

The Structure of Manganese(II) Sulfite

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Abstract. β -MnSO₃, monoclinic, $P2_1/a$, $a = 8.227$ (1), $b = 12.199$ (2), $c = 5.4193$ (5) Å, $\beta = 79.741$ (7)°, $Z = 8$, $M_r = 135.00$, $D_c = 3.55$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 5.65$ mm⁻¹, $R = 0.030$ for 1523 reflections. The S–O distances in the two sulfite ions are 1.537 (3), 1.546 (3), 1.529 (3) and 1.534 (3), 1.544 (3), 1.541 (3) Å. The Mn–O distances range from 2.147 (3) to 2.381 (3) Å.

Introduction. As part of a study of transition-metal sulfites, the structure of β -MnSO₃ has been determined by X-ray methods. The compound has not been characterized previously. The synthesis was accomplished in the following way: 1.0 g of α -MnSO₃·3H₂O (Johansson & Lindqvist, 1980) and 3 ml of water containing 0.4M SO₂(aq) were sealed in a glass ampoule. The ampoule was heated to 416 (±1) K for three days. Two crystalline compounds could be identified, one pink and the other yellow. The two phases were separated by hand and analyzed by IR spectroscopy and thermogravimetry, which indicated that both had the composition MnSO₃. Powder diffractometry showed the pink compound to be isostructural with FeSO₃ (Bugli & Carré, 1980). This compound was designated α -MnSO₃ while the yellow compound was called β -MnSO₃.

A crystal of β -MnSO₃, 0.10 × 0.10 × 0.07 mm, was mounted on a Syntex $P2_1$ four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. 1764 reflections with $2\theta \leq 60^\circ$ were collected. Integrated intensities and $\sigma(I)$ values were obtained from the Lehmann & Larsen (1974) method. Corrections were performed for Lorentz and polarization effects but not for absorption. A ψ scan over the 230 reflection showed that the intensity decreased by 20% when the crystal was rotated from the least to the most absorbing position. The systematic absences $h = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ indicated space group $P2_1/a$. A standard reflection measured after every fiftieth reflection showed no abnormal fluctuation. The crystals are stable in dry air.

Cell parameters were determined from a Guinier focused powder photograph with Pb(NO₃)₂ as internal standard ($a = 7.8566$ Å at 294 K; *International Tables for X-ray Crystallography*, 1962). The refine-

Table 1. Atomic parameters for β -MnSO₃

The temperature factors are given as B_{eq} values. The thermal isotropic equivalents of the anisotropic thermal parameters were calculated (Hamilton, 1959) from $B_{eq} = \frac{4}{3} \sum_i \sum_j b_{ij} (a_i \cdot a_j)$.

	x	y	z	B_{eq} (Å ²)
Mn(1)	0.34645 (7)	0.74451 (5)	0.11880 (10)	0.76 (3)
Mn(2)	0.88292 (7)	0.42092 (5)	0.32919 (10)	0.85 (3)
S(1)	0.7568 (1)	0.0217 (1)	0.0873 (1)	0.83 (3)
S(2)	0.9841 (1)	0.1743 (1)	0.4758 (1)	0.82 (3)
O(1)	0.2392 (3)	0.0947 (2)	0.0222 (5)	1.27 (8)
O(2)	0.1607 (3)	0.1563 (2)	0.5224 (5)	1.56 (9)
O(3)	0.4197 (3)	0.2578 (2)	0.7135 (5)	1.22 (8)
O(4)	0.1580 (3)	0.4203 (2)	0.9078 (5)	1.16 (8)
O(5)	0.1326 (3)	0.4823 (2)	0.3332 (5)	1.21 (8)
O(6)	0.5019 (3)	0.7582 (2)	0.7395 (5)	1.34 (9)

ment of cell parameters was based on 21 lines* and carried out with *POWDER* (Lindqvist & Wengelin, 1967). The Mn positions were determined from a Patterson synthesis, and the S and O positions from a subsequent electron density summation. Block-diagonal refinement of positional and anisotropic thermal parameters gave a final $R = 0.030$ based on 1523 reflections with $I/\sigma(I) > 3.0$ ($R = 0.038$ including unobserved reflections).

Six strong reflections were noticeably affected by extinction and were excluded in the final refinement. No other correction for extinction was performed. The F values were weighted according to $w = [\sigma^2(F) + 0.00015F^2]^{-1}$. Scattering factors (Doyle & Turner, 1968) for Mn⁰, S⁰ and O⁰ were used. Final atomic coordinates are given in Table 1. The anisotropic thermal parameters have reasonable values.*

Discussion. The crystal structure is shown in Figs. 1 and 2. In Table 2 some atomic distances and angles are listed.

* Powder data and lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35867 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

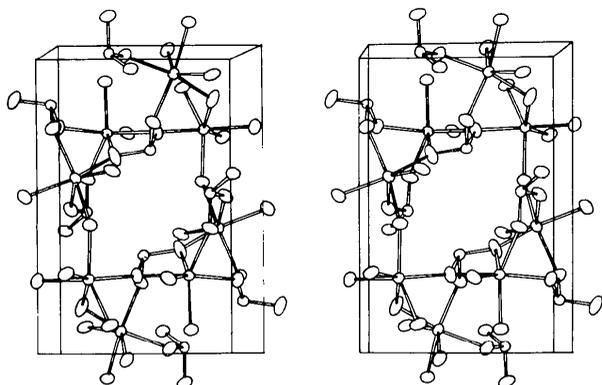


Fig. 1. A stereoscopic picture of the structure. The *c* axis is perpendicular to the paper (ORTEP; Johnson, 1965).

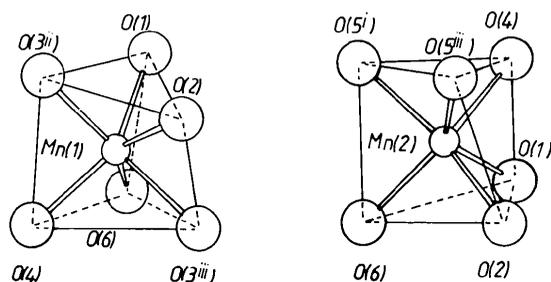


Fig. 2. The coordination polyhedra of Mn(1) and Mn(2).

The structure consists of a three-dimensional network of MnO_6 polyhedra and SO_3 groups sharing O atoms; each O atom is coordinated to two Mn^{2+} ions. Each of the two SO_3 groups in the asymmetric unit coordinates five Mn atoms, acting as a bidentate ligand towards one Mn and as a monodentate ligand towards the other four. The coordination around Mn is rather irregular for both Mn(1) and Mn(2). In both cases the polyhedron can be described as a distorted trigonal prism, but O(4) has a considerably greater coordination distance than the other five for Mn(2).

This unusual coordination of Mn^{2+} (Table 2) is no doubt responsible for the yellow color of the compound. Compounds containing Mn^{2+} coordinated to six O atoms are almost invariably pink, but in these cases the coordination polyhedron is more or less octahedral. Also in pink $\alpha\text{-MnSO}_3$ (Magnusson & Johansson, 1981) the coordination is distorted octahedral. On the other hand, the average Mn—O distances for Mn(1) and Mn(2) are in close agreement with the value found in $\alpha\text{-MnSO}_3$, 2.210 Å.

The average values of bond angles and lengths in the SO_3 groups are similar to those found for other sulfites of divalent cations, e.g. in $\alpha\text{-FeSO}_3 \cdot 3\text{H}_2\text{O}$ (Johansson & Lindqvist, 1979), with average values of 1.536 Å and 103.8°, respectively.

However, the sulfite groups in $\beta\text{-MnSO}_3$ are rather strongly distorted from ideal C_{3v} symmetry. The

Table 2. Interatomic distances (Å) and angles (°)

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

The coordination around Mn(1)

Mn(1)—O(1)	2.147 (3)	Mn(1)—O(4)	2.150 (3)
Mn(1)—O(2)	2.214 (3)	Mn(1)—O(6)	2.225 (3)
Mn(1)—O(3 ⁱⁱ)	2.222 (3)	Mn(1)—O av	2.205
Mn(1)—O(3 ⁱⁱⁱ)	2.269 (3)		
O(1)—O(2)	2.990 (4)	O(3 ⁱⁱⁱ)—O(4)	3.226 (4)
O(1)—O(3 ⁱⁱ)	2.842 (4)	O(1)—O(6)	2.994 (4)
O(2)—O(3 ⁱⁱ)	2.817 (4)	O(2)—O(3 ⁱⁱⁱ)	2.318 (4)
O(6)—O(3 ⁱⁱⁱ)	3.150 (4)	O(3 ⁱⁱ)—O(4)	2.978 (4)
O(6)—O(4)	2.898 (4)		
O(2)—O(1)—O(3 ⁱⁱ)	57.7 (1)	O(3 ⁱⁱ)—O(2)—O(3 ⁱⁱⁱ)	106.2 (1)
O(1)—O(2)—O(3 ⁱⁱ)	58.5 (1)	O(2)—O(3 ⁱⁱ)—O(4)	82.9 (1)
O(1)—O(3 ⁱⁱ)—O(2)	63.8 (1)	O(1)—O(3 ⁱⁱ)—O(4)	89.4 (1)
O(3 ⁱⁱⁱ)—O(6)—O(4)	64.3 (1)	O(1)—O(6)—O(4)	89.0 (1)
O(6)—O(4)—O(3 ⁱⁱⁱ)	61.6 (1)	O(1)—O(6)—O(3 ⁱⁱⁱ)	77.3 (1)
O(6)—O(3 ⁱⁱⁱ)—O(4)	54.1 (1)	O(2)—O(3 ⁱⁱⁱ)—O(6)	98.4 (1)
O(2)—O(1)—O(6)	89.4 (1)	O(2)—O(3 ⁱⁱⁱ)—O(4)	86.0 (1)
O(3 ⁱⁱ)—O(1)—O(6)	91.4 (1)	O(3 ⁱⁱ)—O(4)—O(3 ⁱⁱⁱ)	83.1 (1)
O(1)—O(2)—O(3 ⁱⁱⁱ)	90.8 (1)	O(3 ⁱⁱ)—O(4)—O(6)	89.6 (1)

Mn(2)—O(1)	2.215 (3)	Mn(2)—O(5 ⁱⁱ)	2.162 (3)
Mn(2)—O(2)	2.155 (3)	Mn(2)—O(6)	2.203 (3)
Mn(2)—O(4)	2.381 (3)	Mn(2)—O av	2.218
Mn(2)—O(5 ⁱ)	2.190 (3)		

O(1)—O(2)	2.776 (4)	O(5 ⁱⁱⁱ)—O(5 ⁱ)	2.609 (4)
O(1)—O(6)	3.226 (4)	O(1)—O(4)	2.346 (4)
O(2)—O(6)	3.067 (4)	O(2)—O(5 ⁱⁱⁱ)	2.913 (4)
O(4)—O(5 ⁱ)	3.153 (4)	O(6)—O(5 ⁱ)	3.001 (4)
O(4)—O(5 ⁱⁱⁱ)	3.247 (3)		

O(1)—O(2)—O(6)	66.8 (1)	O(6)—O(2)—O(5 ⁱⁱⁱ)	81.3 (1)
O(2)—O(6)—O(1)	52.3 (1)	O(2)—O(6)—O(5 ⁱ)	87.4 (1)
O(2)—O(1)—O(6)	60.9 (1)	O(1)—O(6)—O(5 ⁱ)	80.3 (1)
O(4)—O(5 ⁱⁱⁱ)—O(5 ⁱ)	64.1 (1)	O(1)—O(4)—O(5 ⁱⁱⁱ)	92.7 (1)
O(5 ⁱⁱⁱ)—O(5 ⁱ)—O(4)	67.8 (1)	O(1)—O(4)—O(5 ⁱ)	91.8 (1)
O(5 ⁱⁱⁱ)—O(4)—O(5 ⁱ)	48.1 (1)	O(2)—O(5 ⁱⁱⁱ)—O(4)	79.8 (1)
O(6)—O(1)—O(4)	99.0 (1)	O(2)—O(5 ⁱⁱⁱ)—O(5 ⁱ)	98.6 (1)
O(2)—O(1)—O(4)	96.6 (1)	O(6)—O(5 ⁱ)—O(4)	88.0 (1)
O(1)—O(2)—O(5 ⁱⁱⁱ)	91.1 (1)	O(6)—O(5 ⁱ)—O(5 ⁱⁱⁱ)	87.7 (1)

The SO_3 groups

S(1)—O(1)	1.537 (3)	S(1)—O(5)	1.529 (3)
S(1)—O(4)	1.546 (3)	S(1)—O av	1.537

O...O distance

O(1)—S(1)—O(4)	99.1 (2)	2.346 (4)
O(1)—S(1)—O(5)	105.8 (2)	2.446 (4)
O(4)—S(1)—O(5)	102.6 (2)	2.400 (4)
O—S(1)—O av	102.5	

S(2)—O(2)	1.534 (3)	S(2)—O(6)	1.541 (3)
S(2)—O(3)	1.544 (3)	S(2)—O av	1.540

O...O distance

O(2)—S(2)—O(3)	97.7 (2)	2.318 (4)
O(2)—S(2)—O(6)	105.9 (2)	2.445 (4)
O(3)—S(2)—O(6)	104.1 (2)	2.443 (4)
O—S(2)—O av	102.6	

O—S—O angle between the O atoms coordinated to the same Mn^{2+} ion is significantly smaller than the other O—S—O angles within the group.

Two other structures have been reported where sulfite groups act as chelating ligands, coordinating the

same cation through two O atoms, namely $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Schröpfer, 1973) and $\text{CdSO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ (Kiers & Vos, 1978). Also, in these structures the chelating O—S—O angle is smaller than the other O—S—O angles. Thus, for $\text{CdSO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ average values are 101.6 and 105.5° and for $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ 101.6 and 105.1° for chelating and non-chelating O—S—O angles, respectively.

This distortion obviously occurs because of attractive forces between the cation and the O atoms in question.

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The Structure of Boron Trifluoride Dihydrate, a Redetermination*

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Abstract. $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, monoclinic, $P2_1/c$, $a = 5.562$ (5), $b = 7.334$ (8), $c = 8.746$ (8) Å, $\beta = 90.30$ (8)°, $M_r = 103.84$, $Z = 4$, $D_x = 1.93$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.28$ mm⁻¹. Final $R = 0.056$ for 1194 reflections. With all atoms now directly located and refined the title compound in the solid state at 173 K is firmly established as hydroxytrifluoroboric acid monohydrate, $\text{BF}_3\text{OH}_2 \cdot \text{H}_2\text{O}$, as opposed to the ionic alternative, oxonium hydroxytrifluoroborate, $\text{H}_3\text{O}[\text{BF}_3\text{OH}]$, which could not be entirely excluded by a previous analysis of the crystal structure [Bang & Carpenter (1964). *Acta Cryst.* 17, 742–745].

Introduction. The title compound was prepared by introducing a stoichiometric amount of boron trifluoride into water. A liquid sample (melting point 279 K; Pawlenko, 1959) was sealed in a thin-walled glass capillary of 0.3 mm diameter. Single-crystal growth was achieved on a diffractometer (Syntex $P2_1$ with low-temperature attachment LT-1 modified for optimal performance) in a stream of cold nitrogen gas. The space group was determined from axial photographs

and systematic absences. With the crystal at 173 K the positions of 15 high-order reflections used for lattice parameter refinement were measured as well as the intensities of 1567 independent reflections up to $2\theta_{\text{max}} = 70^\circ$ (ω scan, Mo $K\alpha$, graphite monochromator). Of these, 1194 with $|F_o| \geq 3.0\sigma_F$ were classified as observed and used in the structure determination. Starting from the non-H atom parameters of the previous analysis at 276 K (Bang & Carpenter, 1964)† full-matrix least-squares refinement followed by a difference synthesis led to the positions of all H atoms. Refinement of the complete structure, anisotropic for the non-H atoms and isotropic for H (71 parameters), converged at $R = 0.056$ (0.068) and $R_w = 0.072$ (0.071) for the observed (all) reflections. The reflections were weighted according to $1/w = \sigma_F^2 +$

† With the angle β very close to 90° an axial setting by chance was adopted in the present analysis which is different from that in the previous one. Direct comparability is obtained with an acute angle (89.55 instead of the reported 90.45°) for the Bang & Carpenter unit cell and all its atomic x coordinates inverted at $x = \frac{1}{2}$, the position of a pseudo mirror of the structure. This, therefore, amounts to the same as starting from the unchanged coordinates and interchanging only the elemental assignments (and symbols) of O(4), called O(1) in the present analysis, and F(3), which was actually done.

* Crystal Structures of Acid Hydrates and Oxonium Salts. XIX. A preliminary report has been given (Mootz & Steffen, 1979). For Part XVIII see Mootz, Ohms & Poll (1981).