Rhombohedral Manganese(II) Sulfite

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Abstract. $MnSO_3$, $M_r = 135.00$, rhombohedral, $R\bar{3}$, $a = 7.912$ (1) Å, $\alpha = 109.241$ (5)°, $Z = 6$, $D_c = 3.50$ Mg m^{-3}, μ(Mo $K\alpha$) = 5.90 mm^{-1}. $R = 0.029$ for 1152 unique reflections. Mn^{2+} is coordinated by six O from different SO_3^{2-} ions in a distorted octahedral configuration, Mn—O ranging from 2.151 (2)–2.242 (2) Å. The sulfite ion has S—O of 1.541 (2), 1.540 (2) and 1.536 (2) Å and O—S—O of 103.23 (9), 103.35 (9) and 103.52 (10)°.

Introduction. In connection with studies on sulfites of Fe and Mn, the crystal structure of pink, rhombohedral $MnSO_3$ has been determined. The preparation of this compound, then designated α-$MnSO_3$, has been described elsewhere (Magnusson, Johansson & Lindqvist, 1981). The compound is isostructural with $FeSO_3$, hereafter called α-$FeSO_3$ (Bugli & Carré, 1980).

Intensities from a crystal, 0.22 × 0.22 × 0.22 mm, were measured with a Syntex $P2_1$ diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. Data were collected for sin $\theta \leq 0.58$ with the θ–2θ scan technique and a variable scan rate from 2 to 14° min^{-1}. A total of 1217 unique reflections were measured. Of these, 1152 had $I \geq 3\sigma(I)$ and were used in subsequent calculations. Integrated intensities were obtained using a profile-analysis procedure (*LELA*; Lindqvist & Ljungström, 1979) based on the Lehmann & Larsen (1974) method. A standard reflection measured after every fiftieth reflection showed no abnormal fluctuation. The intensities were corrected for Lorentz and polarization effects but not for absorption. A ψ scan over the $2\bar{2}1$ reflection showed that the intensity decreased 35% when the crystal was rotated from the least to the most absorbing position. Of the space groups consistent with no systematically absent reflections, $R\bar{3}$ was selected from the location and heights of the peaks in a Patterson synthesis, the position of Mn thus also being determined. The S and O atoms were located in a subsequent Fourier summation (*FOUR*; *XTL*, 1973). Positional and anisotropic thermal parameters were refined to $R = 0.029$; $R = 0.031$ including unobserved reflections (*BLOCK*; Lindgren, 1977). Atomic coordinates and equivalent isotropic thermal parameters are

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j) \text{ (Hamilton. 1959).}$$

	x	y	z	B_{eq}
Mn	0.36530 (5)	0.18610 (5)	0.68143 (5)	0.680 (6)
S	0.35000 (7)	0.02485 (7)	0.21003 (8)	0.605 (9)
O(1)	0.5535 (2)	0.2301 (3)	0.3405 (2)	0.88 (3)
O(2)	0.3101 (3)	−0.0203 (3)	0.3725 (2)	1.05 (4)
O(3)	0.4127 (2)	−0.1322 (2)	0.1190 (3)	0.95 (4)

given in Table 1.* The structure factors were weighted according to $w = (25 + F_o + 0.025F_o^2)^{-1}$. Scattering factors (Doyle & Turner, 1968) for Mn^0, S^0 and O^0 were used. Cell parameters were determined from powder diffractometer data with $Pb(NO_3)_2$ as internal standard [$a_{Pb(NO_3)_2} = 7.8566$ Å at 294 K; *International Tables for X-ray Crystallography*, 1962].* Least-squares refinement of the unit-cell parameters was based on 25 reflections and carried out with the program *POWDER* (Lindqvist & Wengelin, 1967).

Discussion. α-$MnSO_3$ is isomorphous with α-$FeSO_3$ (Bugli & Carré, 1980), and its structure is illustrated in Figs. 1 and 2. In contrast to the yellow β-$MnSO_3$ (Magnusson *et al.*, 1981), α-$MnSO_3$ has the pink color typical of Mn^{2+} salts, reflecting the distorted octahedral environment of Mn^{2+}. The structure consists of MnO_6 octahedra and SO_3 groups linked together in a three-dimensional network, each Mn^{2+} being coordinated by six O from different sulfite groups and each O coordinating two Mn^{2+} ions.

Mn—O distances in α-$MnSO_3$ are significantly longer than the corresponding Fe—O distances in α-$FeSO_3$ (Bugli & Carré, 1980), the average values in the two compounds being 2.203 (1) and 2.158 Å respectively. This agrees well with reported values for the ionic radii

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* 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 35984 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography. 5 Abbey Square. Chester CH1 2HU. England.
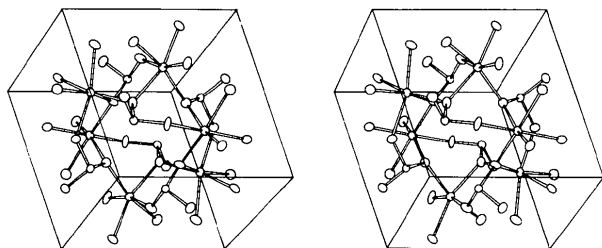
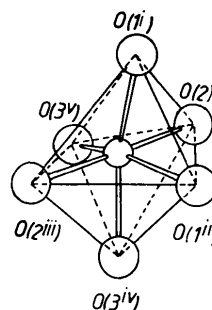Fig. 1. A stereoscopic view of the structure (ORTEP; Johnson, 1965).

Fig. 2. The coordination of the Mn^{2+} ion. Symmetry code as in Table 2.

Table 2. Some interatomic distances (Å) and angles (°)

Mn—O(1^i)	2·151 (2)	Mn—O(3^v)	2·181 (2)
Mn—O(1^{ii})	2·228 (2)	S—O(1)	1·540 (2)
Mn—O(2^{iii})	2·210 (2)	S—O(2)	1·541 (2)
Mn—O(2)	2·242 (2)	S—O(3)	1·536 (2)
Mn—O(3^{iv})	2·207 (2)		

		O···O distances
O(1^i)—Mn—O(1^{ii})	85·58 (8)	2·919 (3)
O(1^i)—Mn—O(2^{iii})	98·46 (6)	3·303 (2)
O(1^i)—Mn—O(2)	90·25 (6)	3·114 (2)
O(1^i)—Mn—O(3^{iv})	161·16 (6)	4·299 (3)
O(1^i)—Mn—O(3^v)	111·43 (6)	3·579 (3)
O(1^{ii})—Mn—O(2^{iii})	97·43 (6)	3·335 (2)
O(1^{ii})—Mn—O(2)	96·10 (7)	3·325 (3)
O(1^{ii})—Mn—O(3^{iv})	79·93 (6)	2·849 (2)
O(1^{ii})—Mn—O(3^v)	162·02 (6)	4·356 (3)
O(2^{iii})—Mn—O(2)	164·63 (7)	4·413 (3)
O(2^{iii})—Mn—O(3^{iv})	74·86 (6)	2·685 (2)
O(2^{iii})—Mn—O(3^v)	90·27 (6)	3·113 (3)
O(2)—Mn—O(3^{iv})	100·46 (6)	3·420 (2)
O(2)—Mn—O(3^v)	74·72 (6)	2·685 (2)
O(3^{iv})—Mn—O(3^v)	86·49 (3)	3·007 (1)
O(1)—S—O(2)	103·23 (9)	2·415 (2)
O(1)—S—O(3)	103·35 (9)	2·413 (2)
O(2)—S—O(3)	103·52 (10)	2·417 (2)

Symmetry code: (i) y,z,x; (ii) $1 - z, 1 - x, 1 - y$; (iii) $z, x, 1 + y$; (iv) $1 - x, -y, 1 - z$; (v) $-y, -z, 1 - x$.

of Mn^{2+} and Fe^{2+} of 0·80 and 0·76 Å respectively (Pauling, 1960). The sulfite ion in α-MnSO$_3$ is only slightly distorted from the ideal C_{3v} symmetry (cf. Table 2), which is in marked contrast to the sulfite ion in β-MnSO$_3$ (Magnusson et al., 1981). This may be ascribed to differences in Mn—sulfite coordination in the two phases. In α-MnSO$_3$ no two O belonging to the same sulfite group coordinate the same Mn^{2+}, as is the case in β-MnSO$_3$. Average values of S—O distances [1·540 (1) Å] and O—S—O angles [103·4 (1)°] are quite similar to those reported for α-FeSO$_3$ (1·543 Å and 103·0°).

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