The Crystal Structure of Iron(II) Sulfite Trihydrate, α-FeSO$_3$.3H$_2$O

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Abstract

α-FeSO$_3$.3H$_2$O crystallizes in space group $P2_1/n$ with $a = 6\cdot604$ (2), $b = 8\cdot693$ (1), $c = 8\cdot714$ (2) Å, $\beta = 96\cdot05$ (2)° and $Z = 4$, and was refined to $R = 0\cdot033$ for 2430 observed reflections. The Fe^{2+} ion has a distorted octahedral coordination involving O atoms from three water molecules and three different SO$_3^{2-}$ ions. The Fe–O distances range from 2·068 (2) to 2·250 (2) Å. The sulfite anion has S–O distances of 1·530 (1), 1·534 (1) and 1·545 (1) Å, and O–S–O angles of 102·9 (1), 104·1 (1) and 104·5 (1)°.

Introduction

In connection with research at this department on atmospheric corrosion and air pollution, interest has been focused on metal sulfites. In polluted air, ambient concentrations of SO$_2$ (0·01–0·2 p.p.m.) markedly increase the corrosion of Fe (Schikorr, 1941). At very high SO$_2$ concentrations, *e.g.* 100 p.p.m. as in oil-tanker inert gas (*i.e.* diesel-engine exhausts deficient in O$_2$), on the other hand, corrosion of Fe is inhibited (Johansson & Vannerberg, 1979). The role of compounds occurring in the system Fe^{3+}–Fe^{2+}–SO$_4^{2-}$–SO$_3^{2-}$–S^{2-}–H$_2$O is under investigation, and it is evident that the reactivities of Fe^{II} sulfite complexes are of great importance in the mechanism for the corrosion of Fe at high SO$_2$ concentrations.

A central problem in air-pollution research is to determine mechanisms for the catalytic oxidation SO$_2$ + $\frac{1}{2}$O$_2$ + H$_2$O → H$_2$SO$_4$. Junge & Ryan (1958) have shown that Mn^{2+}, Fe^{2+} and Cu^{2+} catalyze the oxidation of SO$_2$, and Georgii & Barrie (1976) have shown that aqueous solutions of Mn^{2+} and Fe^{2+} have very high catalytic activity (SO$_2$ adsorption rate up to 10^{-5} M min^{-1} at 1 p.p.m. SO$_2$ and Me^{2+} concentrations of ~10^{-5} M). Brosset (1975, 1978) proposed that uncharged Me sulfite complexes (Me = Fe and/or Mn) are involved in the rate-determining step of the oxidation of SO$_2$.

The monoclinic FeSO$_3$.3H$_2$O phase described in this paper occurs as a corrosion product of Fe at high concentrations of SO$_2$. A detailed knowledge of its

structure is valuable for the understanding of the reactivity of SO$_3^{2-}$ in complexes with Fe^{2+}. The crystal structures of two other Fe^{II} sulphite trihydrates, also formed as corrosion products of Fe, are under investigation.

Experimental

Crystals of α-FeSO$_3$.3H$_2$O were prepared according to Bugli & Pannetier (1968) who found the crystals to be monoclinic, space group $P2_1/n$, with $a = 6\cdot59_1$, $b = 8\cdot69_1$, $c = 8\cdot70_9$ Å and $\beta = 96\cdot00°$. The cell parameters have been reinvestigated in this work (Table 1). Thirty reflections were measured on a Guinier focused powder photograph with PbNO$_3$ as internal standard ($a_{PbNO_3} = 7\cdot8566$ Å at 294 K; *International Tables for X-ray Crystallography*, 1962).* Refinement of the cell

Table 1. *Experimental data*

(*a*) Physical and crystallographic data

Formula	α-FeSO$_3$.3H$_2$O	$a = 6\cdot604$ (2) Å
M_r	189·96	$b = 8\cdot693$ (1)
Space group	$P2_1/n$	$c = 8\cdot714$ (2)
μ	3·45 mm^{-1}	$\beta = 96\cdot05$ (2)°
d_c	2·54 Mg m^{-3}	$V = 497\cdot4$ (2) Å^3
Crystal habit	Light-green parallelepipeds	$Z = 4$
		$F(000) = 384$

(*b*) Data collection

Crystal dimensions	0·10 × 0·20 × 0·20 mm
Radiation	Mo $K\alpha$
Monochromator	Graphite crystal
Maximum 2θ angle	75·0°
Scan interval ($\Delta\omega$)	1·2–1·5°
Standard reflection	135 at intervals of 25 reflections; 15 000 ± 200 − 14 100 ± 200, slow decomposition
Recorded reflections	2938
Significant reflections	2430 [$I/\sigma(I) > 3\cdot0$]
Cell refinement	Guinier powder data

parameters was carried out with *POWDER* (Lindqvist & Wengelin, 1967).

The crystals are not stable in air and their color changes slowly from very light green to light brown prior to decomposition. The crystal used for data collection was sealed in a glass capillary and mounted on a Syntex $P2_1$ diffractometer.

General crystallographic data and parameters relevant to the data collection are given in Table 1. Integrated intensities and $\sigma(I)$ values were obtained from the Lehmann & Larsen (1974) profile-analysis method (*LELA*; Lindqvist & Ljungström, 1979). Corrections for Lorentz and polarization effects were performed with a local Lp program. No absorption correction was considered necessary. A ψ scan over the 002 reflection showed that the intensity decreased 25% when the crystal was rotated from the least to the worst absorbing position.

Structure determination

The space-group extinctions corresponding to $P2_1/n$ were checked by measurements on the diffractometer. The Fe and S atomic positions were determined from a Patterson synthesis, and the O atoms were located from a subsequent electron density summation. The Fourier summations were carried out with *FOUR* in the *XTL* (1973) structure determination system. The non-hydrogen atomic parameters were refined to an R of 0·033 with *BLOCK* (Lindgren, 1977) and are given in Table 2.* In a final difference summation, some peaks appeared which might correspond to the water H atoms. However, it was not possible to refine the isotropic temperature factors of the H atoms to reasonable values, and they are therefore excluded from the description of the structure. A neutron diffraction study to resolve the hydrogen-bonding system in detail is planned. There were no evident deviations between F_o and F_c due to absorption or extinction. The structure

* See previous footnote.

factors were weighted according to $w = [\sigma^2(F) + 0·00025F^2]^{-1}$. Scattering factors (Doyle & Turner, 1968) for Fe⁰, S⁰ and O⁰ were used.

Discussion

Details of the structure of α-FeSO₃.3H₂O are presented in Fig. 1 and Table 3. Each Fe atom is coordinated to three different sulfite ions and three water molecules. Each sulfite ion is bonded to three Fe atoms, resulting in a three-dimensional net of Fe—O—S interactions, stabilized by hydrogen bonds. The precision of the atomic positions of the H atoms does not permit a detailed discussion of the hydrogen bonding. However, the directions of probable hydrogen links are given in Table 4, and the relative strengths of the hydrogen bonds can be related to the corresponding O···O distances (Hamilton & Ibers, 1968).

Table 3. *Distances (Å) and angles (°)*

Fe—O(1)	2·171 (2)	Fe—O(6)	2·192 (2)
Fe—O(2)	2·137 (1)	S—O(1)	1·545 (1)
Fe—O(3)	2·068 (1)	S—O(2)	1·530 (1)
Fe—O(4)	2·250 (1)	S—O(3)	1·534 (1)
Fe—O(5)	2·098 (2)		

		O···O distance
O(1)–Fe–O(2)	92·11 (5)	3·103 (2)
O(1)–Fe–O(3)	96·76 (6)	3·170 (2)
O(1)–Fe–O(4)	94·15 (5)	3·238 (2)
O(1)–Fe–O(5)	88·59 (6)	2·982 (2)
O(1)–Fe–O(6)	171·03 (5)	4·350 (2)
O(2)–Fe– O(3)	95·75 (6)	3·120 (2)
O(2)–Fe–O(4)	173·68 (5)	4·381 (2)
O(2)–Fe–O(5)	95·54 (6)	3·136 (2)
O(2)–Fe–O(6)	91·14 (5)	3·092 (2)
O(3)–Fe–O(4)	84·29 (5)	2·901 (2)
O(3)–Fe–O(5)	167·31 (6)	4·141 (2)
O(3)–Fe–O(6)	91·22 (6)	3·045 (2)
O(4)–Fe–O(5)	83·85 (6)	2·908 (2)
O(4)–Fe–O(6)	82·55 (5)	2·930 (2)
O(5)–Fe–O(6)	82·79 (6)	2·837 (2)
O(1)–S–O(2)	104·48 (8)	2·431 (2)
O(1)–S–O(3)	104·07 (8)	2·428 (2)
O(2)–S–O(3)	102·92 (8)	2·397 (2)

Table 2. *Atomic parameters for α-FeSO₃.3H₂O*

Positional parameters are given as fractions of the lattice transition.
E.s.d.'s are in parentheses.

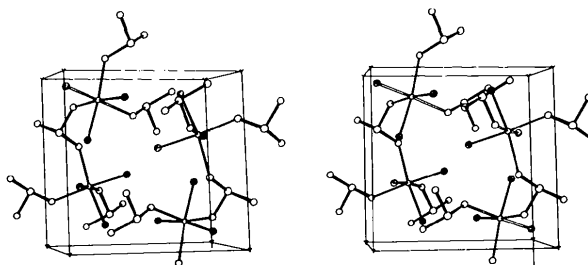|	x	y	z	B (Å²)
Fe	0·42781 (4)	0·24819 (3)	0·14689 (3)	0·77 (1)
S	0·82351 (7)	0·07072 (5)	0·32541 (5)	0·82 (1)
O(1)	0·9551 (2)	0·2002 (2)	0·4060 (1)	1·09 (3)
O(2)	0·7226 (2)	0·1446 (2)	0·1771 (1)	1·15 (4)
O(3)	0·5210 (2)	0·4608 (1)	0·2342 (1)	1·02 (3)
O(4)	0·1131 (2)	0·3481 (1)	0·1415 (1)	1·06 (3)
O(5)	0·2716 (3)	0·0463 (2)	0·0753 (2)	1·49 (4)
O(6)	0·3638 (2)	0·1702 (2)	0·3761 (1)	1·14 (4)

Fig. 1. A stereoscopic picture of the structure projected along a (*ORTEP*; Johnson, 1965). The shaded circles denote the atoms in water molecules.

The Fe^{2+} ions have an approximately octahedral O atom coordination with O—Fe—O angles in the range $90 \pm 7°$. However, the Fe—O distances deviate considerably from ideal octahedral symmetry and vary from 2·068 to 2·250 Å. There is no distinct correlation between the Fe—O length and the nature of the ligand. However, on average, Fe—O$_{sulphite}$ bonds are shorter (2·125 Å) than Fe—O$_{aq}$ bonds (2·180 Å). A comparable Fe^{2+} coordination is present in $FeSO_4.4H_2O$ (Baur, 1962), but in this case the average value of the Fe—O$_{aq}$ bond distances (2·145 Å) is closer to the corresponding Fe—O$_{sulphate}$ value (2·123 Å). The Fe—O$_{aq}$ bonds in α-FeSO$_3$.3H$_2$O are also slightly longer than those in FeCl$_2$.4H$_2$O, mean 2·100 Å (Meunier-Piret & Van Meerssche, 1972), and in FeSO$_4$.7H$_2$O, mean 2·124 Å (Baur, 1964). The longest Fe—O$_{aq}$ distance in α-FeSO$_3$.3H$_2$O [Fe—O(4) = 2·250 (1) Å] is consequently significantly longer than in any of the other structures mentioned. This is probably because O(4) is involved in three short O···O contacts (Table 3).

The structures of and bonding in metal sulfites have been reviewed by Kirkegaard, Larsson & Nyberg (1972). Normal S—O bonds in the SO_3^{2-} ion are close to 1·50 Å, e.g. 3×1.504 (3) Å in Na$_2$SO$_3$ (Larsson & Kirkegaard, 1969). When the sulphite O atoms are involved in hydrogen bonds or interact more or less covalently with metal atoms, a significant elongation of the S—O bonds occurs. In NiSO$_3$.6H$_2$O the three S—O bonds are all 1·536 (7) Å (Baggio & Becka, 1969) and values of 1·49, 1·51 and 1·55 Å have been found in (NH$_4$)$_9$Fe(SO$_3$)$_6$ (Larsson & Niinistö, 1973). In ZnSO$_3$.2·5H$_2$O (Nyberg, 1973) they are 1·502, 1·518 and 1·537 Å.

The S—O bonds of 1·530 (3)–1·545 (1) Å in α-FeSO$_3$.3H$_2$O indicate that the electron distribution in the SO_3^{2-} ion is influenced by interaction with Fe^{2+} and by hydrogen bonding.

The difference between the S—O bonds in α-FeSO$_3$.3H$_2$O, i.e. S—O(1) is significantly longer than the others, does not correlate with a corresponding shortening of the Fe—O(1) bond. On the other hand, O(1) is involved in two hydrogen bonds to water molecules, while O(2) and O(3) each participate in only one such bond (Table 4).

Kirkegaard et al. (1972) have also investigated the O—S—O angle in sulfates and sulfites as a function of

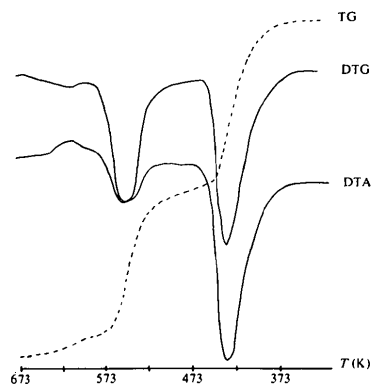Fig. 2. IR spectrum of α-FeSO$_3$.3H$_2$O with characteristic peaks at 48·4, 62·4, 89·3 and 95·6 mm^{-1} (KBr disc).

Fig. 3. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermoanalytical (DTA) curves for α-FeSO$_3$.3H$_2$O in nitrogen. The heating rate was 8 K min^{-1}.

the S—O distance, and have found an approximately linear decrease from 114° at 1·45 Å to 102° at 1·55 Å. The dimensions of the sulfite ion in α-FeSO$_3$.3H$_2$O fit this line well.

The IR spectrum of α-FeSO$_3$.3H$_2$O is shown in Fig. 2. As might be expected, it is similar to the spectrum of the isomorphous MnSO$_3$.3H$_2$O (Lutz, El-Suradi & Engelen, 1977). IR spectra of metal sulfites have been examined by Nyberg & Larsson (1973), who have correlated the S—O stretching frequencies with the S—O distance. The S—O stretching frequencies in α-FeSO$_3$.3H$_2$O fall within the range 89·0–96·0 mm^{-1}, as predicted for a sulfite ion without Me—S interactions (Nyberg & Larsson, 1973). The crystals were powdered in an agate mortar. The powder (approximately 20 mg) was then studied by thermoanalytical techniques. DTA, DTG and TG curves for α-FeSO$_3$.3H$_2$O in N$_2$ are shown in Fig. 3. Dehydration starts at about 363 K, all three water molecules being lost in a single step and not in three steps as for the isomorphous MnSO$_3$.3H$_2$O (Butler & Mitchell, 1976; Lutz et al., 1977). The dehydrated sulfite starts to decompose above 473 K losing SO$_2$. The isomorphous Mn compound shows much greater thermal stability (Lutz et al., 1977).

Table 4. Possible hydrogen bonding

	O···O(W)	O(W)···O	∠O—O(W)—O
O(2)···O(W5)···O(3)	2·758 (2) Å	2·781 (2) Å	112·6 (1)°
Alternative (I)			
O(1)···O(W4)···O(W6)	2·927 (2)	2·695 (2)	114·3 (1)
O(1)···O(W6)···O(W4)	2·754 (3)	2·811 (2)	99·2 (1)
Alternative (II)			
O(1)···O(W4)···O(W6)	2·927 (2)	2·811 (2)	110·5 (1)
O(1)···O(W6)···O(W4)	2·754 (2)	2·695 (2)	116·1 (1)

The crystal structure of the isomorphous MnSO₃.3H₂O phase has been refined completely (Johansson & Lindqvist, 1979).

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The Crystal Structure of *fac*-Triamminetrinitrocobalt(III), *fac*-[Co(NH₃)₃(NO₂)₃]

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Abstract

fac-[Co(NH₃)₃(NO₂)₃], monoclinic, $P2_1$, $a = 7.051$ (3), $b = 10.264$ (2), $c = 10.819$ (2) Å, $\beta = 92.74$ (2)°, $Z = 4$. The Co atoms are octahedrally coordinated by three NO₂ and three NH₃ ligands arranged facially. The structure was refined to $R = 0.055$ for 1165 independent reflections.

Introduction

[Co(H₂O)₃(NH₃)₃]³⁺ (I) reacts with NaNO₂ primarily to give the trinitrito complex *fac*-[Co(NH₃)₃(ONO)₃] (II). Spontaneous isomerization leads to the mixed nitrito–nitro complexes *fac*[Co(NH₃)₃NO₂(ONO)₂] (III) and *fac*-[Co(NH₃)₃(NO₂)₂(ONO)] (IV). From warm aqueous solutions of the latter compounds *fac*-[Co(NH₃)₃(NO₂)₃] (V) is formed (Siebert, 1978). For a long time (V) has been the subject of investigations and communications but unlike its *mer* isomer (VI) (Laing,

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