Structure of Iron(II) Sulfite 2½-Hydrate

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Abstract. $FeSO_3.2\frac{1}{2}H_2O$, tetragonal, $P4_12_12$, $a = 9\cdot535$ (3), $c = 10\cdot333$ (3) Å, $Z = 8$, $M_r = 180\cdot95$, $D_x = 2\cdot56$ Mg m^{-3}, μ(Mo $K\alpha$) = 3·64 mm^{-1}; $R = 0\cdot016$ for 778 unique reflexions. The S—O distances in the sulfite ion are 1·527 (2), 1·540 (2) and 1·534 (2) Å; the Fe—O distances in the Fe—O octahedron range from 2·037 (2) to 2·284 (1) Å.

Introduction. In connexion with research on SO_2-induced atmospheric corrosion and on the catalytic oxidation of SO_2 in polluted air, interest has been focused on transition-metal sulfites. As part of this work the structure of Fe^{II} sulfite 2½-hydrate has been solved by X-ray methods. The compound was first synthesized by Bugli (1977). 1·0 g of α-$FeSO_3.3H_2O$ and *ca* 3 ml of water saturated with SO_2 at room temperature were placed in a glass ampoule, which was then sealed. The ampoule was heated overnight to *ca* 373 K. The crystals formed were light-green octahedra with two pairs of opposite corners truncated. They were oxidized slowly in air, their color changing to yellow-brown. The synthesis may be carried out at temperatures between approximately 363 and 393 K. Below *ca* 363 K α-$FeSO_3.3H_2O$ remains unchanged, and above *ca* 393 K anhydrous $FeSO_3$ forms. $FeSO_3.2\frac{1}{2}H_2O$ cannot be synthesized from aqueous solution at atmospheric pressure.

Diffracted intensities were measured from a crystal $0\cdot17 \times 0\cdot13 \times 0\cdot13$ mm on a Syntex $P2_1$ diffractometer with the ω–2θ scan technique. Graphite-mono-chromated Mo $K\alpha$ radiation was used and data were collected for $h,k,l \geq 0$ with $\sin\theta/\lambda \leq 0\cdot7$ Å^{-1}. Intensities were calculated after the data collection from the 96-point intensity profile collected for each reflexion (Lindqvist & Ljungström, 1979; originally from Lehmann & Larsen, 1974). A standard reflexion measured after every fiftieth reflexion showed no abnormal fluctuation. Symmetry-related reflexions were averaged. 782 of the 867 unique reflexions had $I > 3\sigma(I)$ and were considered observed. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Cell parameters were determined by least squares from the diffractometer setting angles of 15 reflexions.

No restrictions were imposed on the cell parameters but parameters determined by symmetry were found to be within 2σ of their expected values. The structure was solved with *MULTAN* (Main, Woolfson, Germain & Declercq, 1977). The 110 strongest E values ($E_{min} = 1\cdot43$) were used to calculate 770 $\sum_2$ relations. The phases of two general reflexions represented with magic integers, one reflexion with restricted phase, the two origin-fixing reflexions and one with known phase from $\sum_1$ relations were permuted to give 24 different starting sets for the tangent-formula phase determination. The set of phases with the highest combined figure of merit revealed all atoms (except the water H). Block-diagonal refinement of positional and anisotropic thermal parameters followed by a difference synthesis revealed the five H atoms among the seven highest peaks. Full-matrix least-squares refinement of a scale factor, and positional and anisotropic thermal parameters (isotropic for H) for all atoms (89 parameters) gave a final $R = 0\cdot016$ based on 778 reflexions. (R was $0\cdot022$ when the unobserved reflexions were included.)

Three strong reflexions were noticeably affected by extinction and were excluded. No other correction was performed for extinction. The F values were weighted according to $w = (30 + F_o + 0\cdot012F_o^2)^{-1}$, which gave an acceptable weight analysis. The scattering factors

Table 1. *Atomic coordinates with their e.s.d.'s*

O(1) to O(3) are sulfite O atoms. H(1) and H(2) belong to O(4), H(3) and H(4) to O(5), while H(5) belongs to O(6).

	x	y	z
Fe	0·13113 (3)	0·16981 (3)	0·27374 (3)
S	0·46296 (5)	0·20190 (5)	0·22230 (5)
O(1)	0·0722 (2)	0·3140 (2)	0·4206 (2)
O(2)	0·3309 (2)	0·2557 (2)	0·2922 (2)
O(3)	0·1677 (2)	0·0049 (2)	0·3944 (2)
O(4)	0·0756 (2)	0·3266 (2)	0·1278 (2)
O(5)	0·1916 (2)	0·0302 (2)	0·1164 (2)
O(6)	0·4050 (2)	0·4050	0·5000
H(1)	0·128 (4)	0·396 (4)	0·125 (4)
H(2)	0·996 (6)	0·363 (5)	0·141 (5)
H(3)	0·226 (5)	0·044 (5)	0·047 (4)
H(4)	0·364 (5)	0·460 (5)	0·148 (4)
H(5)	0·375 (4)	0·359 (4)	0·426 (4)

for Fe^0, S^0 and O^0 were those of Doyle & Turner (1968) while the scattering factors of Stewart, Davidson & Simpson (1965) were employed for H. The final atomic coordinates are given in Table 1. The anisotropic thermal parameters appear to have reasonable values and the B values of H atoms range from 3 to 5 $Å^2$.*

Discussion. The crystal structure of $FeSO_3.2\frac{1}{2}H_2O$ is shown in Fig. 1. Some interatomic distances and angles are given in Table 2. The structure may be described in terms of FeO_6 octahedra and sulfite ions. Each sulfite ion is coordinated through O(1), O(2) and O(3) to three different Fe atoms forming a three-dimensional network. The approximately octahedral configuration around Fe consists of three sulfite O atoms, O(1), O(2) and O(3), belonging to different sulfite ions. The remaining three positions are occupied by water O atoms. The octahedra are linked in pairs by the sharing of a water O(6). There is extensive hydrogen bonding involving all the H atoms. The sulfite ions are situated along the fourfold screw axis, turning their lone pairs towards the axis, forming channels through the structure in the **c** direction. There are also channels along the twofold screw axis. The average S—O distance and O—S—O angle of 1·534 Å and 103·95° are in agreement with values found in related structures; for example, α-$FeSO_3.3H_2O$ (Johansson & Lindqvist, 1979) and β-$FeSO_3.3H_2O$ (Johansson & Ljungström, 1979) where the corresponding values are 1·536 Å and 103·8°, and 1·533 Å and 104·02°, respectively. The sulfite ion is rather strongly distorted from the ideal C_{3v} symmetry found in Na_2SO_3 (Larsson & Kirkegaard, 1969).

Table 2 shows that O(2) and O(3) approach each other rather closely, resulting in a small O(2)—S—O(3) angle. The same two O atoms also approach the Fe

Table 2. *Some interatomic distances* (Å) *and angles* (°) *in* $FeSO_3.2\frac{1}{2}H_2O$ *with e.s.d.'s*

O(1), O(2) and O(3) belong to the sulfite group.

The sulfite ion

S—O(1)	1·527 (2)	O(1)—S—O(2)	104·53 (9)
S—O(2)	1·540 (2)	O(1)—S—O(3)	106·41 (10)
S—O(3)	1·534 (2)	O(2)—S—O(3)	100·92 (10)
O(1)—O(2)	2·425 (2)		
O(1)—O(3)	2·451 (2)		
O(2)—O(3)	2·370 (2)		

The Fe—O octahedron

Fe—O(1)	2·124 (2)	Fe—O(4)	2·188 (2)
Fe—O(2)	2·082 (2)	Fe—O(5)	2·179 (2)
Fe—O(3)	2·037 (2)	Fe—O(6)	2·284 (1)
O(1)—Fe—O(2)	85·52 (7)	O(2)—Fe—O(6)	174·97 (7)
O(1)—Fe—O(3)	96·16 (7)	O(3)—Fe—O(4)	172·15 (7)
O(1)—Fe—O(4)	89·21 (7)	O(3)—Fe—O(5)	86·57 (7)
O(1)—Fe—O(5)	177·24 (7)	O(3)—Fe—O(6)	89·23 (6)
O(1)—Fe—O(6)	91·66 (8)	O(4)—Fe—O(5)	88·12 (7)
O(2)—Fe—O(3)	95·20 (7)	O(4)—Fe—O(6)	84·89 (8)
O(2)—Fe—O(4)	90·91 (7)	O(5)—Fe—O(6)	88·79 (6)
O(2)—Fe—O(5)	93·83 (7)		

Water

O(4)—H(1)	0·83 (4)	H(1)—O(4)—H(2)	103 (4)
O(4)—H(2)	0·85 (5)	H(3)—O(5)—H(4)	103 (4)
O(5)—H(3)	0·80 (4)	H(5)—O(6)—H(5)	112 (5)
O(5)—H(4)	0·87 (5)		
O(6)—H(5)	0·93 (4)		

Hydrogen bonds

H(1)···O(5)	2·15 (4)	O(5)—H(1)··O(4)	163 (4)
O(4)···O(5)	2·950 (3)		
H(2)···O(1)	1·86 (5)	O(1)—H(2)—O(4)	175 (5)
O(4)···O(1)	2·711 (3)		
H(3)···O(4)	2·06 (4)	O(4)—H(3)—O(5)	176 (4)
O(5)···O(4)	2·866 (3)		
H(4)···O(3)	1·82 (5)	O(3)—H(4)—O(5)	165 (4)
O(5)···O(3)	2·662 (3)		
H(5)···O(2)	1·75 (4)	O(2)—H(5)—O(6)	174 (4)
O(6)···O(2)	2·671 (2)		

atom closely. The Fe—O distances are 2·037 (2) and 2·082 (2) Å, compared to the ionic radii (Shannon & Prewitt, 1969) of 0·77 Å for Fe^{2+} and 1·40 Å for O^{2-}. Thus it seems as if O(2) and O(3) are repelled by the Fe ions, resulting in distortion of the ideal symmetry of the sulfite ion.
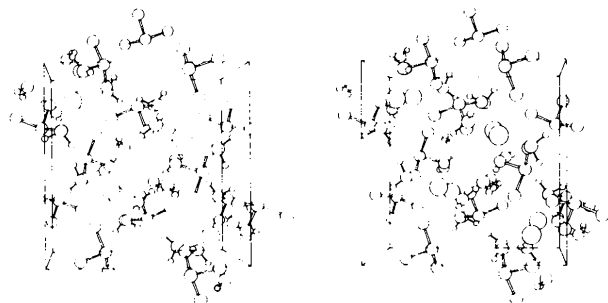
Fig. 1. Stereoscopic projection of $FeSO_3.2\frac{1}{2}H_2O$. The **c** axis is perpendicular to the plane of the paper.

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