



Crystal structure of hydrazine iron(III) phosphate, the first transition metal phosphate containing hydrazine

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The title compound, poly[(μ_2 -hydrazine)(μ_4 -phosphato)iron(III)], $[\text{Fe}(\text{PO}_4)(\text{N}_2\text{H}_4)]_n$, was prepared under hydrothermal conditions. Its asymmetric unit contains one Fe^{III} atom located on an inversion centre, one P atom located on a twofold rotation axis, and two O, one N and two H atoms located on general positions. The Fe^{III} atom is bound to four O atoms of symmetry-related PO_4 tetrahedra and to two N atoms of two symmetry-related hydrazine ligands, resulting in a slightly distorted FeO_4N_2 octahedron. The crystal structure consists of a three-dimensional hydrazine/iron phosphate framework whereby each PO_4 tetrahedron bridges four Fe^{III} atoms and each hydrazine ligand bridges two Fe^{III} atoms. The H atoms of the hydrazine ligands are also involved in moderate $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding with phosphate O atoms. The crystal structure is isotypic with the sulfates $[\text{Co}(\text{SO}_4)(\text{N}_2\text{H}_4)]$ and $[\text{Mn}(\text{SO}_4)(\text{N}_2\text{H}_4)]$.

1. Chemical context

During the last century, transition metal phosphates have been studied intensively not only for their rich crystal- and magneto-chemistry (Kabbour *et al.*, 2012), but also for their various potential applications. For example, $\text{NH}_4\text{M}^{\text{II}}\text{PO}_4\cdot\text{H}_2\text{O}$ phases, where M is a transition metal, are used as pigments for protective paint finishes on metals, as fire retardants in paints

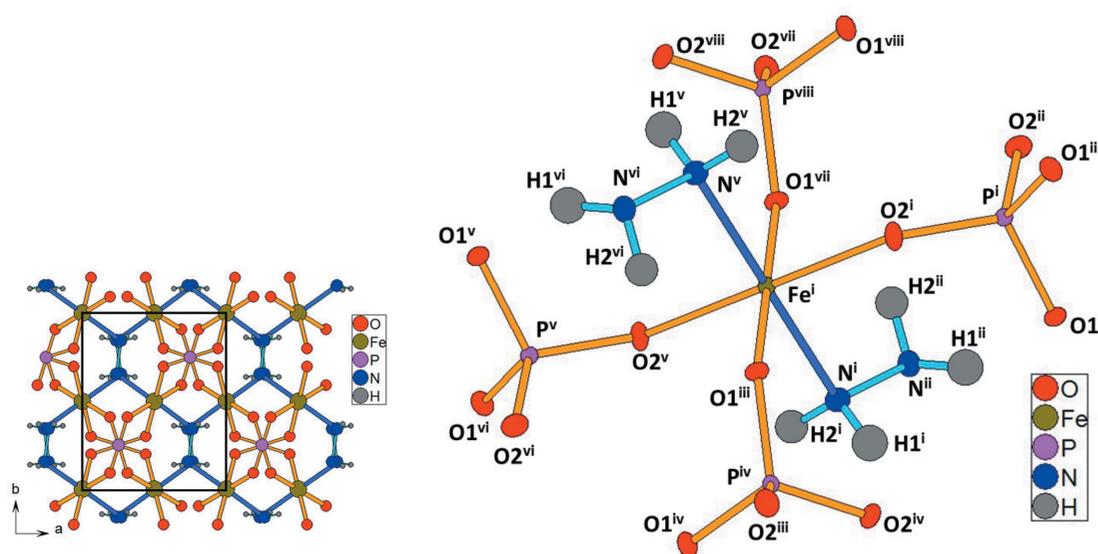


Figure 1
The coordination environment of the Fe^{III} atom in the structure of $[\text{Fe}(\text{PO}_4)(\text{N}_2\text{H}_4)]$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) x, y, z ; (ii) $0.5-x, 0.5-y$; (iii) $-x, y + 0.5, 0.5-z$; (iv) $x + 0.5, -y, 0.5-z$; (v) $-x, -y, -z$; (vi) $x + 0.5, y + 0.5, -z$; (vii) $x, 0.5-y, z + 0.5$; (viii) $0.5-x, y, z + 0.5$.]

Table 1
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|----------|-------------|-------------|---------------|
| $N-H1\cdots O1^i$ | 0.85 (3) | 2.36 (2) | 3.086 (2) | 144 (2) |
| $N-H1\cdots O2^{ii}$ | 0.85 (3) | 2.27 (3) | 2.974 (2) | 141 (2) |
| $N-H2\cdots O1^{iii}$ | 0.85 (3) | 2.19 (3) | 2.873 (2) | 137 (2) |

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, -y, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y, z - \frac{1}{2}$.

and plastics but may also be applied as catalysts, fertilizers and magnetic devices (Erskine *et al.*, 1944; Bridger *et al.*, 1962; Barros *et al.*, 2006; Ramajo *et al.*, 2009). More recently, it was demonstrated by Goodenough and co-workers that in electrodes the presence of PO_4 groups results in higher positive potentials (Padhi *et al.*, 1997), leading to an intensive research on $LiFePO_4$, one of the most promising materials for the new generation of Li batteries (Ouvrard *et al.*, 2013).

2. Structural commentary

The structure of the title compound, $[Fe(PO_4)(N_2H_4)]$, is isotopic with the sulfates $[Co(SO_4)(N_2H_4)]$ and $[Mn(SO_4)(N_2H_4)]$ (Jia *et al.*, 2011). The Fe^{III} atom is bound to four PO_4 tetrahedra and to two N atoms of hydrazine ligands, resulting in a slightly distorted FeO_4N_2 octahedron (Fig. 1). The crystal structure consists of a three-dimensional network made up of Fe^{III} atoms which are interconnected through neutral hydrazine (N_2H_4) ligands and phosphate (PO_4^{3-}) anions (Fig. 2). If the phosphate and sulfate structures are isotopic, the presence of phosphate implies an oxidation state of +III for the transition metal compared to +II for the sulfate analogues. The replacement of sulfate for phosphate leads to a change in the coordination sphere of the metal. These differences are mainly associated with the metal–oxygen bond lengths. The average $Fe^{III}-O$ bond length is 1.97 Å for $[Fe(PO_4)(N_2H_4)]$ and the average $Co^{II}-O$ bond length is 2.12 Å for $[Co(SO_4)(N_2H_4)]$, whereas the average $M-N$ bond lengths involving the N atom of the hydrazine ligand are

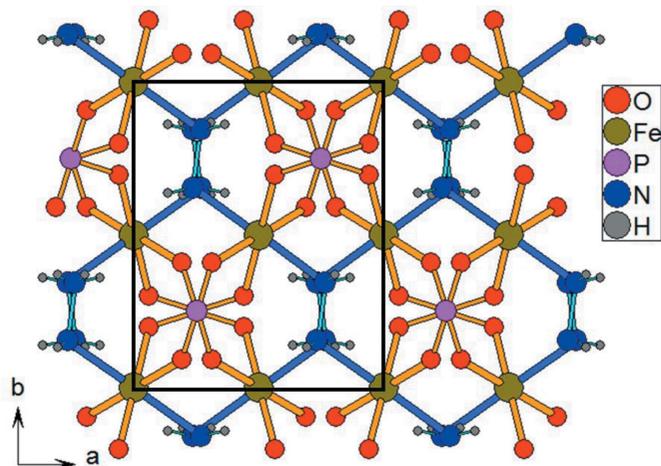


Figure 2
The crystal structure of $[Fe(PO_4)(N_2H_4)]$ in a projection along [001].

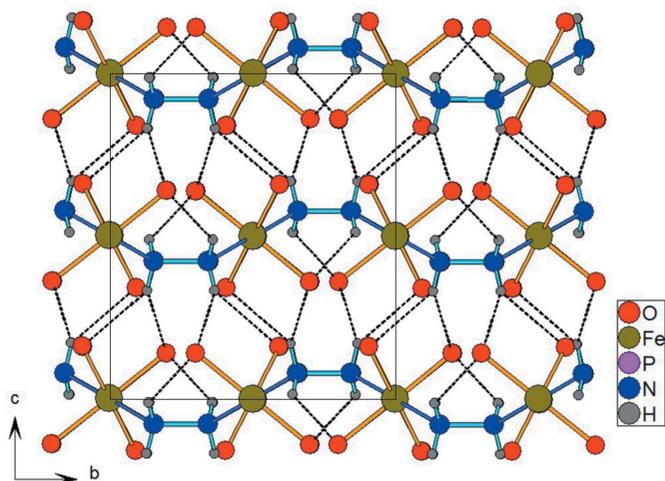


Figure 3
The crystal structure of $[Fe(PO_4)(N_2H_4)]$ in a projection along [100], emphasizing the hydrogen bonding between the components (black dotted lines). P atoms have been omitted for clarity.

similar, with values of 2.17 and 2.12 Å, respectively. As a consequence, the FeN_2O_4 octahedron is more distorted, appearing like an FeO_4 square additionally bound by two *trans* hydrazine ligands in axial positions.

It should be noted that it seems rather surprising to stabilize Fe^{III} with hydrazine, since the latter is a powerful reducing agent. Efforts are currently underway to obtain the title compound as a pure phase to perform magnetic measurements. It could be a way, by comparison with the results reported for $[Co(SO_4)(N_2H_4)]$ (Jia *et al.*, 2011), to study the ability of hydrazine to transmit magnetic coupling.

3. Supramolecular features

The three-dimensional framework structure of $[Fe(PO_4)(N_2H_4)]$ is consolidated by $N-H\cdots O$ interactions between the hydrazine ligands and phosphate O atoms (Fig. 3). One of the two hydrogen bonds is bifurcated. Considering the $N\cdots O$ distances and the values of the $N-H\cdots$ angles (Table 1), this type of hydrogen bonding can be considered as moderately strong.

4. Synthesis and crystallization

Iron(II) chloride tetrahydrate (>99.0%, Sigma–Aldrich), hydrazine monohydrate (99+%) and KH_2PO_4 (both VWR International) were used as received without further purification. Iron(II) chloride tetrahydrate (2 g) was dissolved in water (20 ml) before adding hydrazine monohydrate (2 ml). The obtained solution was stirred for 5 min. Then, KH_2PO_4 (11.5 g) was added. After 10 min of stirring for homogenization, the obtained solution (15 ml) was incorporated in a 23 ml autoclave. The autoclave was then heated at 433 K for 10 h before being cooled to room temperature at a rate of 10 K h^{-1} . The obtained mixture, consisting of orange crystals of the title phase and yellow crystals of an additional phase, was washed with water. The obtained crystals were very small

(around 20 μm) and well isolated from the others. Details of the composition and structure of the yellow crystals will be described in a forthcoming article.

5. Refinement details

Crystal data, data collection and structure refinements are summarized in Table 2. All H atoms were located in a difference Fourier map and were refined freely with isotropic displacement parameters.

Acknowledgements

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Table 2
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | [Fe(PO ₄)(N ₂ H ₄)] |
| M_r | 182.87 |
| Crystal system, space group | Orthorhombic, <i>Pccn</i> |
| Temperature (K) | 293 |
| a, b, c (Å) | 6.3114 (13), 7.6680 (15), 8.6485 (18) |
| V (Å ³) | 418.55 (15) |
| Z | 4 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 3.89 |
| Crystal size (mm) | 0.05 × 0.03 × 0.03 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2013) |
| T_{\min} , T_{\max} | 0.668, 0.746 |
| No. of measured, independent and observed [$I > 3\sigma(I)$] reflections | 13820, 601, 457 |
| R_{int} | 0.065 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.717 |
| Refinement | |
| $R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, S | 0.020, 0.027, 1.46 |
| No. of reflections | 601 |
| No. of parameters | 47 |
| H-atom treatment | All H-atom parameters refined |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.40, -0.33 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014) and *DIAMOND* (Brandenburg & Putz, 2010).

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2010); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2014).

Poly[(μ_2 -hydrazine)(μ_4 -phosphato)iron(III)]

Crystal data

[Fe(PO₄)(N₂H₄)]
 $M_r = 182.87$
 Orthorhombic, *Pccn*
 Hall symbol: -P 2ab 2ac
 $a = 6.3114$ (13) Å
 $b = 7.6680$ (15) Å
 $c = 8.6485$ (18) Å
 $V = 418.55$ (15) Å³
 $Z = 4$

$F(000) = 364$
 $D_x = 2.902$ Mg m⁻³
 Mo *K* α radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2128 reflections
 $\theta = 4.2$ – 26.9°
 $\mu = 3.89$ mm⁻¹
 $T = 293$ K
 Parallelepiped, orange
 0.05 × 0.03 × 0.03 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: X-ray tube
 phi scan
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2013)
 $T_{\min} = 0.668$, $T_{\max} = 0.746$
 13820 measured reflections

601 independent reflections
 457 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\max} = 30.6^\circ$, $\theta_{\min} = 4.2^\circ$
 $h = -9 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F
 $R[F > 3\sigma(F)] = 0.020$
 $wR(F) = 0.027$
 $S = 1.46$
 601 reflections
 47 parameters
 0 restraints

0 constraints
 All H-atom parameters refined
 Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(F) + 0.0001F^2)$
 $(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.40$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|-------------|--------------|--------------|----------------------------------|
| O1 | -0.0604 (2) | 0.30096 (17) | 0.36016 (16) | 0.0093 (4) |
| Fe | 0 | 0 | 0 | 0.00652 (11) |
| P | -0.25 | 0.25 | 0.25868 (8) | 0.00567 (17) |
| O2 | -0.1898 (2) | 0.09269 (19) | 0.15978 (16) | 0.0111 (4) |
| N | 0.2656 (3) | 0.1556 (2) | 0.0781 (2) | 0.0103 (5) |
| H1 | 0.306 (4) | 0.132 (3) | 0.169 (3) | 0.024 (7)* |
| H2 | 0.364 (4) | 0.139 (3) | 0.012 (3) | 0.020 (7)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|--------------|------------|--------------|---------------|--------------|---------------|
| O1 | 0.0089 (6) | 0.0090 (7) | 0.0099 (7) | 0.0001 (5) | -0.0032 (5) | -0.0013 (5) |
| Fe | 0.00692 (19) | 0.0059 (2) | 0.00678 (19) | -0.00013 (13) | 0.00010 (16) | -0.00054 (16) |
| P | 0.0059 (3) | 0.0053 (3) | 0.0057 (3) | -0.0001 (3) | 0 | 0 |
| O2 | 0.0135 (6) | 0.0096 (7) | 0.0101 (7) | 0.0003 (5) | 0.0030 (6) | -0.0033 (6) |
| N | 0.0110 (8) | 0.0074 (8) | 0.0123 (9) | -0.0017 (7) | -0.0012 (8) | 0.0010 (7) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------------------------------------|-------------|--|-------------|
| O1—Fe ⁱ | 1.9843 (14) | P—O2 ⁱⁱⁱ | 1.5268 (15) |
| O1—P | 1.5346 (15) | N—N ^{iv} | 1.461 (2) |
| Fe—O2 | 1.9621 (15) | N—H1 | 0.85 (3) |
| Fe—O2 ⁱⁱ | 1.9621 (15) | N—H2 | 0.85 (3) |
| P—O2 | 1.5268 (15) | | |
| Fe ⁱ —O1—P | 133.97 (8) | O1—P—O2 ⁱⁱⁱ | 108.25 (7) |
| O1 ^v —Fe—O1 ^{vi} | 180.0 (5) | O1 ⁱⁱⁱ —P—O2 | 108.25 (7) |
| O1 ^v —Fe—O2 | 88.09 (6) | O1 ⁱⁱⁱ —P—O2 ⁱⁱⁱ | 109.13 (7) |
| O1 ^v —Fe—O2 ⁱⁱ | 91.91 (6) | O2—P—O2 ⁱⁱⁱ | 111.85 (9) |
| O1 ^{vi} —Fe—O2 | 91.91 (6) | Fe—O2—P | 146.37 (9) |
| O1 ^{vi} —Fe—O2 ⁱⁱ | 88.09 (6) | N ^{iv} —N—H1 | 104.6 (18) |
| O2—Fe—O2 ⁱⁱ | 180.0 (5) | N ^{iv} —N—H2 | 104.2 (18) |
| O1—P—O1 ⁱⁱⁱ | 110.23 (8) | H1—N—H2 | 112 (2) |
| O1—P—O2 | 109.13 (7) | | |

Symmetry codes: (i) $-x, y+1/2, -z+1/2$; (ii) $-x, -y, -z$; (iii) $-x-1/2, -y+1/2, z$; (iv) $-x+1/2, -y+1/2, z$; (v) $-x, y-1/2, -z+1/2$; (vi) $x, -y+1/2, z-1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N—H1 \cdots O1 ^{iv} | 0.85 (3) | 2.36 (2) | 3.086 (2) | 144 (2) |
| N—H1 \cdots O2 ^{vii} | 0.85 (3) | 2.27 (3) | 2.974 (2) | 141 (2) |
| N—H2 \cdots O1 ^{viii} | 0.85 (3) | 2.19 (3) | 2.873 (2) | 137 (2) |

Symmetry codes: (iv) $-x+1/2, -y+1/2, z$; (vii) $x+1/2, -y, -z+1/2$; (viii) $-x+1/2, y, z-1/2$.