

# Synthesis, structure and magnetic properties of a new one-dimensional iron phosphite, [Fe<sup>III</sup>(1,10-phenanthroline)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)]

Sukhendu Mandal<sup>1</sup>, Mark A. Green<sup>2</sup> and Srinivasan Natarajan<sup>1,\*</sup>

<sup>1</sup>Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

<sup>2</sup>Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albermarle Street, London W1S 4BS, UK

A new iron phosphite, [Fe<sup>III</sup>(1,10-phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)], **I**, has been synthesized hydrothermally from a mixture containing iron powder, phosphorous acid, 1,10-phenanthroline and water at 125°C for 7 days. The structure consists of an edge-shared four-membered rings formed by the connectivity between FeO<sub>4</sub>N<sub>2</sub> octahedra and pseudo pyramidal HPO<sub>3</sub> units, connected through their edges forming a one-dimensional structure. The 1,10-phenanthroline molecules and H<sub>2</sub>PO<sub>3</sub> pseudo-tetrahedral units bound with the Fe centre project into the inter-chain spaces. Magnetic investigations reveal that the iron is present in +3 oxidation state, and at low-temperature the sample orders antiferromagnetically with  $T_N \sim 16$  K. Crystal data: **I**, monoclinic, space group = P2(1)/m (no. 11),  $a = 10.180(3)$ ,  $b = 6.424(1)$ ,  $c = 11.6668(5)$  Å,  $\beta = 115.59(1)^\circ$ ,  $V = 668.2(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.880$  g/cm<sup>3</sup>,  $m_{\text{Mo K}\alpha} = 3.456$  mm<sup>-1</sup>,  $R_1 = 0.0313$  and  $wR_2 = 0.0725$  data [ $I > 2s(I)$ ].

**Keywords:** Antiferromagnetic interactions, iron-phosphite,  $p \dots p$  interaction, single crystal structure, synthesis.

THE many potential applications in the areas of catalysis, selective sorption, etc. continue to be the driving force for research in open-framework solids. Intense research during the last two decades has clearly indicated that the metal phosphates are an important class of open-framework materials<sup>1-5</sup>. Recently, the phosphite group, (HPO<sub>3</sub>), has been investigated as a possible replacement for the more traditional phosphate in framework structures, resulting in a new family of solids. Thus, open-framework phosphites of V<sup>6</sup>, Cr<sup>7</sup>, Mn<sup>8</sup>, Fe<sup>9</sup>, Co<sup>10</sup>, Zn<sup>11-14</sup>, Al<sup>15</sup>, Ga<sup>16</sup>, Be<sup>17</sup> and Mo<sup>18</sup> have been synthesized and their structures determined. Many of these compounds have been prepared employing a structure-directing organic amine. Use of simple ligand amines such as 1,10-phenanthroline, 2,2'-bipyridine, and 4,4'-bipyridine has been shown to give new and novel structures in metal phosphates<sup>3-5</sup>. We have been interested in the use of such ligand amines in phosphite networks. During the course of this study, we have now isolated a new iron phosphite with 1,10-phenanthroline, [Fe<sup>III</sup>(1,10-phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)], **I**, possessing a one-dimensional

structure. Here, we present the synthesis, structure and magnetic properties of **I**.

## Experimental

The iron phosphite, [Fe<sup>III</sup>(1,10-Phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)], **I**, was synthesized under hydrothermal conditions using iron metal powder as the source of iron. In a typical synthesis, 0.108 g of Fe-powder was dispersed in 7 ml of deionized water. To this, 0.477 g of H<sub>3</sub>PO<sub>3</sub> and 0.303 g of 1,10-phenanthroline (1,10-phen) were added and the mixture was homogenized for 30 min at room temperature. The final mixture with the composition 1.0 Fe:3.0 H<sub>3</sub>PO<sub>3</sub>:0.86 (1,10-phen):200 H<sub>2</sub>O, was transferred into a 23 ml acid-digestion bomb and heated at 125°C for 7 days. After the reaction, the autoclaves were removed from the oven and left to cool to room temperature at ambient conditions. The resulting product, containing large quantities of yellow-coloured rod-like single crystals was filtered, washed with deionized water and dried at ambient conditions. The yield of the product was ~70% based on Fe. The initial and final pH of the reaction mixture was ~2.

The initial characterizations were carried out using elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and infrared spectroscopic (IR) measurements. An EDAX analysis on many single crystals indicated a Fe:P ratio of 1:2. Elemental analysis: obsd. (calc.) C 35.47 (36.4%), H 2.90 (2.5%), N 6.32 (7.0%). The results agree well with the formula [Fe<sup>III</sup>(1,10-phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)] obtained from the single-crystal data. The powder XRD patterns were recorded on crushed single crystals in the  $2\theta$  range 5–50° using CuK $\alpha$  radiation (Philips, X'pert, Pro). The pattern was entirely consistent with the structure determined using the single-crystal XRD (Figure 1).

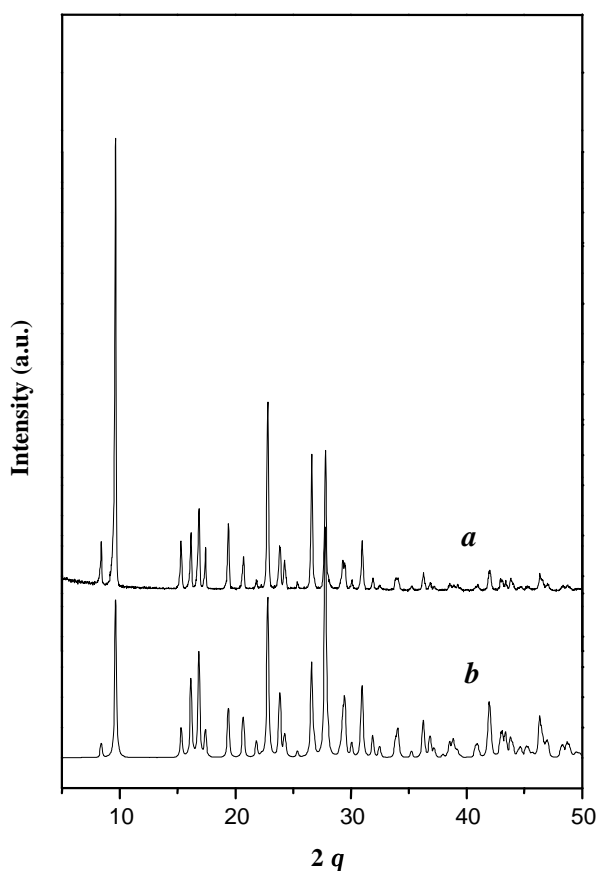
TGA of the title compound, in an atmosphere of flowing air (flow rate = 50 ml/min) was carried out in the temperature range 30–850°C (heating rate = 5°C/min). Studies show a broad weight loss in the range 400–850°C. The total observed weight loss was found to be 40.1%. This weight loss under the flow of air, generally corresponds to the loss of organic amine. The final decomposed products, identi-

\*For correspondence. (e-mail: snatarajan@sscu.iisc.ernet.in)

fied by powder XRD, were  $\text{Fe}^{\text{III}}\text{P}^{\text{V}}_3\text{O}_9$  (JCPDS 38-0109) and  $\text{Fe}_2^{\text{III}}\text{O}_3$  (JCPDS 39-1346). The calculated weight loss based on the removal of 1,10-phen would be 45%. The discrepancy in the observed and calculated weight losses can be explained by considering the oxidation of  $\text{P}^{\text{III}}$  to  $\text{P}^{\text{V}}$  during the decomposition. The calculated weight gain due to the oxidation of  $\text{P}^{\text{III}}$  to  $\text{P}^{\text{V}}$  was 4.04%. Thus, during TGA studies, there is competition between weight loss due to decomposition of the bonded amine and weight gain due to oxidation of  $\text{P}^{\text{III}}$  ions resulting in a net lower weight loss. Taking this into account, the net weight loss would be 44.14 (40.1 + 4.04)%, which matches well with the calculated weight loss (45.00%).

IR spectroscopic studies were carried out in the range 400–4000  $\text{cm}^{-1}$  using KBr pellet method (Perkin Elmer, SPECTRUM 1000). The IR spectrum of **I** shows characteristic peaks, IR bands:  $\nu(\text{NH}) = 2988 \text{ cm}^{-1}$ ,  $\nu(\text{CH}) = 3058 \text{ cm}^{-1}$ ,  $\nu(\text{PH}) = 2403 \text{ cm}^{-1}$ ,  $\delta(\text{NH}) = 1583 \text{ cm}^{-1}$ ,  $\delta(\text{CH}) = 1425 \text{ cm}^{-1}$ ,  $\delta(\text{HP}) = 936 \text{ cm}^{-1}$ ,  $d_s(\text{PO}_3) = 645 \text{ cm}^{-1}$ ,  $d_{\text{as}}(\text{PO}_3) = 573 \text{ cm}^{-1}$ .

Temperature variation of the magnetic susceptibility studies has been carried out on powdered single crystals in the range 2–300 K with a SQUID magnetometer (Quantum Design Inc, USA).



**Figure 1.** Powder X-ray diffraction pattern (Cu K $\alpha$ ) for  $[\text{Fe}^{\text{III}}(\text{C}_{12}\text{N}_2\text{H}_8)(\text{HPO}_3)(\text{H}_2\text{PO}_3)]$ , **I**, (a) experimental and (b) simulated.

### Single crystal structure determination

A suitable yellow-coloured single crystal was carefully selected under a polarizing microscope and glued to a thin glass fibre. The single crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 293(2) K. The X-ray generator was operated at 50 kV and 35 mA using MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Data were collected with  $\omega$  scan width of  $0.3^\circ$ . A total of 606 frames were collected in three different settings of  $j$  (0, 90,  $180^\circ$ ) keeping the sample-to-detector distance fixed at 6.03 cm and the detector position ( $2\theta$ ) fixed at  $-25^\circ$ . Pertinent experimental details of the structure determination of **I** are presented in Table 1.

The data were reduced using SAINTPLUS<sup>19</sup>, and an empirical absorption correction was applied using the SADABS program<sup>20</sup>. The crystal structure was solved and refined<sup>21</sup> using SHELXL97 present in the WinGx suite of programs (Version 1.63.04a)<sup>22</sup>. We have not been able to locate all the hydrogen positions from the difference Fourier map. We have made use of detailed bond valence sum calculations<sup>23</sup> to arrive at the hydrogen positions for the hydroxyl groups. The idealized hydrogen positions were then placed geometrically and refined using the riding model. The last cycles of refinement included atomic positions, 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 package of programs<sup>21</sup>. Selected bond distances and angles for **I** are listed in Table 2.

**Table 1.** Crystal data and structure refinement parameters for  $[\text{Fe}^{\text{III}}(1,10\text{-phen})(\text{HPO}_3)(\text{H}_2\text{PO}_3)]$ , **I**

Empirical formula	$\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_6\text{P}_2\text{Fe}_1$
Formula weight	397.019
Crystal system	Monoclinic
Space group	$\text{P}2_1/\text{m}$ (no. 11)
$a$ ( $\text{\AA}$ )	10.180 (3)
$b$ ( $\text{\AA}$ )	6.424 (1)
$c$ ( $\text{\AA}$ )	11.668(5)
$\beta$ (deg)	115.59 (1)
Volume ( $\text{\AA}^3$ )	688.2 (4)
$Z$	4
$T$ (K)	293(2)
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.880
$m$ ( $\text{mm}^{-1}$ )	3.456
$q$ range (deg)	1.94 to 23.28 $^\circ$
$\lambda$ (Mo K $\alpha$ ) ( $\text{\AA}$ )	0.71073
Reflections collected	1194
Unique reflections	829
Number of parameters	160
Goodness of fit (S)	1.079
$R$ indexes [ $I > 2s(I)$ ]	$R_1 = 0.0313$ , $wR_2 = 0.0725$
$R$ (all data)	$R_1 = 0.0347$ , $wR_2 = 0.0750$
Largest diff. peak and hole $\text{e}\text{\AA}^{-3}$	0.396 and $-0.304$

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; \quad wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}; \quad w = 1 / [r^2(F_o^2) + (aP)^2 + bP]; \quad P = [\max(F_o, O) + 2(F_c)^2] / 3, \quad \text{where } a = 0.0168 \text{ and } b = 1.7907.$$

**Table 2.** Selected bond distances and angles in [Fe<sup>III</sup>(1,10-phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)], **I**

Bond	Distance (Å)	Bond	Distance (Å)
Fe(1)–O(1)	1.901(4)	P(1)–O(1)	1.506(4)
Fe(1)–O(2)	1.941(4)	P(1)–O(3)#2	1.514(3)
Fe(1)–O(3)#1	1.987(3)	P(1)–O(3)#3	1.514(3)
Fe(1)–O(3)	1.987(3)	P(2)–O(2)	1.490(4)
Fe(1)–N(1)	2.189(5)	P(2)–O(4)#1	1.496(5)
Fe(1)–N(2)	2.203(5)	P(2)–O(4)	1.496(5)
Moiety	Angle (°)	Moiety	Angle (°)
O(1)–Fe(1)–O(2)	102.83(18)	O(3)#1–Fe(1)–N(2)	85.04(8)
O(1)–Fe(1)–O(3)#1	94.19(8)	O(3)–Fe(1)–N(2)	85.04(8)
O(2)–Fe(1)–O(3)#1	93.41(9)	N(1)–Fe(1)–N(2)	75.32(18)
O(1)–Fe(1)–O(3)	94.19(9)	O(1)–P(1)–O(3)#2	113.59(14)
O(2)–Fe(1)–O(3)	93.41(9)	O(1)–P(1)–O(3)#2	113.59(14)
O(3)#1–Fe(1)–O(3)	167.77(14)	O(3)#2–P(1)–O(3)	109.5(2)
O(1)–Fe(1)–N(1)	93.62(18)	O(2)–P(2)–O(4)#1	109.1(2)
O(2)–Fe(1)–N(1)	163.55(18)	O(2)–P(2)–O(4)	109.1(2)
O(3)#1–Fe(1)–N(1)	85.29(8)	O(4)#1–P(2)–O(4)	113.2(4)
O(3)–Fe(1)–N(1)	85.29(8)	P(1)–O(1)–Fe(1)	164.8(3)
O(1)–Fe(1)–N(2)	168.94(19)	P(2)–O(2)–Fe(1)	142.4(3)
O(2)–Fe(1)–N(2)	88.23(19)	P(1)#3–O(3)–Fe(1)	138.80(15)

Symmetry transformations used to generate equivalent atoms: #1,  $x, -y + 1/2, z$ ; #2  $-x, y + 12, -z + 1$ ; #3  $-x, -y, z + 1$ .

## Results and discussion

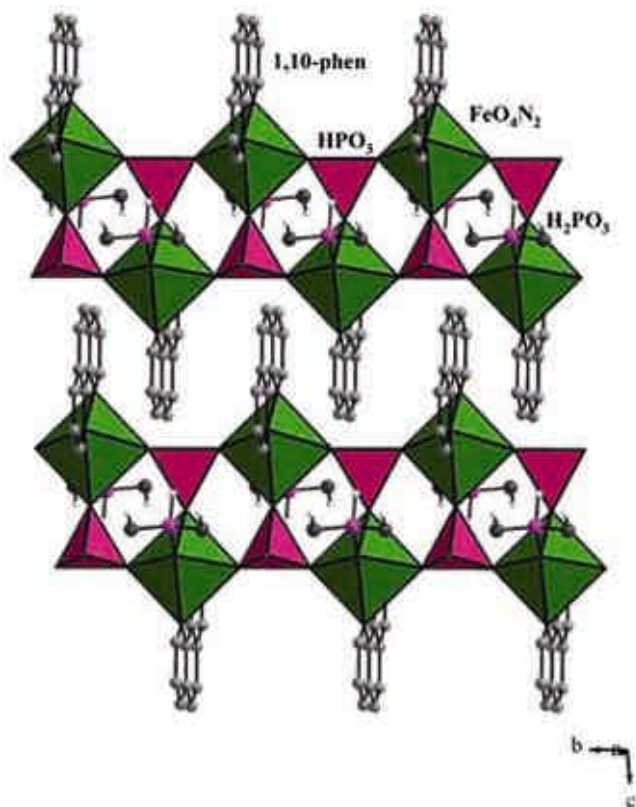
The asymmetric unit of **I** contains 21 non-hydrogen atoms, of which one iron and two phosphorous atoms are crystallographically independent. The iron atom is octahedrally coordinated by two nitrogen atoms of the 1,10-phenanthroline ligand and four oxygen atoms of the phosphite groups. The Fe–O bond lengths are in the range 1.901(4)–1.987(3) Å [av. 1.954 Å] and Fe–N bonds have an average distance of 2.196 Å. The O/N–Fe–O/N bond angles are in the range 85.04°(8)–168.94°(19). The iron atom is connected to two distinct phosphorous atoms through Fe–O–P bonds. Among the two P atoms, P(1) is connected to iron through three P–O–Fe bonds, and P(2) is connected by one P–O–Fe bond and possesses two terminal P–O bonds. The P–O bond distances are in the range 1.504(4)–1.514(3) Å for P(1) atom [av. 1.511 Å] and 1.490(4)–1.496(5) Å for P(2) atom [av. 1.494 Å] respectively. Bond valence sum calculations show a value of 2.986 for Fe, indicating that Fe is in +3 state. The bond valence sum values for the oxygens, O(1)–O(3), are in the range 1.86–2.02 and that of O(4) is 1.38. It is likely that O(4) is protonated, giving rise to the molecular formula of [Fe<sup>III</sup>(1,10-phen)(HPO<sub>3</sub>)(H<sub>2</sub>PO<sub>3</sub>)].

The FeO<sub>4</sub>N<sub>2</sub> octahedral and HP(1)O<sub>3</sub> pseudo-tetrahedral units are connected through their vertices, giving rise to a four-membered ring. The four-membered rings are connected through their edges forming a one-dimensional structure. The H<sub>2</sub>P(2)O<sub>3</sub> units and the 1,10-phenanthroline ligands are connected with the chain by bonding with the iron centre (Figure 2). The hanging 1,10-phenanthroline ligands from two different chains, projecting into the

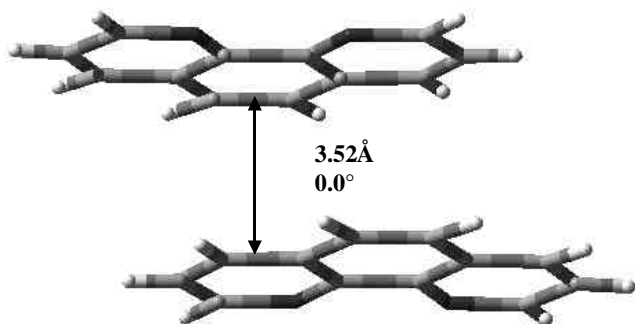
interchain spaces, are separated by 3.52 Å. This indicates that there exist considerable *p...p* interactions between the 1,10-phen molecules. The 1,10-phenanthroline ligands appear to be stacked exactly one over the other, the angle ( $q$ ) suspended between the neighbouring ones is zero (Figure 3). The stacking is anti-parallel in nature. For a better understanding of the role of the *p...p* interactions in these structures, we carried out preliminary calculations using the AM1-parameterized Hamiltonian available in the Gaussian program suite<sup>24,25</sup>. From these calculations, the dipole moment of the independent 1,10-phenanthroline molecule was found to be 2.73 debye and the dipole moment value for the stacked arrangement was found to be zero. This possibly resulted from the anti-parallel arrangement of the 1,10-phenanthroline molecules leading to the cancellation of dipole moment. We have also calculated the strength of the *p...p* interactions based on single-point energy calculations, without the symmetry constraints, on the basis of the crystal structure geometry. The calculated *p...p* interaction energy was found to be 10.2 kcal/mol. This energy is of the order of intermediate hydrogen-bond strengths (approx 10–15 kcal/mol) observed generally in N–H...O and O–H...O hydrogen-bonded systems<sup>26</sup>.

The thermal variation of  $c_m$  is shown in Figure 4 and the inset shows the  $c^{-1}$  versus temperature plot. The molar magnetic susceptibility increases with decreasing temperature and reaches a sharp maximum around 16 K. If  $T$  is reduced further, the susceptibility decreases sharply. At high temperature ( $T > 100$  K), the thermal evolution of  $c_m$  follows a Curie–Weiss law,  $c = C/(T - q)$  with  $C_m = 0.0870$  cm<sup>3</sup>k/mol and  $q_p = -35$  K. At room temperature,

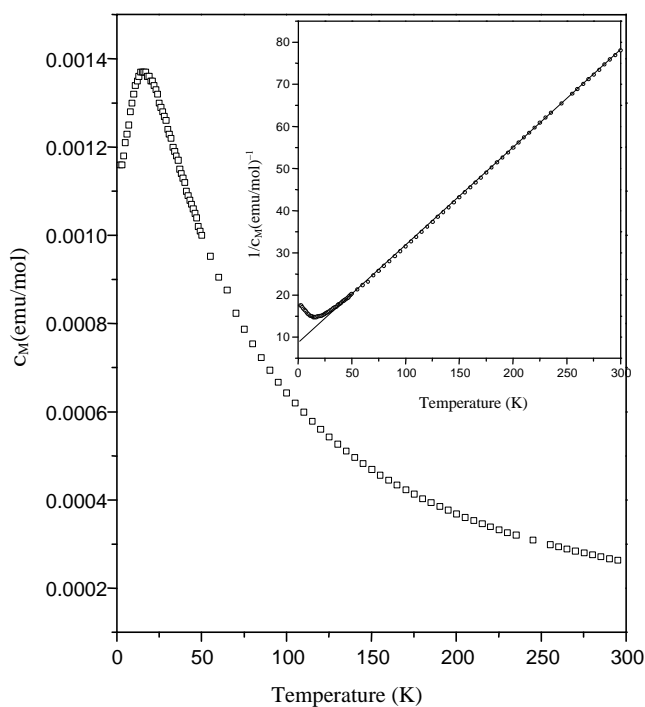
the observed effective magnetic moment ( $m_{\text{eff}}$ ) saturates to a value of  $5.57 m_B$ , which is close to the calculated paramagnetic spin-only value of Fe in +3 state ( $5.92 m_B$ ). The negative Weiss constant together with the continuous decrease in the  $c_m T$  vs  $T$  curve, imply that the dominant interactions between the neighbouring  $\text{Fe}^{3+}$  species are antiferromagnetic in nature. The antiferromagnetic ordering temperature ( $T_N$ ), estimated from the inverse susceptibility versus temperature plot is 16 K.



**Figure 2.** Polyhedral view of structure of **I**, in the  $bc$  plane showing arrangement of one-dimensional chains. Hanging phosphite units are shown as ball-stick view.



**Figure 3.** Arrangement of 1,10-phenanthroline molecules in **I**. Note that the phenanthroline molecules are stacked in anti-parallel arrangement.



**Figure 4.** Temperature variation of magnetic susceptibility of **I**. (Inset) Temperature variation of inverse susceptibility.

The structure of **I**, appears to have a close relationship to the iron phosphite-phosphate  $[\text{Fe}^{\text{III}}(2,2'\text{-bipyridine})(\text{HPO}_3)(\text{H}_2\text{PO}_4)]^{27}$ , and the iron phosphate  $[\text{Fe}^{\text{III}}(1,10\text{-phen})(\text{HPO}_4)(\text{H}_2\text{PO}_4) \cdot 0.5\text{H}_2\text{O}]^3$ , structures. In the iron phosphite-phosphate structure, the  $\text{FeO}_4\text{N}_2$  and  $\text{HPO}_3$  units are linked to give rise to the edge-shared one-dimensional chains. The  $\text{H}_2\text{PO}_4$  and the 2,2'-bipyridine groups hang from the iron centre. In **I**, we have an identical situation with  $\text{FeO}_4\text{N}_2$  and  $\text{HP}(1)\text{O}_3$  units linked to form the one-dimensional chain, with 1,10-phen and  $\text{H}_2\text{P}(2)\text{O}_3$  molecules hanging from the Fe centre. In  $[\text{Fe}^{\text{III}}(1,10\text{-phen})(\text{HPO}_4)(\text{H}_2\text{PO}_4) \cdot 0.5\text{H}_2\text{O}]$ , the  $\text{FeO}_4\text{N}_2$  and  $\text{HPO}_4$  units form the edge-shared one-dimensional chains with 1,10-phen molecules and  $\text{PO}_2(\text{OH})_2$  units hanging from the iron centre. Similar structural features have also been encountered in the one-dimensional cadmium phosphate  $[\text{Cd}(2,2'\text{-bipyridine})(\text{H}_2\text{PO}_4)_2]^{28}$ .

Crystallographic data for this compound has been deposited with Cambridge Crystallographic Data Centre (CCDC No. 275931). The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: [deposit@ccdc.cab.ac.uk](mailto:deposit@ccdc.cab.ac.uk)).

- Cheetham, A. K., Ferey, G. and Loiseau, T., Open-framework inorganic materials. *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 3268–3292.
- Cavellec, M., Riou, D., Greneche, J. M. and Ferey, G., Hydrothermal synthesis, structure and magnetic properties of a novel

- monodimensional iron phosphate:  $[\text{FeF}(\text{HPO}_4)_2, \text{N}_2\text{C}_3\text{H}_{12}, (\text{H}_2\text{O})_x]$  ( $x = 0.20$ ) (ULM-14). *Inorg. Chem.*, 1997, **36**, 2187–2190.
3. Meng, H., Li, G., Liu, Y., Cui, Y. and Pang, W., Hydrothermal synthesis and characterization of a new iron phosphate structure of ladder-like chains and coordination directly by an organo-nitrogen ligand:  $[\text{Fe}(\text{Phen})(\text{HPO}_4)(\text{H}_2\text{PO}_4) \cdot 0.5\text{H}_2\text{O}]$  (1,10-phenanthroline). *J. Solid State Chem.*, 2004, **177**, 4459–4464.
  4. Chang, W.-J., Chen, C.-Y. and Lii, K.-H., Synthesis and characterization of two-dimensional fluorinated metal phosphate incorporating 2,2'-bipyridine ligands:  $\text{M}_2\text{F}_2(2,2'\text{-bipy})(\text{HPO}_4)_2(\text{H}_2\text{O})$  ( $\text{M} = \text{Fe}, \text{Ga}$ ). *J. Solid State Chem.*, 2003, **172**, 6–11.
  5. Jiang, Y.-C., Lai, Y.-C., Wang, S.-L. and Lii, K.-H.,  $[\text{Ni}(4,4'\text{-bipy})_2(\text{HPO}_4)_2] \cdot \text{C}_4\text{H}_9\text{OH} \cdot \text{H}_2\text{O}$ : a novel metal phosphate that exhibits interpenetration of 2D net into 3D framework. *Inorg. Chem.*, 2001, **40**, 5320–5321.
  6. Fernandez, S., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I. and Rojo, T., Two new three-dimensional vanadium(III) and iron(III) phosphite templated by ethylenediamine:  $(\text{C}_2\text{H}_{10}\text{N}_2)_{0.5}[\text{M}(\text{HPO}_3)_2]$ . *Ab initio* structure determination, spectroscopic and magnetic properties. *Chem. Mater.*, 2002, **14**, 2300–2307.
  7. Fernandez, S., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I. and Rojo, T.,  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cr}(\text{HPO}_3)\text{F}_3]$ : The first organically templated fluorochromium(III) phosphite. *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 3683–3685.
  8. Fernandez, S., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I., Olazcuaga, R. and Rojo, T., A new layered inorganic-organic hybrid manganese(II) phosphite:  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Mn}_3(\text{HPO}_3)_4]$ . Hydrothermal synthesis, crystal structure, and spectroscopic and magnetic properties. *Chem. Mater.*, 2000, **12**, 2092–2098.
  9. Fernandez-Armas, S., Mesa, J. L., Pizarro, J. L., Garitaonandia, J. S., Arriortua, M. I. and Rojo, T.,  $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Fe}^{\text{II}}_{0.86}\text{Fe}^{\text{III}}_{1.14}(\text{HPO}_3)_{1.39}(\text{HPO}_4)_{0.47}(\text{PO}_4)_{0.14}\text{F}_3]$ : A fluoro-phosphite-hydrogen-phosphate-phosphate iron(II, III) mixed-valence organically templated compound. *Angew. Chem. Int. Ed. Engl.*, 2004, **43**, 977–980.
  10. Fernandez, S., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I. and Rojo, T., Hydrothermal synthesis of a new layered inorganic-organic hybrid cobalt(II) phosphite:  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Co}_3(\text{HPO}_3)_4]$ : Crystal structure and spectroscopic and magnetic properties. *Int. J. Inorg. Mater.*, 2001, **3**, 331–336.
  11. Fu, W. S., Shi, Z., Li, G. N., Zhang, D., Dong, W. J., Chen, X. B. and Feng, S. H., Synthesis and characterization of an organically templated zincophosphate:  $[\text{C}_6\text{H}_{16}\text{N}_2][\text{Zn}_3(\text{HPO}_3)_4]$ . *Solid State Sci.*, 2004, **6**, 225–228.
  12. Gorden, L. E. and Harrison, W. T. A., Amino acid templating of inorganic networks: Synthesis and structure of L-asparagine zinc phosphite,  $\text{C}_4\text{N}_2\text{O}_3\text{H}_8 \cdot \text{ZnHPO}_3$ . *Inorg. Chem.*, 2004, **43**, 1808–1809.
  13. Lin, Z. E., Zhang, M., Zheng, S. T. and Yang, G. Y., A novel open-framework zinc phosphite,  $\text{Zn}_3(\text{HPO}_3)_4 \cdot \text{Ni}(\text{en})_2(\text{H}_2\text{O})_2$ , templated by a transition-metal complex. *Eur. J. Inorg. Chem.*, 2004, 953–955.
  14. Liang, J., Wang, Y., Yu, J. H., Li, Y. and Xu, R. R., Synthesis and characterization of a new layered zinc phosphite  $(\text{C}_5\text{H}_6\text{N}_2)\text{Zn}(\text{HPO}_3)$  containing helical chains. *Chem. Commun.*, 2003, **7**, 882–883.
  15. Harvey, H. G., Hu, J. and Attfield, M. P., Synthesis, structural characterization, and readsorption behavior of a solid solution aluminum phosphite/ethylenediphosphonate series. *Chem. Mater.*, 2003, **15**, 179–188.
  16. Fernandez-Armas, S., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I. and Rojo, T., A new organically templated gallium(III)-doped chromium(III) fluorophosphite,  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ga}_{0.98}\text{Cr}_{0.02}(\text{HPO}_3)\text{F}_3]$  hydrothermal synthesis, crystal structure and spectroscopic properties. *J. Solid State Chem.*, 2004, **177**, 765–771.
  17. Fu, W. S. *et al.*, The first organically templated beryllium phosphite  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3] \cdot \text{Be}_3(\text{HPO}_3)_4$ : Hydrothermal synthesis and X-ray crystal structure. *Cryst. Growth Des.*, 2004, **4**, 297.
  18. Lyxell, D. G., Bostrom, D., Hashimoto, M. and Petterson, L., Multicomponent polyanions. 54. Crystal structure of tetraesium monohydrogen phosphato(phosphito)pentamolybdate dihydrate,  $\text{Cs}_4[\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}] \cdot 2\text{H}_2\text{O}$ . *Acta Chem. Scand.*, 1998, **52**, 425–430.
  19. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
  20. Sheldrick, G. M., Siemens area correction absorption correction program, University of Göttingen, Göttingen, Germany, 1994.
  21. Sheldrick, G. M., SHELXL-97 program for crystal structure solution and refinement, University of Göttingen, Göttingen, Germany, 1997.
  22. Farrugia, J. L., WinGx suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
  23. Brown, I. D. and Altermatt, D., Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
  24. Gaussian 03, Revision B. 05, Gaussian Inc. Pittsburg PA, 2003.
  25. Dewar, M. J. S., Zebisch, E. G., Healy, E. F. and Stewart, J. J. P., Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. *J. Am. Chem. Soc.*, 1985, **107**, 3902.
  26. Desiraju, G. R. and Steiner, T., *The Weak Hydrogen Bond. In Structural Chemistry and Biology*, Oxford University Press, 1999.
  27. Mandal, S., Pati, S. K., Green, M. A. and Natarajan, S., The first one-dimensional iron phosphite-phosphate,  $[\text{Fe}^{\text{III}}(2,2'\text{-bipyridine})(\text{HPO}_3)(\text{H}_2\text{PO}_4)]$ : Synthesis, structure and magnetic properties. *Chem. Mater.*, 2005, **17**, 638–643.
  28. Lin, Z. E., Sun, Y. Q., Zhang, J., Wei, Q. H. and Yang, G. Y.,  $\text{Cd}(2,2'\text{-bipy})(\text{H}_2\text{PO}_4)_2$ : the first cadmium phosphate with an organic amine acting as a ligand. *J. Mater. Chem.*, 2003, **13**, 447–449.

ACKNOWLEDGEMENTS. S.M. acknowledges financial support from the University Grants Commission, Government of India through the award of research fellowship. S.N. thanks the Department of Science and Technology, Government of India for award of research grant. We also thank DST-IRHPA, India for CCD facility.

Received 24 June 2005; revised accepted 5 October 2005