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The Structure of a Monoclinic Phase of Iron(II) Sulfite Trihydrate

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Abstract. β-$FeSO_3.3H_2O$, monoclinic, $P2_1/c$, a = 7·313 (1), b = 7·985 (1), c = 9·229 (1) Å, β = 104·46 (1)°, $Z = 4$, D_x = 2·42 Mg m^{-3}, μ(Mo $K\alpha$) = 3·29 mm^{-1}. Refinement (2266 reflections, 97 parameters) gave a final R of 0·027. The sulfite ion has S—O distances of 1·551 (1), 1·521 (1) and 1·526 (1) Å. The Fe ion is approximately octahedrally surrounded by sulfite and water O atoms with Fe—O distances ranging from 2·051 to 2·227 Å.

Introduction. Research on SO_2-induced atmospheric corrosion and on the catalytic oxidation of SO_2 in polluted air, in progress in this department, indicates that solid transition-metal sulfites and sulfite complexes in solution may play a role as intermediates in such processes. As part of this work, a phase of iron(II) sulfite trihydrate not described previously has been prepared and its crystal structure solved by X-ray methods.

A pure iron plate partly covered by ferric corrosion products was immersed in an aqueous solution containing 0·5 M SO_2(aq.). Care was taken to exclude air so as to avoid oxidation to the sulfate. After 48 h the plate was removed from the solution, washed with ethanol and dried in nitrogen. The surface of the specimen was found to be covered by amorphous iron sulfide and by two crystalline phases, one of which was identified as α-$FeSO_3.3H_2O$ (Johansson & Lindqvist, 1979*a*). The other phase, which consisted of rather large, crystalline plates, was isolated under the microscope and analyzed by powder diffraction, IR spectroscopy, thermogravimetry and wet chemical methods. The results of the analyses are in agreement with the composition $FeSO_3.3H_2O$. Crystals of the new phase, β-$FeSO_3.3H_2O$, are initially transparent and colorless but become brown after a few days in contact with air, probably due to oxidation of Fe^{2+} to Fe^{3+}. The oxidation would, however, appear to be very slow since there is no sign of decomposition (*e.g.* change in X-ray powder pattern) over a period of six months. Slow decomposition has been noted for the α-phase (Johansson & Lindqvist, 1979*a*).

Intensities from a crystal 0·25 × 0·17 × 0·13 mm were measured with a Syntex $P2_1$ diffractometer by the ω–2θ scan technique. Graphite-monochromated Mo $K\alpha$ radiation was used and data were collected for $\sin\theta/\lambda \le 0{\cdot}808$ Å^{-1}. 2594 reflexions with $h \ge 0$ and $k \ge 0$ were measured. Of these, 2266 had $I \ge 3\sigma(I)$ and were used in subsequent calculations. Integrated intensities were obtained with a profile-analysis procedure (program *LELA*; Lindqvist & Ljungström, 1979) based on the Lehmann & Larsen (1974) method. Normal geometric and polarization corrections were applied but no correction was made for absorption. A standard reflexion measured after every fiftieth reflexion showed no significant fluctuation. Cell parameters were determined from refined diffractometer setting angles for 14 reflexions by least squares. No constraints were imposed on α and γ but these angles were found to be 90° within 3σ.

The structure was solved from Patterson and electron density calculations. Block-diagonal least-squares refinement of a scale factor and positional and anisotropic thermal parameters for Fe, S and the six O atoms gave R = 0·030. A difference synthesis showed a number of rather high (0·7–1·0 e Å^{-3}) peaks which were identified as probable H atoms. When all these positions were inserted as H atoms with isotropic temperature factors in a subsequent cycle, only six of the H atoms retained reasonable thermal parameters.

Table 1. *Atomic coordinates for* β-$FeSO_3.3H_2O$

E.s.d.'s are given in parentheses. O(1), O(2) and O(3) belong to sulfite groups while O(4), O(5) and O(6) are water O atoms.

	x	y	z
Fe	0·84392 (3)	0·14489 (2)	0·02097 (2)
S	0·84817 (5)	0·79579 (4)	0·18960 (4)
O(1)	0·9013 (2)	0·8823 (1)	0·0553 (1)
O(2)	0·9794 (2)	0·1901 (2)	0·2402 (1)
O(3)	0·3022 (2)	0·1685 (2)	0·3839 (1)
O(4)	0·5778 (2)	0·1731 (2)	0·0946 (1)
O(5)	0·3463 (2)	0·9263 (1)	0·1880 (1)
O(6)	0·7914 (2)	0·1021 (2)	0·4555 (2)
H(1)	0·498 (5)	0·223 (4)	0·033 (4)
H(2)	0·533 (6)	0·095 (5)	0·123 (4)
H(3)	0·325 (6)	0·001 (5)	0·249 (4)
H(4)	0·377 (5)	0·835 (5)	0·246 (4)
H(5)	0·834 (4)	0·081 (4)	0·389 (3)
H(6)	0·762 (6)	0·016 (5)	0·498 (4)

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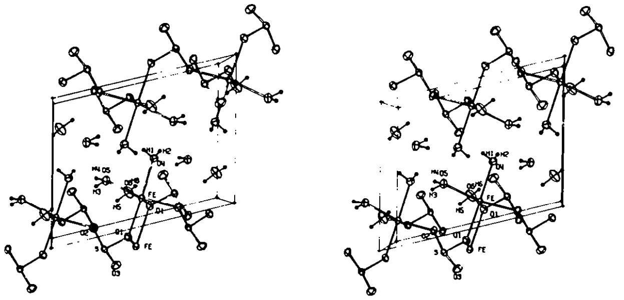

Fig. 1. Stereoscopic view of β-FeSO$_3$.3H$_2$O. The thermal ellipsoids enclose 50% probability. The *a* axis is vertical and *b* is directed away from the viewer.

Since, moreover, distances and angles involving these six atoms were in good agreement with expected values, these atoms were accepted. Although the H atom parameters have high e.s.d.'s the positions of these atoms confirm the directions of hydrogen bonds. In the final full-matrix least-squares refinement a scale factor, positional parameters and anisotropic thermal parameters for Fe, S and O and isotropic thermal parameters for H were refined giving $R = 0{\cdot}027$ for 97 parameters and 2266 reflexions ($R = 0{\cdot}034$ when the 328 unobserved reflexions were included).* The positional parameters are given in Table 1, the numbering being in accordance with Fig. 1. The *B* values for the H atoms lie between 2·7 and 5·3 Å^2 while the thermal motion of the other atoms is illustrated in Fig. 1. Scattering factors for Fe^0, S^0 and O^0 were taken from Doyle & Turner (1968) while the values of Stewart, Davidson & Simpson (1965) were used for H. The structure factors were weighted according to $w = (30 + F_o + 0{\cdot}025F_o^2)^{-1}$ which yielded a satisfactory weight analysis.

Discussion. The crystal structure of β-FeSO$_3$.3H$_2$O is illustrated in Fig. 1. Some interatomic distances and angles are given in Table 2. The structure may be described in terms of layers of FeO$_6$ octahedra parallel to the *bc* plane. Each sulfite ion is coordinated to two different Fe ions through O(1) and to yet another Fe ion through O(2). The third sulfite oxygen, O(3), is not within coordination distance of any Fe ion but is involved in extensive hydrogen bonding. The approximately octahedral configuration around Fe consists of two O(1) atoms from different sulfite ions and one O(2) atom from a third sulfite ion. The remaining three positions are occupied by water O atoms. The octahedra are linked in pairs by edge sharing, each such pair being further linked through the sulfite ions to four other pairs of octahedra forming puckered layers. The layers are held together by hydrogen bonds.

Table 2. *Some interatomic distances* (Å) *and angles* (°) *in* β-FeSO$_3$.3H$_2$O *with their e.s.d.'s*

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

The sulfite ion			
S—O(1)	1·551 (1)	O(1)—S—O(2)	103·94 (6)
S—O(2)	1·521 (1)	O(1)—S—O(3)	103·75 (7)
S—O(3)	1·526 (1)	O(2)—S—O(3)	104·36 (7)
O(1)—O(2)	2·420 (2)		
O(1)—O(3)	2·421 (2)		
O(2)—O(3)	2·408 (2)		
The iron—oxygen octahedron			
Fe—O(1)	2·146 (1)	Fe—O(1′)	2·161 (1)
Fe—O(2)	2·051 (1)	Fe—O(4)	2·227 (1)
Fe—O(5)	2·153 (1)	Fe—O(6)	2·116 (1)
O(1)—Fe—O(1′)	78·30 (5)	O(1)—Fe—O(2)	89·89 (5)
O(1)—Fe—O(4)	101·96 (5)	O(1)—Fe—O(5)	86·16 (4)
O(1)—Fe—O(6)	171·74 (5)	O(1′)—Fe—O(2)	95·49 (5)
O(1′)—Fe—O(4)	178·79 (4)	O(1′)—Fe—O(5)	95·68 (4)
O(1′)—Fe—O(6)	96·47 (5)	O(2)—Fe—O(4)	85·69 (5)
O(2)—Fe—O(5)	167·15 (5)	O(2)—Fe—O(6)	97·02 (6)
O(4)—Fe—O(5)	83·18 (5)	O(4)—Fe—O(6)	83·15 (6)
O(5)—Fe—O(6)	88·03 (5)		
Water			
O(4)—H(1)	0·81 (3)	O(4)—H(2)	0·78 (4)
O(5)—H(3)	0·86 (4)	O(5)—H(4)	0·90 (4)
O(6)—H(5)	0·77 (3)	O(6)—H(6)	0·84 (4)
H(1)—O(4)—H(2)	110 (4)	H(3)—O(5)—H(4)	103 (4)
H(5)—O(6)—H(6)	113 (4)		
Hydrogen bonds			
O(2)—O(6)	2·773 (2)	O(2)···H(5)	2·12 (3)
O(2)—H(5)—O(6)	143 (3)		
O(3)—O(4)	2·736 (2)	O(3)···H(1)	1·93 (3)
O(3)—H(1)—O(4)	177 (3)		
O(3)—O(5)	2·722 (2)	O(3)···H(3)	1·86 (4)
O(3)—H(3)—O(5)	175 (4)		
O(3)—O(6)	2·800 (2)	O(3)···H(6)	1·96 (4)
O(3)—H(6)—O(6)	174 (4)		
O(4)—O(5)	2·805 (2)	O(4)···H(4)	1·92 (4)
O(4)—H(4)—O(5)	166 (4)		
O(5)—O(4)	2·867 (2)	O(5)···H(2)	2·11 (4)
O(5)—H(2)—O(4)	164 (4)		

The average S—O distance and O—S—O angle in β-FeSO$_3$.3H$_2$O of 1·533 Å and 104·02° are in excellent agreement with the average values found in α-FeSO$_3$.3H$_2$O (Johansson & Lindqvist, 1979*a*) of 1·536 Å and 103·8° and in α-MnSO$_3$.3H$_2$O of 1·535 Å and 104·0° (Johansson & Lindqvist, 1979*b*). The O(1)—S distance is significantly longer than the other two O—S distances. This is in agreement with the proposals of Kirkegaard, Larsson & Nyberg (1972) since O(1) is in close contact with two Fe ions, O(2) is in contact with only one Fe ion and O(3) participates solely in hydrogen bonding. The Fe—O distances within the FeO$_6$ octahedron are consistent with the sum of the ionic radii for Fe^{2+} and O^{2-} of 0·77 and 1·40 Å (Shannon & Prewitt, 1969).

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34652 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure du Dichromate de Baryum, Forme α

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Abstract. α-$BaCr_2O_7$, monoclinic, $C2/c$, $a = 16{\cdot}31$ (2), $b = 16{\cdot}67$ (2), $c = 9{\cdot}474$ (5) Å, $\beta = 95{\cdot}53$ (5)°, $Z = 16$. The crystal structure of this salt has been solved using 5964 independent reflexions and $Ag(K\alpha_1\alpha_2)$ radiation: the 2508 highest values give a final R value of 0·039. The structure can be described as a layer structure with Cr_2O_7 anions on the planes $z = 0$ and $\frac{1}{2}$ and Ba cations on the planes $z = \frac{1}{4}$ and $\frac{3}{4}$.

Introduction. Le dichromate de baryum cristallise sous les formes α (température ambiante) et β (haute température).

La préparation chimique de la forme α ainsi que les données cristallographiques sur les formes α et β font l'objet d'une autre publication (Blum, 1979).

Le cristal utilisé était un fragment approximativement cubique de dimensions 0,16 × 0,13 × 0,15 mm. 5964 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre Philips PW 1100 en utilisant la longueur d'onde de l'argent $K\alpha_1\alpha_2$ (0,5608 Å) monochromatisée par une lame de graphite. Chaque réflexion était mesurée en balayage ω dans un domaine de 1,20° à la vitesse de 0,02° s^{-1}. Le fond continu était mesuré durant 10 s à chaque extrémité de ce domaine. Le domaine angulaire exploré s'étendait de 3 à 25° (θ). Les deux réflexions de référence utilisées ($0,10,\bar{4}$ et $0,\overline{10},4$) n'ont pas subi de variations significatives durant la période de mesure.

L'analyse structurale a été effectuée selon des méthodes directes. Le programme *MULTAN* (Main, Woolfson & Germain, 1971) a permis d'obtenir une première synthèse de Fourier qui nous a conduit à la localisation des atomes de baryum et de chrome. Les pics interatomiques déduits de ces positions ont pu être vérifiés par l'examen de la fonction de Patterson. Quelques cycles d'affinement (Prewitt, 1966), alternés avec des synthèses de Fourier successives, permettent alors de préciser la totalité de l'arrangement atomique. De nouveaux cycles d'affinement, effectués, après élimination d'un très grand nombre (2456) de raies très faibles et mal mesurées ($F_o < 10$ dans notre échelle de mesure), en utilisant des paramètres thermiques aniso-

Tableau 1. *Paramètres des positions atomiques et* $B_{éq}$ *pour* $BaCr_2O_7$

	Sites	x	y	z	$B_{éq}$ (Å^2)
Ba(1)	4(*e*)	0	0,45992 (3)	0,25	1,14
Ba(2)	4(*e*)	0	0,04261 (3)	0,25	1,49
Ba(3)	8(*f*)	0,20500 (2)	0,75605 (2)	0,71895 (4)	1,19
Cr(1)	8(*f*)	0,17106 (6)	0,42198 (5)	0,5028 (1)	1,15
Cr(2)	8(*f*)	0,30709 (6)	0,44080 (6)	0,0070 (1)	1,24
Cr(3)	8(*f*)	0,41862 (6)	0,32566 (6)	0,4593 (1)	1,26
Cr(4)	8(*f*)	0,43633 (5)	0,19075 (5)	0,0614 (1)	1,03
O(*E*11)	8(*f*)	0,4041 (3)	0,0208 (3)	0,4527 (6)	2,41
O(*E*12)	8(*f*)	0,1361 (3)	0,3631 (3)	0,3750 (6)	2,33
O(*E*13)	8(*f*)	0,2905 (4)	0,1265 (3)	0,3647 (6)	2,77
O(*L*12)	8(*f*)	0,2467 (3)	0,4821 (3)	0,4288 (6)	2,23
O(*E*21)	8(*f*)	0,1366 (3)	0,0991 (3)	0,1137 (6)	2,18
O(*E*22)	8(*f*)	0,2452 (3)	0,3736 (4)	0,0615 (8)	3,43
O(*E*23)	8(*f*)	0,3623 (4)	0,4775 (4)	0,1339 (7)	3,67
O(*E*31)	8(*f*)	0,0778 (3)	0,1796 (3)	0,3683 (5)	2,26
O(*E*32)	8(*f*)	0,4579 (4)	0,4114 (3)	0,4179 (7)	3,12
O(*E*33)	8(*f*)	0,3257 (3)	0,3155 (4)	0,4002 (8)	3,98
O(*L*34)	8(*f*)	0,4743 (3)	0,2458 (3)	0,3898 (6)	2,40
O(*E*41)	8(*f*)	0,3543 (3)	0,2430 (3)	0,0839 (6)	2,31
O(*E*42)	8(*f*)	0,0613 (3)	0,3286 (3)	0,1078 (5)	2,05
O(*E*43)	8(*f*)	0,4360 (3)	0,1089 (3)	0,1513 (6)	2,21

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