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Rietveld refinement of the Tutton salt K₂[Fe(H₂O)₆](SO₄)₂

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Dipotassium hexaaquairon(II) bis(sulfate), $K_2[Fe(H_2O)_6](SO_4)_2$, is a member of the isotypic series of Tutton salts with general formula $M^I_2[M^{II}(H_2O)_6](XO_4)_2$, where X = S, Se or Cr. The structure contains centrosymmetric $Fe(H_2O)_6$ octahedra, with an average Fe—O distance of 2.14 (4) Å. Each octahedron is surrounded by isolated SO_4 tetrahedra [average S—O distance = 1.483 (15) Å] and distorted $KO_6(H_2O)_2$ polyhedra with an average K—O distance of 2.96 (15) Å. The polyhedra are linked *via* common O atoms and a system of medium-strength hydrogen bonds.

Comment

The title compound is a member of the isotypic series $M^I_2[M^{II}(H_2O)_6](XO_4)_2$, also known as Tutton salts, where X = S, Se or Cr. The structure consists of $M^{II}(H_2O)_6$ octahedra, with M^{II} located at a centre of symmetry, linked to four M^IO_8 polyhedra *via* the equatorial O atoms that belong to water molecules, and to eight XO_4 tetrahedra *via* medium-strength hydrogen bonds (Fig. 1 and Table 2). Whereas the $M^I = NH_4$ series has been fully structurally characterized (Cotton *et al.*,
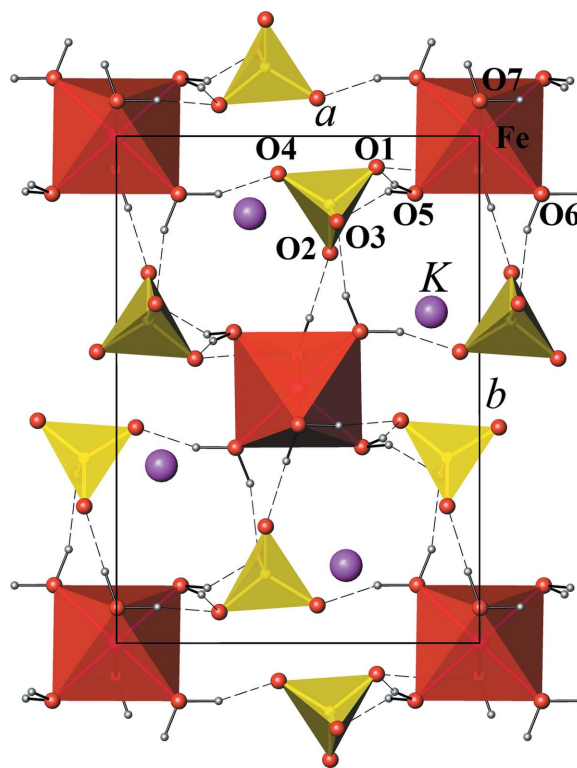
Figure 1
Crystal structure of $K_2[Co(H_2O)_6](SO_4)_2$ as seen along [001]. FeO₆ octahedra are red, SO₄ tetrahedra are yellow, K atoms are purple, O atoms are red and H atoms are grey.
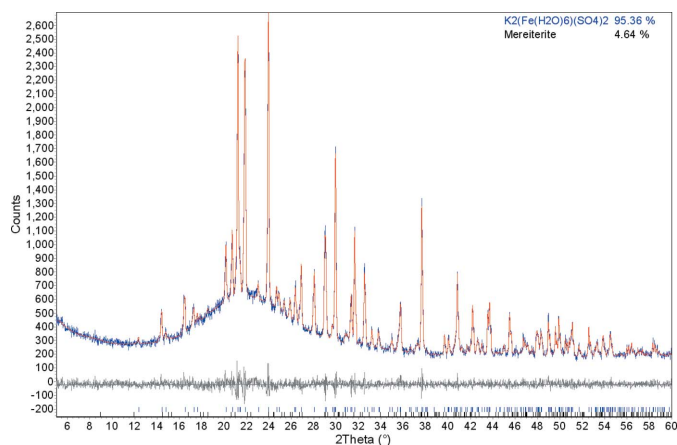
Figure 2
Experimental (blue line) and calculated (red line) intensities of $K_2[Fe(H_2O)_6](SO_4)_2$ in the range 5–60° 2θ. The difference plot appears below. Vertical markers refer to calculated position of Bragg reflections of $K_2[Fe(H_2O)_6](SO_4)_2$ (blue) and $K_2Fe(SO_4)_2{\cdot}4H_2O$ (mereiterite; black).

1993), the M^I = K series has been investigated only for M^{II} = Co (Kirfel *et al.*, 1998), Cu (Robinson & Kennard, 1972), Mg (Kannan & Viswamitra, 1965), Ni (Pietraszko *et al.*, 2000) and Zn (Whitnall *et al.*, 1975). We report here the structure refinement for M^I = K and M^{II} = Fe by the Rietveld method based on conventional X-ray data (Fig. 2).

The average Fe—O distance within the $Fe(H_2O)_6$ octahedron is 2.14 (4) Å. This value compares well with that of 2.13 (2) Å for $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$ (Cotton *et al.*, 1993), and with that of 2.13 (4) Å reported by Euler *et al.* (2000) for $Rb_2[Fe(H_2O)_6](SO_4)_2$. The $Fe(H_2O)_6$ octahedron is slightly distorted, with three different bond distances (Table 1), which are caused by the fact that O7 is linked only to Fe whereas both O5 and O6 are bonded to Fe and K. In the sulfate tetrahedron, as in other Tutton salts, the S—O4 distance is slightly smaller [1.464 (13) Å] than the remaining three [1.482 (16)–1.496 (15) Å] owing to bond-valence requirements. Atoms O4 and O2 are acceptors for a single hydrogen bond, while both O1 and O3 are acceptors for two hydrogen bonds each. Despite the fact that both O2 and O4 are bonded to two K atoms, O4 is only weakly bonded to one of the two cations. The K atom is coordinated by six O atoms and two water molecules with an average K—O distance of 2.96 (15) Å, which is identical to that reported for $K_2[Co(H_2O)_6](SO_4)_2$ (Kirfel *et al.*, 1998). A similar trend is observed in $Rb_2[Fe(H_2O)_6](SO_4)_2$ (average Rb—O distance = 3.07 (12) Å; Euler *et al.*, 2000) and $Rb_2[Co(H_2O)_6](SO_4)_2$ (average Rb—O distance = 3.06 (12) Å; Euler *et al.*, 2000).

Experimental

The title compound was prepared by dissolving K_2SO_4 (Merck, p.A.) and $FeSO_4{\cdot}7H_2O$ (Carlo Erba, p.A.) in distilled water with a salt fraction, defined as mol K_2SO_4/(mol K_2SO_4 + mol $FeSO_4$) = 0.3, acidified with sulfuric acid (pH = 2.05) and ensuing slow evaporation at 294 K. The resulting crystals, in equilibrium with the mother solution, were removed and dried at room temperature. The product consisted of a fine pale-green powder of $K_2[Fe(H_2O)_6](SO_4)_2$ that was found to be unstable in air as it quickly dehydrates to

$K_2Fe(SO_4)_2{\cdot}4H_2O$ (synthetic mereiterite). The sample became yellow during X-ray irradiation.

Crystal data

$K_2[Fe(H_2O)_6](SO_4)_2$	$Z = 2$
$M_r = 434.29$	$D_x = 2.170$ Mg m^{-3}
Monoclinic, $P2_1/a$	Cu $K\alpha$ radiation
$a = 9.0766\ (3)$ Å	$\mu = 18.36$ mm^{-1}
$b = 12.2646\ (4)$ Å	$T = 298$ K
$c = 6.1689\ (2)$ Å	Specimen shape: cylinder
$\beta = 104.5478\ (16)°$	Particle morphology: prism, pale
$V = 664.71\ (4)$ Å^3	green

Data collection

Bruker AXS D8Focus diffractometer	Scan method: step
Specimen mounting: borosilicate glass capillary	Absorption correction: for a cylinder mounted on the φ axis (Sabine *et al.*, 1998)
Specimen mounted in transmission mode	$2\theta_{min} = 5.0$, $2\theta_{max} = 155.0°$
	Increment in $2\theta = 0.02°$

Refinement

$R_p = 5.04$	95 parameters
$R_{wp} = 6.40$	H-atom parameters not refined
$R_{exp} = 6.16$	$w = 1/Y_i$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.01$
Wavelength of incident radiation:	Preferred orientation correction:
Cu $K\alpha_{1a}$ 1.540596, Cu $K\alpha_{1b}$ 1.541058, Cu $K\alpha_{2a}$ 1.544410, Cu $K\alpha_{2b}$ 1.544721, satellites 1.534753 Å	Spherical Harmonics Order 4 y00, 1 y20, −0.077(12) y22m, −0.039(11) y22p, −0.023(12) y40, −0.063(17) y42m, −0.018(11) y42p, −0.041(12) y44m, −0.014(12) y44p, −0.011(14)
Profile function: FPA (Cheary & Coelho, 1992)	

Table 1
Selected geometric parameters (Å, °).

Fe—O5	2.183 (11)	K—O3^v	2.844 (13)
Fe—O5^i	2.183 (11)	K—O4^{ii}	3.238 (12)
Fe—O6	2.140 (12)	K—O4^{iv}	2.946 (15)
Fe—O6^i	2.140 (12)	K—O5	3.121 (12)
Fe—O7	2.081 (12)	K—O6^{vi}	2.978 (13)
Fe—O7^i	2.081 (12)	S—O1	1.493 (13)
K—O1^{ii}	2.731 (13)	S—O2	1.496 (15)
K—O2^{iii}	2.942 (13)	S—O3	1.482 (16)
K—O2^{iv}	2.890 (15)	S—O4	1.464 (13)
O1—S—O2	108.6 (7)	O2—S—O3	112.9 (8)
O1—S—O3	108.4 (6)	O2—S—O4	108.9 (6)
O1—S—O4	107.6 (6)	O3—S—O4	110.5 (7)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H11$\cdots$O3	0.98	1.82	2.73 (2)	152
O5—H12$\cdots$O1^{iii}	0.96	1.86	2.78 (2)	162
O6—H21$\cdots$O3^v	0.95	1.98	2.79 (2)	142
O6—H22$\cdots$O4^{vii}	0.96	1.92	2.70 (1)	136
O7—H31$\cdots$O2^v	0.97	1.85	2.64 (1)	137
O7—H32$\cdots$O1	0.98	1.86	2.70 (1)	142

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

Powder diffraction data were analysed by the Rietveld method using the fundamental parameter approach (FPA) as described by

Cheary & Coelho (1992). This convolutive approach has proved to be able to reproduce the peak shape more closely than the conventional approach. Starting atomic positions of non-H atoms were those of $K_2[Co(H_2O)_6](SO_4)_2$ (Kirfel *et al.*, 1998) in space group $P2_1/a$. For better comparison with other Tutton salts we also used this non-standard setting of space group $P2_1/c$. Careful scrutiny of the difference plot indicated the presence of minor amounts of $K_2Fe(SO_4)_2 \cdot 4H_2O$ (synthetic mereiterite), which was included to the refinement. Structural parameters for mereiterite were used from single-crystal data (Giester & Rieck, 1995), but only cell parameters were refined for this phase, leading to $a = 11.849\,(3)$ Å, $b = 9.550\,(3)$ Å, $c = 9.949\,(4)$ Å and $\beta = 94.90\,(3)°$, which is in very good agreement with the single-crystal data $[a = 11.841\,(3)$ Å, $b = 9.553\,(2)$ Å, $c = 9.942\,(2)$ Å, $\beta = 94.87\,(1)°]$. Refinement of individual scale factors revealed the presence of 5 (1) wt% mereiterite. H-atom positions for $K_2[Fe(H_2O)_6](SO_4)_2$ were calculated on the basis of the $K_2[Co(H_2O)_6](SO_4)_2$ hydrogen-bond network. Inclusion of the H atoms (no positions refined; $U_{eq}(H) = 0.05$ Å^2 for all H atoms) improved significantly the quality of the fit, especially with respect to the Fe—O bond distances that otherwise resulted in being larger than expected.

Data collection: *DiffracPlus* (Bruker, 2004); cell refinement: *TOPAS* (Bruker, 2005); data reduction: *DiffracPlus*; program(s) used to solve structure: coordinates taken from isotypic compound; program(s) used to refine structure: *TOPAS*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *TOPAS*.

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