

Cs₃Fe₅O(OH)(AsO₄)₅: A novel iron(III) arsenate containing four-, five- and six-coordinated iron atoms

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A novel iron(III) arsenate is synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, which reveals a framework structure of vertex- and edge-sharing Fe–O polyhedra crosslinked by vertex-sharing AsO₄ tetrahedra in a manner that generates tunnels and cavities occupied by Cs⁺ cations.

Iron phosphates have shown a rich crystal chemistry owing to the accessibility of more than one oxidation state and the ability of iron–oxygen polyhedra and phosphate tetrahedra to form a variety of complex network structures. These compounds are of interest because they present a challenge to complete structural characterization from a basic research point of view. We have recently synthesized a number of new ternary iron phosphates by hydrothermal techniques. The structures of these phosphates cover discrete FeO₆ octahedra, FeO₅ trigonal bipyramids, dimers of corner-sharing, edge-sharing, or face-sharing FeO₆ octahedra, trimeric, tetrameric units of Fe–O polyhedra, and infinite chains of FeO₆ octahedra sharing either *trans* or skew edges. They include iron(II), -(III) and mixed-valence compounds.¹ In contrast to the phosphates, few compounds are known in the ternary iron arsenate system. Therefore, we have undertaken an investigation of the alkali metal–iron–arsenate phase space. This paper reports the results of our exploratory synthesis and structural characterization of a novel iron(III) arsenate, Cs₃Fe₅O(OH)(AsO₄)₅. Its structure consists of four-, five- and six-coordinated iron atoms.

High-temperature, high-pressure hydrothermal syntheses were performed in gold ampoules contained in a Leco Tem-Pre autoclave where pressure was provided by water. Chemicals of reagent grade or better were used as received. Cs₂HAsO₄₍₅₎ was prepared from a solution of As₂O₃ dissolved in H₂O₂ with caesium hydroxide. The arsenate Cs₃Fe₅O(OH)(AsO₄)₅ was synthesized by heating Cs₂HAsO₄ (0.329 g), H₃AsO₄ (0.1 ml, 3 mol dm⁻³), FeO (0.011 g) and H₂O (0.45 ml) (molar ratio Cs : As = 0.8 : 1) in a sealed gold ampoule (6.7 cm × 0.485 cm inside diameter) at 550 °C and an estimated pressure of 30 000 psi for 12 h, cooled at 5 °C h⁻¹ to 250 °C, and quenched to room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol and dried in a desiccator at ambient temperature. The product contained light brown crystals of Cs₃Fe₅O(OH)(AsO₄)₅ as the major product, a small amount of pale green crystals of CsFe(HAsO₄)₂² and orange crystals of an unidentified compound. A light brown single crystal was used to determine its structure by X-ray diffraction.[†] Other phases were obtained from similar reactions when Fe₂O₃ was used instead of FeO or the Cs to As mole ratio was 0.6 : 1. An optimum reaction condition to prepare a single-phase product of Cs₃Fe₅O(OH)(AsO₄)₅ was not found. The distinct colour of Cs₃Fe₅O(OH)(AsO₄)₅ crystals allowed for hand sorting of enough sample to carry out physical measurements. The IR spectrum, which was measured by using the KBr pellet technique, showed bands in the region 600–1000 cm⁻¹ associated with Fe–O and As–O resonances, as well as a weak peak at 3180 cm⁻¹ due to

an O–H stretch. The room-temperature Mössbauer spectrum is a symmetric doublet and does not show different Fe components as expected from the crystal structure. The spectral parameters are δ (isomer shift) = 0.357 mm s⁻¹ (relative to iron foil at 300 K), ΔE_Q (quadrupole splitting) = 0.868 mm s⁻¹, and Γ (full width at half-height) = 0.40, 0.44 mm s⁻¹. The linewidths appear broader than those for a thin iron calibration foil. The isomer shift is consistent with those for iron(III) phosphates.³

The framework consists of four different types of polyhedra in an asymmetric unit: one FeO₄ tetrahedron, one FeO₅ square pyramid, four FeO₆ octahedra, and five AsO₄ tetrahedra. Two of the four FeO₆ octahedra sit on inversion centres. The polyhedral representation of the structure along the [010] direction is given in Fig. 1, showing the complex linkage of these polyhedra. Two Fe(3)O₆ and two Fe(5)O₆ octahedra are joined by shared edges in the same way as those in the molecular tetramer [Ti(OEt)₄]₄.⁴ The structure of the Mo^V-As^{III} heteropolyanion Na₄[Mo₄As₆O₂₀(OH)₂]₉H₂O consists of a similar tetranuclear M₄O₁₆ core except for the Mo–Mo bonds in the cluster.⁵ The tetramer in Cs₃Fe₅O(OH)(AsO₄)₅ contains two discrete layers of close-packed oxygen atoms with Fe atoms in octahedral holes. The μ_3 -oxo atom, which coordinates to one Fe(3) and two Fe(5) atoms, is the hydroxy oxygen. The H atom is involved in hydrogen bonding. This tetramer is coordinated by eight arsenate ligands. Four of the eight arsenates form bridges between two neighbouring Fe atoms within a tetramer. The remaining two coordination sites of the tetramer are attached to two Fe(6)O₄ tetrahedra by corner-sharing, forming a hexanuclear iron cluster (Fig. 2). These hexamers are connected by Fe(2)O₆ octahedra, *via* –O–As–O–Fe(2)–O– bonds, to form sheets in the *bc*-plane. These sheets are linked by Fe(1)O₅ square pyramids and Fe(4)O₆ octahedra to form a three-dimensional framework, enclosing infinite tunnels along the the

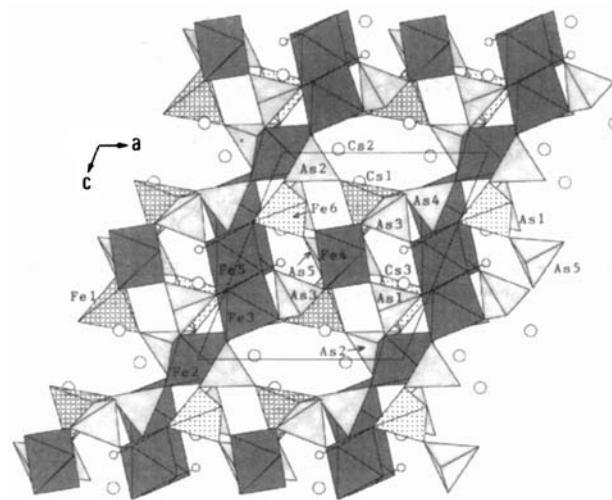


Fig. 1 Polyhedral view of the Cs₃Fe₅O(OH)(AsO₄)₅ structure along the *b*-axis; large and small open circles are Cs and H atoms, respectively

b-axis where Cs(1) and Cs(2) are located. Cs(3) is located in a cavity within the framework. The framework is also characterized by the presence of infinite tunnels along the *a*-axis occupied by Cs(2). The compound therefore adopts an intersecting tunnel structure with Cs(2) located at the intersections of the tunnels. Cations Cs(1), Cs(2) and Cs(3) are ten-, ten- and eight-coordinate with respect to nearby ($d < 3.60$ Å) oxygen atoms with $d_{av}(\text{Cs}-\text{O}) = 3.255(7)$, $3.299(8)$ and $3.086(7)$ Å and bond-valence sums (BVS)⁶ of 1.17, 1.06 and 1.46, respectively. The BVS value for Cs(3) indicates that it is tightly bound.

From the Fe–O bond lengths, the O···O distances, and O–Fe–O bond angles, we see that each FeO₆ octahedron is markedly distorted. Fe(3)O₆ and Fe(5)O₆ octahedra are more distorted than the others because of edge-sharing. The Fe(2) and Fe(4) octahedra share corners with arsenate tetrahedra only. Fe(1) is five-coordinate and its geometry is closer to square-pyramidal than to trigonal-bipyramidal. Octahedral Fe^{III} is the most common coordination polyhedron in iron arsenates and phosphates. Square-pyramidal geometry is not a common stereochemistry for Fe^{III}. The title compound is remarkable for tetrahedral Fe^{III} in the structure, which is hitherto unknown in arsenates. Tetrahedral Fe^{III} is very rare even in phosphates. To our knowledge FePO₄,⁷ which adopts the structure of low-quartz, is the only phosphate containing tetrahedral Fe^{III}. FeAsO₄ has an interesting structure in which the iron atoms are five-coordinated with approximately trigonal-bipyramidal geometry.⁸ Fe(6) in the title compound is tetrahedrally coordinated with an average Fe–O distance of 1.865(7) Å which agrees with the expected value based on ionic radii sum, 1.87 Å.⁹ The Fe(6)O₄ tetrahedron shares three oxygen atoms with three different arsenate tetrahedra with the remaining oxygen being bonded to two Fe atoms within a tetramer. The arsenate groups are tetrahedral with typical $d_{av}(\text{As}-\text{O})$ of 1.680(7)–1.686(7) Å. It is interesting that the polyhedral connectivity of As(1)O₄ is compared to that of Fe(6)O₄, namely, each As(1)O₄ shares corners with three different Fe–O polyhedra with the fourth corner to two Fe atoms in a tetramer.

In summary, the synthesis and crystal structure of a novel iron(III) arsenate, Cs₃Fe₅O(OH)(AsO₄)₅, is reported. The structure is composed of FeO₆ octahedra, FeO₅ square pyramids,

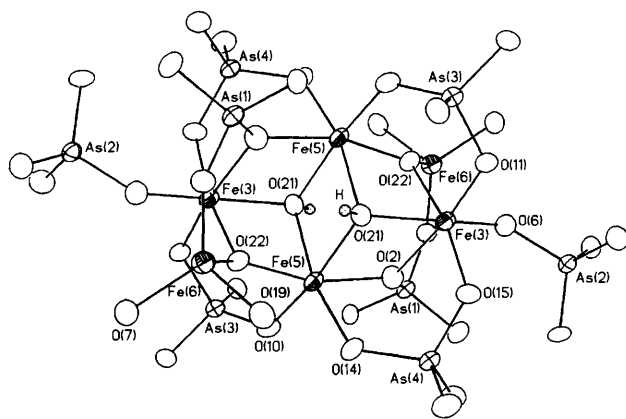


Fig. 2 The hexanuclear iron cluster in Cs₃Fe₅O(OH)(AsO₄)₅; thermal ellipsoids are shown at 60% probability

FeO₄ tetrahedra and AsO₄ tetrahedra, linked *via* Fe–O–Fe and Fe–O–As bonds, enclosing tunnels and cavities occupied by a caesium cations. The framework includes [Fe₄O₁₆] units built up from four FeO₆ octahedra sharing edges.

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Footnote

† *Crystal data* for Cs₃Fe₅O(OH)(AsO₄)₅: triclinic, space group $P\bar{1}$, $a = 10.2086(3)$, $b = 10.3528(3)$, $c = 11.7330(3)$ Å, $\alpha = 110.917(1)$, $\beta = 105.642(1)$, $\gamma = 101.990(1)^\circ$, $U = 1049.78(9)$ Å³, $Z = 2$, $M_r = 1405.59$, $D_c = 4.447$ g cm⁻³, $\mu = 164.3$ cm⁻¹, $\lambda = 0.71073$ Å, graphite monochromator, crystal dimensions: $0.3 \times 0.4 \times 0.5$ mm. The crystal was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 2300 frames with increasing ω (width of 0.3° per frame). The orientation matrix and unit-cell dimensions were determined by a least-squares fit of 7875 reflections with $2\theta > 5^\circ$. Of the 9186 reflections collected ($2\theta_{\max} = 53.3^\circ$), 3794 unique reflections were considered observed [$I > 2.5\sigma(I)$] after Lorentz polarization and absorption correction. Correction for absorption was based on 4236 symmetry-equivalent reflections using the SHELXTL PC program package ($T_{\min, \max} = 0.216, 0.948$).¹⁰ The structure was solved by direct methods: the metal and arsenic atoms were first located and all the oxygen atoms were found in difference Fourier maps. Bond-valence calculations indicated that O(21) had a valence sum of 1.16, and all other oxygen atoms had values close to 2. Because all iron atoms are trivalent, one hydrogen atom must be included to balance charge. The hydrogen atom was located from a difference Fourier map. Refinement (320 parameters) was performed by full-matrix least-squares analysis, using anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. The reliability factors converged to $R = 0.0416$ and $R_w = 0.0524$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/38.

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