Polymorphism and variable structural dimensionality in the iron(III) phosphate oxalate system: a new polymorph of 3D $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2] \cdot 2H_2O$ and the layered material $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]^{\dagger}$

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Two new iron (III) phosphate oxalates have been isolated under hydrothermal conditions as phase-pure samples and their crystal structures determined from single crystal X-ray diffraction. $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]\cdot 2H_2O$, **I**, is a polymorph of a known phase and differs in the local arrangement of hydrophosphate, oxalate and coordinated water about iron, presenting a *mer* orientation of three coordinated phosphates, rather than *fac* as previously seen. The structure of **I** is three-dimensionally connected with similar network connectivity to the known phase but different overall topology. $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]$, **II**, has a layered structure constructed from octahedral Fe(III) centres coordinated by hydrophosphate, oxalate and water in a *fac* arrangement. The amount of water used in synthesis is one of the key experimental parameters in stabilising one phase over the other. Thermogravimetric analysis shows that both **I** and **II** ultimately collapse into dense tridymite type FePO₄ above 600 °C and variable temperature powder XRD shows that this occurs *via* crystalline intermediate phases. Variable temperatures, with similar Néel temperatures (~29 K) despite their long-range structural differences.

Introduction

The study of hybrid organic-inorganic solids continues to be of great interest because of the variety of solid-state structures that can be produced, often with open frameworks that might have applications due to their porosity. The combination of metalcentred polyhedral units with organic ligands offers some scope of design in synthesis by potentially providing choice in the connectivity of an extended structure, by selection of a particular organic ligand, and also by the selection of a metal with a particular preferred coordination environment or specific chemical property. The initial work in this area arose from the possibility of preparing novel zeolite analogues,¹ but currently the focus is in the field of metal-organic framework (MOF) materials.² These solids have porosity that extend from the microporous to the mesoporous with applications in gas purification, separation and shapeselective catalysis,³ and several of these have extreme flexibility in the solid state, giving them distinctly different properties from traditional zeolite materials.4

Rao and co-workers have reviewed the use of carboxylate units in MOFs and other hybrid structures.⁵ When polycarboxylate anions are used, these units can act as bridging linkers between metal centres or more complex inorganic groups, and may coexist with other structural units (e.g. phosphate tetrahedra) in hybrid materials. The simplest dicarboxylate unit, the oxalate anion, is a rigid unit that exhibits a range of co-ordination behaviour. It often acts in a bis-bidentate configuration bridging metal centres and oxalate is particularly effective in providing electronic communication between paramagnetic metal centres producing magnetic ordering and its use as a linker in hybrid materials provides a route to multifunctional magnetic materials.6 A wide range of metal oxalate structures now exist, and oxalate has also been combined with phosphate units to produce hybrid materials giving even greater structural variety.⁷⁻⁹ Here oxalate has been observed to act as a pillar between metal phosphate layers, or it can be part of a layer linking metal phosphate ladders. Other mixed anion frameworks have been reported combining, for example, phosphate and acetate, phosphonate and oxalate and bipyridyl and glutarate. Metals incorporated include vanadium, iron, manganese, cobalt, (with the possibility of each in variable oxidation states) zinc, aluminium and gallium.5 Use has been made of amines in many of these syntheses, where the amine plays a role of structure direction, space filling or charge balance, similar to the templates often used in zeolite synthesis.

In this paper we describe the synthesis and structural characterisation of two new Fe(III) oxalate phosphate materials. Although a variety of oxalate phosphates of transition metals have been reported previously,⁷⁻⁹ our results illustrate the effect that subtle changes in synthesis conditions can have on the material produced: in this case permitting small changes in the local structure of the metal or by adjusting the amount of extra-framework water, that then give a material with a different extended structure. The

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results are potentially of relevance to the future 'design' of open framework hybrid solids.

Results and discussion

Table 2 shows some typical reaction conditions used in the synthesis of Fe(III) oxalate phosphates. Two experiments labelled D and C were found to form reproducibly I and II, respectively, as phase-pure samples. Cyclohexylamine is required under the conditions used here to form the new materials: presumably it is controlling pH as there is no evidence of it in the products, as template, for example. Attempts were also made to synthesise the material $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]\cdot 2H_2O$ reported by Choudhury *et al.*⁷ This material was reported to be formed using polypropylene bottles as reaction vessels, however these were found to be unsatisfactory, since some degree evaporation of water during the hydrothermal reaction often occurred, making synthesis difficult to reproduce. Interestingly, Reaction J (Table 2)

Table 1 Details of single crystal structure solution and refinement for ${\bf I}$ and ${\bf II}$

	Ι	П
Empirical formula	FePO ₈ CH ₅	FePO ₇ CH ₃
T/\hat{K}	120	293
λ	Μο Κα	Μο Κα
Crystal size/mm ³	$0.20 \times 0.10 \times 0.04$	$0.20 \times 0.10 \times 0.10$
Crystal form	Block	Block
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a/Å	8.1041(3)	5.0365(3)
b/Å	6.6254(2)	7.6400(5)
c/Å	12.0431(4)	7.6678(6)
$\alpha /^{\circ}$	90	97.292(6)
β/°	108.423(2)	101.847(6)
$\gamma/^{\circ}$	90	106.380(6)
$V/\text{\AA}^3$	613.49(4)	271.62(3)
Ζ	4	2
μ/mm^{-1}	2.722	3.049
Reflections collected/unique	6105/1402	2581/1277
Reflections $I > 2\sigma(I)$	1322	1193
$R_{int}, R_w (I > 2\sigma(I))$	0.0261, 0.0635	0.0205, 0.0527
GOF	1.056	1.107

Table 2 Examples of reacting ratios in the synthesis of I and II. All reactions were carried out at $110 \degree C$ for 7 days

Experiment	FeCl ₃	${\rm H_3PO_4}$	H_2C_2O	$_{4}$ C ₆ H ₁₁ N	$H_2 H_2O$	Product
A	2	2	1	1	2	II
В	2	2	1		2	II + impurity
С	2	2	1	1	4	П
D	2	2	1	1	8	I
Е	2	2	1	1	16	I
F	2	2	1	1	32	FePO ₄ ·2H ₂ O phosphosiderite (JCPDS 33-0666)
G	1	2	1	1	4	I
Н	1	2	1	1	8	I
Ι	1	2	1	1	16	$I + FeC_2O_4 \cdot 2H_2O$ (JCPDS 23-0293)
Ja	1	2	1	1	122	$\begin{array}{c} FeC_2O_4 \cdot 2H_2O \\ (JCPDS \ 23-0293) \end{array}$
^{<i>a</i>} Reactant (C ₂ O ₄)(H ₂ C	ratios))2]·2H2	from O. ⁷	the re	eported	synthesis	of Fe ₂ (HPO ₄) ₂ -

using the ratios from the work of Choudhury et al. and a steel autoclave, failed to form this material. This suggests that the water content of the reaction mixtures is crucial for obtaining the desired product in hydrothermal synthesis. The water content of these reactions is indeed low for hydrothermal synthesis and II is observed to form with lower reagent water content than I (compare reactions A, C, D and E in Table 2), which is consistent with the different crystal water content of the two materials as discussed below. FePO4·2H2O, phosphosiderite, is formed with higher water content (see reation F); this was also a common product of reactions using the degraded FeCl₃ that had been dried in an oven. Where the ratio of FeCl₃ was reduced, increasing the water ratio resulted instead in the formation of FeC₂O₄·2H₂O (see reactions G-J). Reactions based on the ratios in reaction E were also used to examine the effect of time; after 1 day a very small quantity of lilac crystals were formed, reactions after 2, 5 and 6 days showed that the crystal size first increased and later the yield improved. I and II were not observed at any temperature other than 110 °C: other reaction temperatures of 80, 100, 120, 140 and 200 °C were investigated. At 200 °C iron ammonium phosphates or iron phosphates were formed and the products of the other reactions were soluble in water and dissolved upon washing. Experiments varying the ratios of phosphoric and oxalic acid led to the formation of iron phosphate or iron oxalate.

The iron co-ordination environments in $[Fe_2(HPO_4)_2(C_2O_4) (H_2O)_2$]·2H₂O, I, and [Fe₂(HPO₄)₂(C₂O₄)(H₂O)₂], II, are shown in Fig. 1. For further comparison, the equivalent view of the related material that was reported by Choudhury et al.⁷ is also shown. I and the material reported by Choudhury et al. have identical chemical compositions and hence are polymorphs; they also show very similar Fe³⁺ co-ordination, with each iron connected to three hydrophosphate tetrahedra, one oxalate unit (bidentate) and one water molecule. The O-Fe-O angles vary between 79.2° (O(5)-Fe-O(6)) and 99.8° (O(3)-Fe-O(7)), the smallest angle is part of the bidentate oxalate co-ordination where a five-membered ring is formed. There is an important difference between the two materials, however; in I the phosphate groups are in a mer configuration about the Fe(III) centre, whereas in the previously described material they are oriented in a *fac* configuration. Both materials contain a free water molecule, and one oxygen on the phosphate groups (O(1) and O(7) respectively) is protonated, *i.e.* it is a hydrophosphate group. Each hydrophosphate tetrahedra is co-ordinated to three irons, and each oxalate to two. In both materials this leads to the formation of iron phosphate layers. Considering only the iron and phosphorus atoms (analogous to the way T atoms are represented in a zeolite structure¹⁰) these layers are constructed from four and eight membered rings, as shown in Fig. 2. Bisbidentate oxalate anions bridge the layers in both materials resulting in three-dimensional connectivity, Fig. 3. According to the structural classification proposed by Cheetham et al. for hybrid inorganic-organic materials,11 both I and the material reported by Choudhury et al. have I²O¹ connectivity; that is, the inorganic structure extends in two dimensions and the organic in one dimension, overall giving a three-dimensional structure.

In contrast, **II** is a two-dimensional material. The co-ordination environment around the Fe^{3+} (Fig. 1c) is analogous to that of Choudhury's material, where three phosphate tetrahedra are





Fig. 2 Layers in (a) I and (b) $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2] \cdot 2H_2O^7$ showing Fe (green) and phosphorus (pink) only.

Fig. 1 Co-ordination environment of Fe³⁺ for (a) I, (b) II, and (c) $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2] \cdot 2H_2O \cdot ^7$ Fe green, P pink, O red, C black, H white.

found in a *fac* configuration. The octahedral co-ordination is completed by one water molecule and one bidentate oxalate unit as before. The iron is found in a distorted octahedron as in **I**, with minimum and maximum angles of 78.3° (O(1)-Fe-O(2)) and 103.1° (O(4)-Fe-O(5)). As in **I**, the smallest intra-octahedral angle

is due to the oxalate co-ordination, while the largest angle is found between the oxygen atoms opposite. II also has one protonated oxygen per phosphate (O(6)), but no free water molecules were located in the single crystal structure. Phosphate tetrahedra and iron octahedra form ladders along the *a* axis, Fig. 4a, which are connected into layers in the [01-1] plane by oxalate anions, Fig. 4b. Using the classification of Cheetham *et al.*,¹¹ II has I¹O¹ structural connectivity. The layers in II are stacked in an ABA sequence. There is evidence for hydrogen bonding interactions between





Fig. 3 Three-dimensional structure of (a) I and (b) $[Fe_2(HPO_4)_2(C_2O_4)-(H_2O)_2]\cdot 2H_2O.^7$ FeO₆ octahedra pale green, PO₄ tetrahedra dark blue, O red, C black, H white.

neighbouring layers: the distance between O6 (the P-OH oxygen) and O7 (an oxygen bridging Fe and P in a neighbouring layer) is 2.703 Å, and the distance between O3 (of the water coordinated to Fe) and O5 (another bridging oxygen in a neighbouring layer) is 2.912 Å.

Thermogravimetric analysis of I (shown in Fig. 5) shows an initial mass loss of 8.4% between 100 °C and 220 °C. There is a further rapid loss of 29.7% to 295 °C, followed by a small loss between 515 and 700 °C, bringing the total mass loss to 34.8%. In contrast, II shows no weight change until nearly 200 °C (see Fig. 6). A rapid loss of 25.3% occurs to 350 °C, followed by a

small step similar to I around 500 °C. By 700 °C a further 4.2% is lost, corresponding to a total loss of 29.5%. The absence of an initial loss from II below 200 °C is consistent with the lack of free water in the structure; this water in I accounts for 7.8% by weight which is close to the loss observed (8.4%), bearing in mind the likely presence of surface water. Both materials show a mass at 700 °C consistent with the loss of all the remaining water and oxalate to form FePO₄ (calculated total loss of 35.0% for I, 29.5% for II).

Variable temperature powder X-ray diffraction of both materials is shown in Fig. 6 upon heating the samples in air and recording patterns at intervals of between 25 and 50 °C as shown. The sample was heated at 0.5 °C s⁻¹ and then held for 20 minutes equilibration followed by data collection at the desired temperature. Patterns calculated from the single crystal structures show excellent agreement with the measured room temperature patterns (as shown on Fig. 6) confirming the phase purity of the samples. Bragg peaks of I can be seen up to 175 °C, which would correspond to the loss of water, based on the TGA results. (Note that the heating rate is not directly comparable with the TGA.) Patterns collected at 200 and 250 °C show the appearance of a new crystalline phase. From 300 to 600 °C the material is largely amorphous but the final pattern collected at 700 °C shows the appearance of peaks similar to the tridymite form of quartz. This form of FePO₄ has been reported previously as a result of heating iron phosphate materials.12 The experiment was repeated with heating up to 250 °C where the new crystalline phase was formed, followed by cooling to room temperature. The phase remains stable throughout cooling, however could not be identified by a search of the JCPDS database. Various iron (III) phosphate phases have been reported by Reale et al.12 and Song et al.13 were also considered as candidates for the unknown phase, but none of these match the pattern obtained. Diffraction patterns from II (Fig. 6b) show similar behaviour, with a (different) new phase observed at 300 and 350 °C, and the appearance of the tridymite structure at 700 °C. Again the experiment was repeated, heating to the appearance of the new phase (350 °C) followed by cooling to room temperature. In contrast to I, this intermediate phase was not stable during the cooling process, at which point peaks from a further phase appeared.

Plots of magnetic susceptibility per Fe vs temperature are shown in Fig. 7 where parameters derived from analysis of these traces are shown. (There is possibly evidence of a very small amount of a paramagnetic impurity in II but this does not affect the analysis.) Both materials show antiferromagnetic behaviour, with Néel temperatures of ~29 K, rather similar to other reported iron phosphate oxalates.⁷ In both I and II oxalate is co-ordinated in a bis-bidentate mode to iron; the remaining connectivity provided by corner-sharing phosphate tetrahedra. The same mode of coordination is seen in the four materials reported by Choudhury et al., all of which order antiferromagnetically between 25 and 40 K.7 The iron (III) arsenate oxalate $[NH_3(CH_2)CH(NH_3)CH_3]_3[Fe_6(AsO_4)_2(HAsO_4)_6(C_2O_4)_3]$ also shows antiferromagnetic ordering below 31 K.14 Although this structure is quite different in appearance to those described here, the local connectivity is similar, i.e. bisbidentate oxalate and corner-sharing polyhedra. The Fe(II)containing (N₂C₄H₁₂)[Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] includes oxalate co-ordinating in two different modes (mono- and bidentate) and



Fig. 4 The structure of II (a) ladders showing Fe and P only (b) view of a single layer and (c) showing the stacking of the layers. Colours as for Fig. 1 and 2.

edge-sharing FeO_6 octahedra; this material also shows antiferromagnetism at low temperatures (23 K).⁹

Experimental

Synthesis

Materials were synthesised hydrothermally in deionised water from FeCl₃ (anhydrous, Alfa Aesar, 98%), H_3PO_4 (85% in water

Fisher), $H_2C_2O_4$ ·2 H_2O (BDH, 99%) and cyclohexylamine (Acros, 99%). Reactants were added directly to PTFE autoclave liners with stirring. The stainless steel autoclaves, approximate volume 15 ml, were sealed and placed in an oven at 110 °C for 1 week. After cooling to room temperature the contents of the autoclaves were filtered and washed with deionised water. Anhydrous FeCl₃ was kept in a vacuum desiccator to avoid water uptake. Keeping FeCl₃ at ~70 °C was found to be unsatisfactory as the material degraded



Fig. 5 Thermogravimetric analysis plots of I (solid line) and II (dashed line).

and gave irreproducible synthesis results. Specific details of the synthesis are described below.

Crystal structure analysis

For I, $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]\cdot 2H_2O$, single crystal data were collected at the EPSRC Crystallography Service at the University of Southampton. For II, $[Fe_2(HPO_4)_2(C_2O_4)(H_2O)_2]$, data were collected on an Oxford Diffraction Gemini four-circle system with a Gemini CCD area detector. Details of structure solution and refinement are given in Table 1. Both structures were solved by direct methods using SHELXS¹⁵ and light atoms were located by Fourier methods. Hydrogen atoms were located in a difference map and given isotropic displacement parameters equal to 1.5 times the displacement parameter of the oxygen atoms to which they are attached. All other atoms were refined with anisotropic thermal parameters. Semi-empirical absorption corrections were applied based on symmetry-equivalent and repeated reflections.

Laboratory characterisation

Powder X-ray diffraction patterns were collected on a Bruker D5000 diffractometer with Cu K α radiation, using aluminium sample holders in Bragg-Brentano geometry for phase



Fig. 6 Powder XRD recorded on heating to 700 $^{\circ}$ C for (a) I and (b) II. The simulated powder patterns of I and II were generated from the single crystal structures reported in the text and the Miller indices of the strong peaks of the tridymite form of FePO₄¹² are indicated on the pattern of the final product.



Fig. 7 Magnetic susceptibility vs temperature plots of I (closed spheres) and II (open spheres) with the extracted parameters shown in the inset table.

identification and to verify sample purity. For variable temperature experiments, an MRI TC-Basic furnace was fitted and alumina sample holders were used. The sample was heated to the desired temperature and equilibrated for 20 minutes before data was collected. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 1 from 30–900 °C at 10 °C min⁻¹ in flowing air. Variable temperature magnetisation measurements were taken in an external field of 1000 G between 2 and 350 K using a Quantum Design MPMS-5 SQUID magnetometer. Powdered samples were held in gel-capsules within plastic straws and the diamagnetic contributions from the sample mount and sample (Pascals constants) were corrected for in all calculations.

Conclusions

Small changes in reaction conditions lead to quite dramatic changes in the structures of iron oxalate phosphates that crystallise under hydrothermal conditions. The local coordination about Fe can thus be adjusted in a subtle manner (*fac/mer* arrangements of coordinating groups) and the resulting dimensionality of structure can be affected by changing the relative ratios of reagents, in particular the water content of the synthesis mixture. Although the resulting materials have rather similar magnetic behaviour their long-range crystal structures are clearly dictated by the connectivity induced by the local arrangement about Fe(III) and this would have implications in the "design" of new hybrid organic-inorganic materials by control of reaction conditions.

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