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[12] Single crystal X-ray structure: orthorhombic, space group *Pbcm* (no. 57), $a = 9.1348(6)$, $b = 12.351(1)$, $c = 13.873(1)$ Å, $V = 1565.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.673$ g cm^{-1}. Data collection: STOE IPDS, 8639 reflections, 1446 independent reflections, $R_{int} = 0.0931$, room temperature, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, $-10 \leq h \leq 9$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$, crystal size $0.36 \times 0.30 \times 0.04$ mm^3, numerical absorption correction (X-RED,[13] X-SHAPE[14]). The structure was solved by direct methods and refined against F^2 (SHELX-97[15]). The refinement of 75 parameters converged to $R = 0.0369$ and $wR = 0.0771$ ($I > 2\sigma(I)$) and $R = 0.0545$ and $wR = 0.0816$ (all reflections). Min./max. electron density (final difference Fourier extremes) $-0.995/1.772$ e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411332.
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The Structure of the Fe^{IV}O$_4^{4-}$ Ion**

Mark T. Weller* and Andrew L. Hector

Most of the complex oxide chemistry of iron is restricted to the oxidation states 2 and 3 though tetravalent, pentavalent, and hexavalent iron compounds can be formed in combination with Group 1 and 2 cations. Hexavalent iron is well known as the red-purple tetrahedral ferrate(VI) ion, FeO_4^{2-}, in compounds such as Cs_2FeO_4[1] and Na_2FeO_4.[2] The FeO_4^{3-} ion, containing iron(V), has also been structurally characterized in K_3FeO_4.[3] Iron(IV) compounds include the alkali metal iron oxides such as Sr_2FeO_4,[4] $Sr_3Fe_2O_7$,[5] $SrFeO_3$,[6] and $CaFeO_3$,[7] which contain distorted FeO_6 octahedra sharing vertices; unusual electronic properties are exhibited by some of these d^4 materials due to a spin-pairing mechanism.[8] The existence of a phase of the stoichiometry Ba_2FeO_4, reported by Scholder et al.[9] as adopting the β-Ca_2SO_4 structure on the basis of similarities in the powder X-ray diffraction patterns, has not been substantiated. Fe^{3+} adopts octahedral coordination to oxygen in most of its complex oxides though the tetrahedral FeO_4^{5-} ion is known in the compound Na_5FeO_4.[10]

Scholder et al.[9] reported the synthesis of a sodium iron(IV) oxide of the stoichiometry Na_4FeO_4 but no structural data exist for this material, which might be expected to contain tetrahedral FeO_4^{4-} by analogy with other Na_4MO_4 (M = Ti, Cr, Co, Ge) compounds.[11–14] Indeed the structure of the ferrate(IV) ion has not been described to date. Iron(IV) is isoelectronic with manganese(III) and both ions exhibit Jahn–Teller distortions, due to their high-spin d^4 configurations. The observation of unusual colossal magnetoresistive properties in some Mn^{III} and Fe^{IV} compounds[15] is associated with structural distortions in these d^4 species. Herein we report for the first time the geometry of the FeO_4^{4-} ion as determined in sodium ferrate(IV).

The structure of Na_4FeO_4 consists of discrete FeO_4^{4-} ions separated by sodium ions as shown in Figure 1. Each unit cell contains two ferrate(IV) ions related by a center of symmetry, and the sodium ions coordinate to four (Na1, Na2, and Na3) or five (Na4) oxygen atoms at 2.3–2.5 Å, though Na1 has two and Na3 has one longer, additional interactions to an oxygen atom. The most remarkable feature of the structure is that the FeO_4^{4-} tetrahedron is strongly distorted (Figure 2). The unit is squashed along one C_2 axis to give the ion approximately D_{2d} symmetry, rather than perfect tetrahedral, and two of the

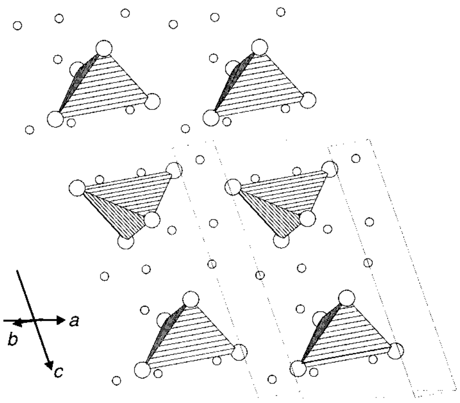

Figure 1. Unit cell of Na_4FeO_4. FeO_4^{4-} units are shown as polyhedra and sodium atoms as spheres.

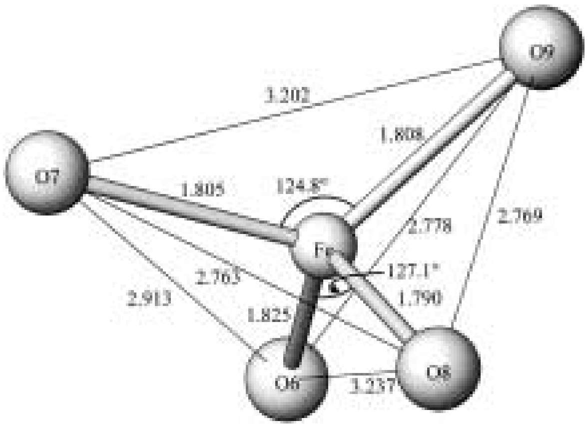

Figure 2. Geometry of the FeO_4^{4-} ion. Other bond angles [°] not shown for clarity are O6-Fe-O7 106.7(2), O6-Fe-O9 99.8(2), O7-Fe-O8 100.5(2), O8-Fe-O9 100.6(2).

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O-Fe-O bond angles open out to 125° and 127°, respectively. Such behavior is well known for d^9 systems, for example tetrahedral copper(II) in species such as $CuCl_4^{2-}$ in Cs_2CuCl_4 and, much more rarely, d^4-centered tetrahedra.[16] The only previous example of a d^4 oxotetrahedral unit is in the MnO_4^{5-} ion present in Na_5MnO_4, where squashed tetrahedral geometry is also adopted with two O-Mn-O bond angles between 130° and 135°.[17] The d^4 Fe^{IV} ion in Na_4FeO_4 evidently displays similar Jahn–Teller-originated distortion. In terms of the unit cell this flattening of the tetrahedron in comparison with other MO_4^{4-} ions in Na_4MO_4 compounds results in a contraction along the *c* direction (e.g. Na_4GeO_4 8.58 Å, Na_4FeO_4 8.24 Å) as the tetrahedra can approach each other more closely.

The average Fe–O distance in the ferrate(IV) ion of 1.807 Å is in line with that expected from other FeO_4^{n-} ions (FeO_4^{2-} 1.647, FeO_4^{3-} 1.720, FeO_4^{5-} 1.889 Å). However all these other ferrate ions are close to perfect tetrahedra.

Experimental Section

Black Na_4FeO_4 was synthesized from FeO (Aldrich, 99.9%) and Na_2O_2 (Aldrich, 97%) (1:2) by heating the mixture at 400 °C for 48 h. The mixture was pelletized, placed in a gold crucible, and sealed under vacuum into a Pyrex tube. All reagents and products were handled in a dry nitrogen glove box. The powder X-ray diffraction pattern (Siemens D5000, $Cu_{K\alpha 1}$ radiation) of the crystalline product showed no evidence of starting materials or other known compounds from the Na-Fe-O system. Time-of-flight neutron diffraction data were collected for 2 h on the POLARIS high-flux diffractometer at the ISIS facility. IR (nujol, Perkin-Elmer Spectrum One): $\tilde{\nu} = 600$ (br), 799 cm^{-1} (br); Fe content (gravimetric with 8-hydroxyquinoline); found: 27.4%; calcd: 26.4%; Fe oxidation state (iodometric): 3.97 ± 0.05.

2θ reflection positions were extracted from the neutron diffraction data and indexed by using the DICVOL91 program.[18] Successful indexing was performed with a triclinic cell of dimensions and volume similar to those reported for other Na_4MO_4 phases though one angle and cell dimension were significantly different indicating a compression of the unit cell along one direction. A Le Bail extraction using this cell and the high-resolution back scattering neutron diffraction data produced an excellent fit (χ^2 ca. 1) demonstrating this as the correct unit cell. Structural models were developed from the published data on Na_4GeO_4 ($P\bar{1}$)[14] and Na_4CoO_4 ($P1$)[13] and these were refined by using the GSAS program suite.[19] After refinement an excellent fit to the profiles was obtained in $P\bar{1}$ and it was found unnecessary to reduce the symmetry to $P1$. Final refined atomic coordinates and profile fit parameters are summarized in Table 1, derived bond lengths and angles of significance relating to the FeO_4 tetrahedron are shown in Figure 2 and the final profile fit achieved is shown in Figure 3.

Table 1. Refined atomic coordinates for Na_4FeO_4 and the parameter B_{iso} for the profile fit (esds are given in parentheses).[a]

Atom	*x*	*y*	*z*	B_{iso} [Å^2]
Na1	0.4061(11)	0.7871(10)	0.1306(7)	1.99(10)
Na2	0.7920(9)	0.2657(9)	0.4835(6)	1.11(10)
Na3	0.7521(10)	0.7702(8)	0.3342(6)	1.37(10)
Na4	0.9502(10)	0.2800(9)	0.0679(6)	1.49(10)
Fe5	0.4083(3)	0.2786(4)	0.2482(2)	0.88(4)
O6	0.2429(7)	0.0979(6)	0.3938(4)	1.60(7)
O7	0.1650(6)	0.5031(6)	0.1708(4)	1.24(7)
O8	0.5630(6)	0.4729(6)	0.2998(4)	1.01(6)
O9	0.6901(6)	0.0282(6)	0.1164(4)	1.05(5)

[a] Space Group $P\bar{1}$, $a = 5.76205(11)$, $b = 5.76188(10)$, $c = 8.24301(15)$ Å, $\alpha = 87.8769(14)$, $\beta = 71.9681(14)$, $\gamma = 69.3396(12)°$, $V = 242.690(8)$ Å^3, $R_{wp} = 0.0205$, $R_p = 0.0366$, $R_I = 0.0305$.

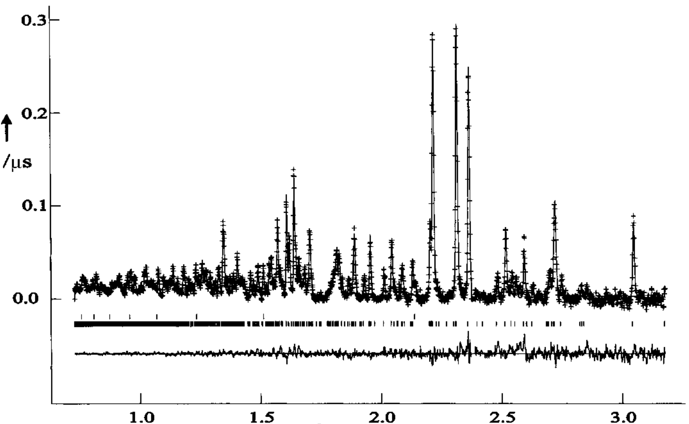

Figure 3. Final profile fit obtained to the powder neutron diffraction data from Na_4FeO_4. Crosses are observed data, upper continuous line the calculated profile and lower continuous line the difference. Tick marks represent peak positions, upper set vanadium from the sample can and lower Na_4FeO_4. *n* is the number of counts.

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