octahedra that form an infinite zigzag chain through edge sharing. Arsenate tetrahedra and As_2O_7 units separate the chains; this creates sheets in the *ab* plane. The piperazinium molecular ions occupy space between these sheets. The structure could also be described as quasi, three-dimensional pore-like, with the arsenate tetrahedra extending strongly into the interlayer space producing a closest contact of only 2.46 Å between two O10 atoms from opposite layers.

This is quite different from (4), which possesses a much more strongly corrugated iron arsenate layer that maintains a regular spacing between layers. A comparison between the two structures is shown in Fig. 4. The corrugation arises from the bonding motif of the iron octahedra. The asymmetric unit contains five iron atoms that form two parallel chains of edge sharing octahedra. The chain motif is not a simple zigzag having a repeating wave-like curve over ten individual octahedra. In contrast to (3) arsenic is present only as AsO₄ tetrahedra with no As₂O₇ units. The arsenate bridges between the chains of iron octahedra making an infinite sheet in the *ac* plane. The iron arsenate framework of (4) has many hydroxide groups present; evidence for the AsO₂(OH)₂ tetrahedra and FeO₄(OH)₂ and two FeO₅(OH) octahedra present comes from differences in bond lengths between these and typical As–O and Fe–O bonds.





Fig. 4 Comparison of the layer structures of $[Fe_4As_6O_{22}H_2]^{2-}$ (piperazinium²⁺), (left) and $[Fe_5As_5O_{24}H_4]^{2-}$ (piperazinium²⁺)·2H₂O, (right). Shading scheme as in previous figures.

A comparison of the unit cell dimensions of materials (3) and (4) highlights the difference in bonding motifs. The long b and c axes of material (4) are due to the large interlayer space and corrugated structure. The structure of material (4) as a whole exhibits a complex hydrogen bonding network, details of which are given in Table S1 (see ESI).† The network is responsible for the location of the piperazinium molecule and water molecules between the framework layers. The piperazinium ion forms five separate bonds to the framework and neighbouring water molecule. By contrast the amine cation in (3) forms only two hydrogen bonds, implying the structure may be more likely to possess ion-exchange properties as the templating cation is less rigidly held in place.

Both structures show relatively small thermal ellipsoids for the templating amine cation and water molecules. This implies a low level of disorder and a fixed position for these molecules. In material (3) hydrogen atoms were given fixed positions for hydroxyl and amine groups. The amine cation in material (4) has fixed positions for C–H bonds but refined N–H bond lengths.

The magnetic susceptibility of material (3) has been analysed; a $\chi(T)$ plot (Fig. 5) shows a broad maximum at about 30(1) K with χ_{max} at 0.061 cm³ mol⁻¹. A plot of $\chi^{-1}(T)$ shows that Curie– Weiss behaviour is followed above ~100 K and a Curie–Weiss fit gives C = 5.6(1) cm⁻³ mol K⁻¹ and $\theta = 25(1)$ K. The positive Weiss constant implies ferromagnetic interactions, although the overall behaviour of the magnetic susceptibility is characteristic of antiferromagnetism. A plot of $\mu_{eff}(T)$ shows a decreasing moment on cooling and a room-temperature moment of 5.50 µ_B.

Iron arsenate piperazinium structures have been previously reported. The material, $As_4Fe_3O_{16}H_2(C_4N_2H_{12})^{11}$ was produced as part of an investigation into an iron arsenate oxalate system. The material was produced by heating the material



Fig. 5 Left: Plot of magnetic susceptibility (black circles) and inverse susceptibility (white circles) *versus* temperature for $Fe_4As_6O_{22}$ (piperazine²⁺).

 $[Fe(OH)(HAsO_4)(C_2O_4)](C_4N_2H_{12})\cdot H_2O, and has a greater structural similarity to (2) than either of these piperazine templated structures. The same units are also observed in another oxalatorion arsenate piperazine structure, ¹⁶ C₈H₁₂As₁₂Fe₈O₆₄(C₄N₂H₁₂)₄. More similar to the structures found in this work for (3) and (4) is that of the fluoro-iron arsenate piperazinium As₃F₅Fe₃O₁₂H₂(C₄N₂H₁₂)_{1.5} which has a 2D framework with intercalated piperazine molecules.¹⁴$

$[Fe_6As_7O_{31}H_5]^{2-}(dabco^{2+})$ (5)

The material $As_7Fe_6O_{31}H_7(C_4N_2H_{14})$ (5) crystallises in the triclinic space group, $P\overline{1}$. Some difficulties were apparent in modelling the diffraction data and these stem from structural disorder at

two sites within the material. The first was the orientation of the templating dabco unit: this unit was finally modelled by positioning the molecule over two sites, related by a centre of inversion so that the four of the six carbon atoms are common to the two possible dabco orientations. The nitrogen and non-shared carbon atoms were assigned as half occupancy sites. All hydrogen atoms were modelled with fixed positions and thermal parameters. The resultant large and highly elliptical thermal parameters still found for all atoms within this unit indicate probable further disorder of the template though the current model replicates the scattering distribution reasonably well.

The second site of disorder is associated with the arsenate unit (As4) that is pendent from the main iron arsenate sheets and which was modelled (together with the associated oxygen atoms O10, O11 and O12) as a half-occupied site; full occupation of this site would produce two adjacent arsenate units (attached and facing towards each other from neighbouring iron arsenate sheets) with impossibly short oxygen to oxygen close contacts.

A large thermal ellipsoid occurs for the oxygen atom O6. The reasons for this are unclear, the short As2-O6 bond length of 1.55(1) Å clearly indicates a terminal double bonded oxygen atom and the reagents used leave few possible alternatives. Evidence for hydroxyl groups was clearly seen by IR spectroscopy, assigning the individual -OH groups was performed on the basis of bond lengths. The terminal oxygen atoms O11, O13 and O16 were obvious likely candidates, whereas the short bond lengths of O6 and O10 ruled out possible hydroxyl groups. In order to form a charge neutral material an additional hydroxyl group was required; investigating the bond lengths further showed the As-O bond lengths for O3, O5, O7, O8, O11, O14 and O15 were all >1.7 Å and therefore possible hydroxyl groups. Of these, all were three coordinate oxygen atoms, apart from O8 and O11. It was therefore decided to assign O8 as the final hydroxyl group by adding a hydrogen atom with fixed bond length and temperature factors.

The structure of (5) is shown in Fig. 6. The iron arsenate layers along the ab plane are made up from zigzag chains of edge sharing iron(III) octahedra separated by isolated corner sharing AsO₄ tetrahedra. The partially occupied As4O₄ tetrahedra is positioned



Fig. 6 Structure of $Fe_6As_7O_{31}H_7(dabco^{2+})$ looking down the *a* direction. Shading scheme as per previous figures.

out of the plane and forms very close O–O distances (O11–O12 = 1.32(2) Å) with those in neighbouring layers. As the sites are half occupied it is likely that the tetrahedra are randomly distributed along the surface of the planes but avoiding opposing units.

The hydrogen bonding, shown in Table S1 (see ESI),† reveals interesting differences between the two possible amine cation positions. The nitrogen atom N1 makes three hydrogen bond links with the framework, connecting to O4, O8 and O17. However these bonds are rather weak with long donor to acceptor distances. By contrast N2 makes only one hydrogen bond to O4, but this bond is likely to be much stronger, being both shorter and closer to 180°.

The magnetic behaviour of the sample was analysed using a SQUID magnetometer in the range 4–300 K. A $\chi(T)$ plot (Fig. 7) shows a broad maximum at about 34(1) K with χ_{max} at 0.0358 cm³ mol⁻¹. A plot of $\chi^{-1}(T)$ shows that Curie–Weiss behaviour is followed above 53 K and a Curie–Weiss fit gives C =3.83(5) cm⁻³ mol K⁻¹ and $\theta = -13.3(3)$ K. A plot of $\mu_{eff}(T)$ shows a decreasing moment on cooling, however the level has not settled by room temperature.



Fig. 7 Left: Plot of magnetic susceptibility (black circles) and inverse susceptibility (white circles) *versus* temperature for $Fe_6As_7O_{31}H_7(dabco^{2+})$.

The negative Weiss temperature and decreasing moment on cooling indicate antiferromagnetic behaviour, and this has been analysed using Fisher's model of S = 5/2 interacting chains, with coupling constants J = -1.49(4) K and J' = 2.22(4) K.

Relatively few dabco templated frameworks containing iron are known. There are three phosphates in the literature $[C_6N_2-H_{14}]_2[Fe_3(OH)F_3(PO_4)(HPO_4)_2]_2\cdot H_2O$, $[C_6N_2H_{14}][Fe_2F_2(HPO_4)_2-(H_2PO_4)_2]\cdot 2H_2O^{27}$ and $[Fe_4(PO_4)_2F_2(H_2O)_3]\cdot [C_6H_{14}N_2]^{28}$ are all 3D open framework materials. One iron arsenate–fluoride material has been reported;²⁹ $[C_6H_{14}N_2][Fe_3(HAsO_4)_2(AsO_4)F_4]\cdot 0.5H_2O$ contains sheets cross-linked by hydrogen–arsenate groups to form a 3D framework. Structure (5) is the first example of a dabco templated iron material that does not contain fluorine.

LiFeAsO₄OH (6)

Compound (6) forms under hydrothermal conditions without the need for an organic template cation; lithium cations act to balance the negative framework charge. The triclinic structure of (6) consists of axially linked chains of corner sharing iron(III) octahedra, meaning the iron centres are in a straight line with an Fe–O–Fe angle of 132° . The chains run perpendicular to the $\langle 111 \rangle$

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plane and are bridged by arsenate tetrahedra, which share all four oxygen atoms with three separate chains of iron octahedra.

The hydroxide group is present on the bridging Fe–O–Fe oxygen. This bridging oxygen possesses tetrahedral co-ordination as it is also one of six oxygen atoms that co-ordinates to the lithium ion within the range 1.97(1)–2.82(5) Å. This close packed arrangement results in the large calculated density of 3.906 g cm⁻³, despite the pore like nature of the structure (Fig. 8). The hydrogen atom H1 forms a bifurcated hydrogen bonding link to oxygen atoms O2 and O3, cutting across the channels viewed parallel to the *b* axis. Details of these bonds are given in Table S1 (see ESI).†



Fig. 8 Structure of LiFeAsO₄·H₂O looking down the *a* direction. Shading scheme as per previous figures; lithium ions are medium grey spheres.

The structure has a phosphate analogue,³⁰ and is also isostructural with the naturally occurring mineral amblygonite. Also reported are stoichiometrically identical manganese equivalents of both the arsenate³¹ and phosphate³² systems, with similar chains of vertex sharing MO_6 , M = Mn, octahedra linked in an identical manner by the TO_4 , T = P, As, tetrahedra. However in these manganese analogues the octahedra are strongly distorted due to the presence of the Jahn–Teller ion Mn(III).

Conclusions

Several new iron arsenate framework structures have been synthesised and their structures elucidated, considerably expanding this class of materials. The framework iron arsenates adopt structures that contrast strongly with those typical of the much more highly developed iron phosphate chemistry. This behaviour is mainly as a result of the prevalence of protonated As(O,OH)₄ tetrahedra in these materials; phosphate in polyhedral frameworks almost invariably links through simple P-O-M bridges, with rarer occurrences of terminal P-OH groups. The presence of such framework-terminating As-OH groups in several of the iron arsenates reported in this work promulgates other structural features in these compounds, such as strong hydrogen bonds that cross-link polyhedral units, as in $[Fe_6As_7O_{31}H_5]^{2-}(dabco^{2+})$ and hydrogen bonds to templating cationic amine units, as in $[Fe_6As_8O_{32}H_4]^{2-}(1,4-butanediamininium^{2+})\cdot 2H_2O$. In common with many transition metal containing frameworks the materials

described in this article show only weak cooperative magnetic interactions between the metal centres, *i.e.* antiferromagnetic ordering only at low temperatures, below 50 K.

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