

The high-temperature β modification of iron(II) sulfate

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{S-O}) = 0.001$ Å; R factor = 0.016; wR factor = 0.044; data-to-parameter ratio = 26.3.

Single crystals of the high-temperature modification of iron(II) sulfate, β -FeSO₄, were grown using chemical transport reactions with HCl as transport agent. The title compound crystallizes in the CuSO₄ structure (space group *Pnma*) and is isotypic with other divalent metal sulfates $M^{II}\text{SO}_4$ adopting this structure type ($M = \text{Mg, Co, Zn}$). The coordination polyhedron of the Fe²⁺ cation is a distorted octahedron ($\bar{1}$ symmetry) with a [2+2+2] distribution of bond lengths. By edge-sharing of the [FeO₆] octahedra, [FeO_{4/2}O_{2/1}]_∞ chains are established parallel to [010]; these are linked into a framework by corner-sharing with slightly distorted SO₄ tetrahedra (m symmetry).

Related literature

For single-crystal growth of β -FeSO₄ using chemical transport reactions, see: Dahmen & Gruehn (1991). Lattice parameters of this polymorph were reported by Kirfel *et al.* (1977). The structure of the α -FeSO₄ polymorph was determined by Samaras & Coing-Boyat (1970). For the isotypic MgSO₄, see: Weil (2007). For the bond-valence model, see: Brown (2002) and Brese & O'Keeffe (1991). Average S—O distances were calculated by Baur (1981) and ionic radii were taken from Shannon (1976).

Experimental

Crystal data

FeSO ₄	$V = 283.38$ (4) Å ³
$M_r = 151.91$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 8.7042$ (8) Å	$\mu = 5.86$ mm ⁻¹
$b = 6.8013$ (5) Å	$T = 293$ (2) K
$c = 4.7868$ (5) Å	$0.50 \times 0.43 \times 0.14$ mm

Data collection

Nonius CAD-4 diffractometer	875 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (<i>HABITUS</i> ; Herrendorf, 1997)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.207$, $T_{\text{max}} = 0.736$	3 standard reflections
6494 measured reflections	frequency: 120 min
922 independent reflections	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	35 parameters
$wR(F^2) = 0.044$	$\Delta\rho_{\text{max}} = 0.61$ e Å ⁻³
$S = 1.15$	$\Delta\rho_{\text{min}} = -0.60$ e Å ⁻³
922 reflections	

Table 1

Selected bond lengths (Å).

Fe—O1 ⁱ	2.0111 (5)	S—O1	1.4613 (5)
Fe—O2	2.1514 (5)	S—O3 ⁱⁱ	1.4778 (8)
Fe—O3 ⁱ	2.2923 (5)	S—O2	1.4924 (8)

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

Data collection: *CAD-4 Software* (Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (implemented in *PLATON*; Spek, 2003); method used to solve structure: coordinates taken from an isotypic structure; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2037).

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Comment

Like many other anhydrous sulfates $M^{\text{II}}\text{SO}_4$ (M = first row transition metal, Mg), anhydrous iron(II) sulfate is dimorphic and crystallizes in a low-temperature modification (α -form; space group $Cmcm$, CrVO_4 structure type) and a high-temperature modification (β -form, space group $Pnma$, CuSO_4 structure type). The refinement of the crystal structure of α - FeSO_4 has already been reported (Samaras & Coing-Bayat, 1970), whereas a detailed structure determination of β - FeSO_4 is still missing, although the single-crystal growth of β - FeSO_4 using chemical transport reactions has been reported some time ago (Dahmen & Gruehn, 1991).

The crystal structure of β - FeSO_4 contains one Fe, one S and three O atoms in the asymmetric unit. The basic structural features are $[\text{FeO}_{4/2}\text{O}_{2/1}]_{\infty}$ chains made up of edge-sharing $[\text{FeO}_6]$ octahedra and SO_4 tetrahedra. The chains run parallel to $[010]$ and are interconnected by corner-sharing with the SO_4 tetrahedra into a framework structure (Fig. 1). The $[\text{FeO}_6]$ octahedron ($\bar{1}$ point symmetry) is considerably distorted and shows a $[2 + 2 + 2]$ coordination, with two short Fe—O distances to the terminal O atoms and two medium and two long distances to the bridging O atoms of the $[\text{FeO}_{4/2}\text{O}_{2/1}]_{\infty}$ chains. However, the average Fe—O distance of 2.105 Å is in good agreement with the sum of the ionic radii (2.15 Å for high-spin Fe^{2+} ; Shannon, 1976).

The SO_4 tetrahedron (m point symmetry) is slightly distorted, with an average S—O bond length of 1.473 Å which is in perfect agreement with the value of 1.473 Å given by Baur (1981) for more than 100 S—O bond lengths in various sulfates(VI).

The O atoms have coordination numbers of 2 (O1) and 3 (O2, O3). O1 has one Fe and one S as neighbours, both with the shortest observed Fe—O and S—O bond lengths. O2 and O3 act as the bridging atoms in the $[\text{FeO}_{4/2}\text{O}_{2/1}]_{\infty}$ chains and thus have two Fe and one S as coordination partner.

Results from the bond valence sum (BVS) calculations (Brown, 2002), using the parameters of Brese & O'Keeffe (1991), are in accordance with the expected values (in valence units) of 2 for Fe, 6 for S and 2 for O: Fe 2.04, S 6.02, O1 2.03, O2 2.07, O3 1.93.

Experimental

Iron powder (Merck, p.A.) was dissolved in half-concentrated sulfuric acid, leading to crystallization of light-blue $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ after evaporation of the solvent. The heptahydrate was dehydrated in a tube furnace at 573 K for 3 h under a flowing N_2/H_2 (90/10) atmosphere. X-ray powder diffraction (XRPD) of the greyish powder revealed a single phase product of the low-temperature modification, α - FeSO_4 (Samaras & Coing-Boyat, 1970). 0.5 g of the polycrystalline material was then mixed with 35 mg NH_4Cl and heated in a sealed and evacuated silica ampoule in a temperature gradient 973 \rightarrow 873 K

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for six days. Under these conditions NH_4Cl is decomposed and the released HCl acts as the actual transport agent. After the reaction time, the ampoule was taken out of the two-zone furnace and was quenched in a cold water bath. Single crystals of $\beta\text{-FeSO}_4$ with mostly plate-like habit, a colourless to light-green colour and maximal edge lengths up to 1 mm were obtained in the colder zone ("sink") of the ampoule, accompanied with a few crystals of hematite ($\alpha\text{-Fe}_2\text{O}_3$). The remaining material at the hotter zone of the ampoule ("source") turned out to be hematite with only small amounts of $\beta\text{-FeSO}_4$.

Refinement

Atomic coordinates were taken from the isotopic compound MgSO_4 (Weil, 2007) as starting parameters. The obtained lattice parameters of $\beta\text{-FeSO}_4$ are in good agreement with those given by Kirfel *et al.* (1977) calculated from powder data ($a = 8.715$, $b = 6.804$, $c = 4.795$ Å; the latter values were transformed from the setting in $Pbnm$).

Figures

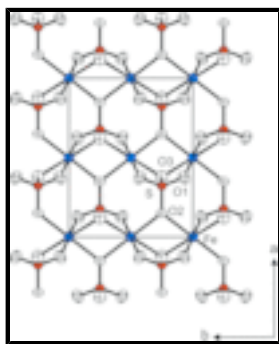


Fig. 1. The crystal structure of $\beta\text{-FeSO}_4$ projected along $[001]$. Displacement ellipsoids are drawn at the 90% probability level.

Iron(II) sulfate

Crystal data

FeSO_4

$M_r = 151.91$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 8.7042$ (8) Å

$b = 6.8013$ (5) Å

$c = 4.7868$ (5) Å

$V = 283.38$ (4) Å³

$Z = 4$

$F_{000} = 296$

$D_x = 3.561$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10.3\text{--}15.9^\circ$

$\mu = 5.86$ mm⁻¹

$T = 293$ (2) K

Plate, light green

$0.50 \times 0.43 \times 0.14$ mm

Data collection

Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 40.0^\circ$

$\theta_{\text{min}} = 4.9^\circ$

$h = -15 \rightarrow 15$

$\omega/2\theta$ scans $k = -12 \rightarrow 12$
 Absorption correction: numerical (HABITUS; Herrendorf, 1997) $l = -8 \rightarrow 8$
 $T_{\min} = 0.207$, $T_{\max} = 0.736$ 3 standard reflections
 6494 measured reflections every 120 min
 922 independent reflections intensity decay: none
 875 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 Primary atom site location: isomorphous structure methods
 Least-squares matrix: full $w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.0945P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $R[F^2 > 2\sigma(F^2)] = 0.016$ $(\Delta/\sigma)_{\max} = 0.003$
 $wR(F^2) = 0.044$ $\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$
 $S = 1.15$ $\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$
 922 reflections Extinction correction: SHELXL,
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 35 parameters Extinction coefficient: 0.447 (10)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe	0.0000	0.0000	0.0000	0.00895 (6)
S	0.32185 (3)	0.2500	0.02339 (4)	0.00617 (6)
O1	0.37412 (6)	0.07077 (8)	0.16234 (11)	0.01162 (10)
O2	0.15045 (9)	0.2500	0.03136 (16)	0.00953 (11)
O3	0.37783 (9)	0.2500	0.73194 (15)	0.01058 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe	0.00881 (8)	0.00821 (8)	0.00984 (8)	-0.00098 (3)	0.00274 (3)	-0.00160 (3)
S	0.00547 (9)	0.00710 (9)	0.00596 (8)	0.000	-0.00039 (5)	0.000
O1	0.0131 (2)	0.01013 (18)	0.01163 (19)	0.00265 (15)	-0.00303 (15)	0.00258 (15)

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O2	0.0056 (2)	0.0089 (3)	0.0141 (3)	0.000	0.00039 (19)	0.000
O3	0.0124 (3)	0.0119 (3)	0.0075 (2)	0.000	0.0027 (2)	0.000

Geometric parameters (Å, °)

Fe—O1 ⁱ	2.0111 (5)	Fe—O3 ⁱ	2.2923 (5)
Fe—O1 ⁱⁱ	2.0111 (5)	S—O1 ^{iv}	1.4613 (5)
Fe—O2 ⁱⁱⁱ	2.1514 (5)	S—O1	1.4613 (5)
Fe—O2	2.1514 (5)	S—O3 ^v	1.4778 (8)
Fe—O3 ⁱⁱ	2.2923 (5)	S—O2	1.4924 (8)
O1 ⁱ —Fe—O1 ⁱⁱ	180.00 (4)	O3 ⁱⁱ —Fe—O3 ⁱ	180.00 (3)
O1 ⁱ —Fe—O2 ⁱⁱⁱ	94.96 (3)	O1 ^{iv} —S—O1	113.07 (5)
O1 ⁱⁱ —Fe—O2 ⁱⁱⁱ	85.04 (3)	O1 ^{iv} —S—O3 ^v	109.09 (3)
O1 ⁱ —Fe—O2	85.04 (3)	O1—S—O3 ^v	109.09 (3)
O1 ⁱⁱ —Fe—O2	94.96 (3)	O1 ^{iv} —S—O2	107.43 (3)
O2 ⁱⁱⁱ —Fe—O2	180.0	O1—S—O2	107.43 (3)
O1 ⁱ —Fe—O3 ⁱⁱ	92.35 (2)	O3 ^v —S—O2	110.72 (4)
O1 ⁱⁱ —Fe—O3 ⁱⁱ	87.65 (2)	S—O1—Fe ^{vi}	137.31 (4)
O2 ⁱⁱⁱ —Fe—O3 ⁱⁱ	105.67 (2)	S—O2—Fe	127.351 (17)
O2—Fe—O3 ⁱⁱ	74.33 (2)	S—O2—Fe ^{vii}	127.351 (17)
O1 ⁱ —Fe—O3 ⁱ	87.65 (2)	Fe—O2—Fe ^{vii}	104.43 (3)
O1 ⁱⁱ —Fe—O3 ⁱ	92.35 (2)	S ^{viii} —O3—Fe ^{vi}	127.61 (2)
O2 ⁱⁱⁱ —Fe—O3 ⁱ	74.33 (2)	S ^{viii} —O3—Fe ^{ix}	127.61 (2)
O2—Fe—O3 ⁱ	105.67 (2)	Fe ^{vi} —O3—Fe ^{ix}	95.76 (3)

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

Fig. 1

