

$$N \simeq (0.6\nu + 2.2) \quad (8)$$

where ν is a typical coordination number for the cation.*

Thus in the case of a cation not given in Table 1, the cation-oxygen bond valence can be calculated using

$$s \simeq \bar{s}(R/\bar{R})^{-(0.6\nu + 2.2)} \quad (9)$$

Some parameters for bonds to other anions have been reported by Brown (1974) [Sn(2), Sb(3), Te(4), I(5) and Xe(6) to F] and Hoggins & Steinfink (1975) [Fe(2), Fe(3) to S].

* An effective coordination number around any cation can be defined as the cation valence divided by the largest bond valence. For regular coordination this procedure yields the normal coordination number but for irregular coordination it treats long bonds as making only a partial contribution to the coordination number. Using this definition, equation (8) predicts better than (7) the smaller value of N found for the lower valence states of the main group elements.

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Crystal Structure and Chemical Bonding of Manganese(II) Sulphite Trihydrate

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$\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ is orthorhombic, $a = 9.72$ (2), $b = 5.63$ (1), $c = 9.53$ (2) Å, $Z = 4$, space group $Pnma$. The structure was solved by the Patterson method and refined by full-matrix least squares to $R = 0.062$. Coordination around Mn atoms is octahedral, the ligands being three oxygen atoms from water molecules and another three from sulphite groups. The anions behave as bridging ligands, linking MnO_6 octahedra together and forming chains parallel to the c unit cell axis. Modifications in SO_3^{2-} geometry are discussed.

Introduction

Several structural studies on metal sulphite compounds have been performed so far. The anion, as was demonstrated in those reports, can behave as a monodentate or as a bridging ligand. In the first case, it generally coordinates through sulphur, sometimes with strong evidence of π -bonding. However, the crystal structure of $(\text{NH}_4)_9\text{Fe}(\text{SO}_3)_6$, where the sulphite group is bonded to the metal atom through an oxygen atom, has recently been reported (Larsson & Niinistö, 1973). As a bridging ligand, the polydentate anion has been found to bind through sulphur and/or oxygen. In this type of compound, polymeric moieties are generally formed.

According to Cruickshank (1961), π -bonding orbitals in sulphur oxy-anions are formed with $3d$ sulphur or-

bitals and $2p$ oxygen orbitals. Robinson (1964) discussed the effect of unshared electrons on sulphur in relation to the S-O bond order, and suggested that the bond order in the SO_3^{2-} ion is only 1.33 (as compared with 1.50 in the sulphate ion) with a lone pair replacing one of the two resonating double bonds in the valence bond formulation. When SO_3^{2-} coordinates through sulphur and its lone pair is engaged in binding to a metal, the effect of the electron pair is reduced and S-O distances should be shorter than found in the free SO_3^{2-} ion. On the other hand, if sulphite coordinates through oxygen, a lengthening of the S-O bond would be expected, since there is a minor availability of $2p$ orbitals for π -bonding. When coordination through sulphur and oxygen occurs, the effects are counteracted and the bonding scheme is obscured.

In order to obtain additional information about the

structure and bonding of sulphite compounds, we have determined the crystal structure of $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$. The infrared spectrum of the solid shows two peaks in the S–O stretching region (940 and 1110 cm^{-1}) suggesting that the anion would have nearly C_{3v} symmetry, without giving indication of the type of coordination, if any (Baggio, 1966).

Experimental

Very good crystals suitable for X-ray work were obtained by allowing solutions of MnSO_4 and Na_2SO_3 to diffuse through a Na_2SO_4 solution for two weeks. Initial mixing was avoided using solutions of different densities. Crystals grew as colourless prisms, elongated along the b axis.

Crystal data

Formula: $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$; name: manganese sulphite trihydrate; F.W. 189.02; crystal system: orthorhombic; cell dimensions: $a = 9.72$ (2), $b = 5.63$ (1), $c = 9.53$ (2) Å, from calibrated precession photographs; unit-cell volume: 521.5 Å^3 ; density: observed 2.40 g cm^{-3} (by flotation), calculated 2.40 g cm^{-3} (from X-ray data, $Z = 4$); $\mu(\text{Mo K}\alpha) = 31.6 \text{ cm}^{-1}$; space group: $Pnma$ or $Pna2_1$, from systematic absences, $Pnma$ was confirmed by the resolution of the structure.

Collection and measurement of the intensities

A crystal of dimensions $0.25 \times 0.25 \times 0.65 \text{ mm}$ was mounted with the b axis parallel to the goniometer axis. Equi-inclination Weissenberg photographs of levels $hk0$ to $hk10$ were obtained using the multiple-film technique with $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107 \text{ Å}$). Precession photographs of $h0l$ and $0kl$ were obtained from the same crystal with $\text{Mo K}\alpha$ radiation. Intensities were measured with a microdensitometer. They were corrected for Lorentz and polarization factors and for absorption, using programs written in this laboratory. The number of intensities measured was 1454, within the ratio 1200:1. Interlayer scaling of intensities was carried out according to Hamilton, Rollett & Sparks (1965). An approximate scale factor and an overall temperature factor were obtained by means of the Wilson plot, and the structure factors were then normalized to $|E|$ values.

With $|E^2 - 1|$ as coefficients, an origin removed Patterson map was computed, where the positions of all non-hydrogen atoms were obtained.

At this point a sequence of full-matrix least-squares refinements was begun, allowing for the simultaneous variation of coordinates, isotropic temperature factors and scale factors, one for each layer line. When convergence was achieved, refinement was continued using anisotropic temperature factors and an overall scale factor. At the end of the process residuals were: $R = 0.062$ and $R'(\sum w\Delta/\sum wF_o) = 0.070$.

The weighting scheme used in the last stages of the least-squares process was

$$\sigma = 1/\sqrt{w} = \{(5.98 + 0.66F_o - 0.09F_o^2)(2.99 + 3.06q^2) \times [1.03 - \exp(2.45q^2)]\}^{-1}$$

where $q = \sin \theta/\lambda$.

Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1968). The final parameters, as obtained from the last cycle of refinement, are given in Table 1.*

Results and discussion

A schematic view of the structure of $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ is shown in Fig. 1. In Table 2 the interatomic distances and angles are listed.

The structure may be described in terms of pyramidal sulphite groups and MnO_6 octahedra. The orientation

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31564 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

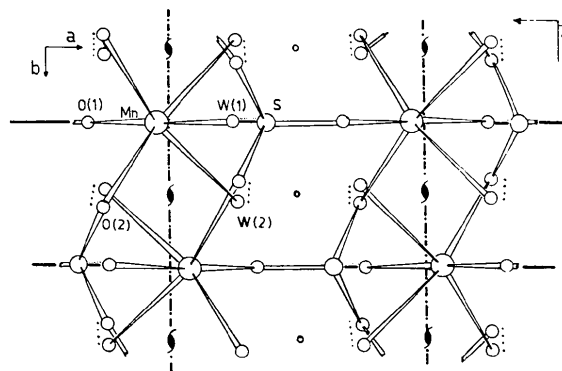


Fig. 1. Schematic view of the structure of $\text{MnSO}_3 \cdot 3\text{H}_2\text{O}$ projected down c .

Table 1. Final positional and thermal parameters ($\times 10^5$), with estimated standard deviations in parentheses

The temperature factor is of the form $\exp[-(\sum \beta_{ij}h_ih_j)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	22340 (6)	25000 (0)	6260 (6)	260 (5)	791 (10)	315 (6)	0.0 (0)	-12 (6)	0.0 (0)
S	6527 (9)	75000 (0)	9052 (9)	254 (10)	744 (18)	221 (9)	0.0 (0)	12 (11)	0.0 (0)
O(1)	91171 (35)	75000 (0)	11714 (39)	305 (34)	2581 (16)	450 (41)	0.0 (0)	-6 (44)	0.0 (0)
O(2)	11909 (30)	53524 (47)	17215 (25)	677 (35)	1321 (92)	394 (32)	-147 (55)	46 (35)	45 (51)
W(1)	63263 (45)	75000 (0)	76451 (41)	612 (53)	2769 (125)	549 (49)	0.0 (0)	-116 (58)	0.0 (0)
W(2)	36254 (24)	50486 (42)	95202 (25)	415 (27)	1222 (86)	373 (29)	-13 (48)	32 (29)	-6 (51)

Table 2. *Bond distances and angles*

Mn-O(1)	2.158 Å	O(1)-Mn-W(1)	177.1°
Mn-O(2)	2.167	O(1)-Mn-W(2)	89.7
Mn-W(1)	2.159	O(2)-Mn-W(2)	91.9
Mn-W(2)	2.235	O(2)-Mn-W(2')	170.3
O(1)-Mn-O(2)	95.6°	O(2)-Mn-W(1)	86.4
O(2)-Mn-O(2')	95.7		
W(1)-Mn-W(2)	88.1		
W(2)-Mn-W(2')	79.9		
S-O(1)	1.513 Å	O(1)-S-O(2)	104.6°
S-O(2)	1.530	O(2)-S-O(2')	104.5

of the moieties is such that the unit cell *c* axis almost coincides with the ternary axis of the ideal MnO₆ octahedra and SO₃²⁻ pyramids.

The distorted octahedral coordination around the metal atom is provided by three oxygen atoms from three independent sulphite groups and three water molecules. As Mn atoms are located on the mirror planes of the cell, MnO₆ groups have *C_s* symmetry. Bond distances in MnO₆ octahedra range from 2.159 to 2.236 Å (with a mean value of 2.189 Å) which is in

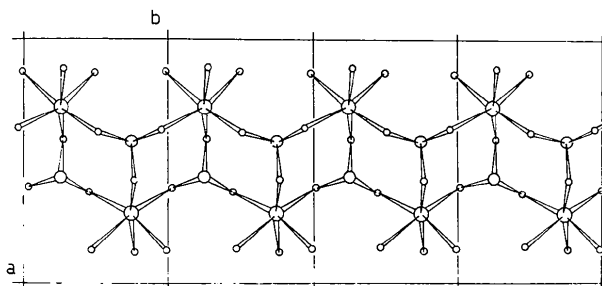


Fig. 2. Projection of the structure down the *c* axis, showing chains parallel to the *b* axis.

good agreement with values reported in other octahedral manganese(II) compounds. For a good table of MnO distances in Mn^{II} octahedral compounds, we refer to Popov, Herak, Prelesnik & Ribar (1973). The MnO₆ polyhedra have no corners in common and they are linked together by sulphite groups, which behave as bridging ligands. Chains parallel to the *b* axis result as a consequence, as schematically depicted in Fig. 2. Adjacent chains are related through glide planes.

In Table 3 some short intermolecular contacts are given which fulfil the angular criterion for hydrogen bonding.

Table 3. *Short intermolecular contacts*

O(2) ··· W(2)	($\frac{1}{2} - x, \frac{1}{2} + y, -z$)	2.68 Å
W(2) ··· W(2)	($x, 1 - y, \frac{1}{2} - z$)	2.82
S(1) ··· W(1)	($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$)	3.44

S(1) ··· W(1) interactions seem to be responsible for joining chains in the *a* direction, while O(2) ··· W(2) and W(2) ··· W(2) contacts account for the connexion along *c*. Dotted lines, in Fig. 1, show how chains are held together through hydrogen bonding.

The sulphite group, as was mentioned before, maintains pyramidal geometry and is linked to three different manganese atoms through oxygen atoms. One of these, namely O(2), also participates in hydrogen bonding with W(2). S-O distances and O-S-O angles are very close to their mean values, 1.525 Å and 104.5° respectively, in good agreement with those found in other O-bonded sulphite complexes. In Table 4 values for S-O bond distances and O-S-O bond angles for a number of sulphite compounds so far studied are given. In order to discuss the effect of coordination on the

Table 4. *Structural data for some sulphite compounds*

When two values are reported for a given compound, they correspond to non-equivalent distances and angles.

Compound	Coordinated by	Type of coordination	S-O (Å)	O-S-O (°)	Reference
Na ₂ SO ₃	ionic		1.504	105.7	Larsson & Kierkegaard (1969)
(NH ₄) ₂ SO ₃ · H ₂ O	ionic		1.536	103.6	Battelle & Trueblood (1965)
NiSO ₃ · 6H ₂ O	ionic		1.524	104.8	Baggio & Becka (1969 <i>b</i>)
[Co(en) ₂ SO ₃ · NCS] · 2H ₂ O	S	monodentate	1.485	110.3	Baggio & Becka (1969 <i>a</i>)
[Co(NH ₃) ₅ SO ₃]Cl · H ₂ O	S	monodentate	1.483	...	Elder & Trkula (1974)
[Co(qp)SO ₃ H ₂ O]NO ₃ · H ₂ O (qp = quaterpyridyl)	S	monodentate	1.457	111.9	Maslen, Raston & White (1975)
[Co(en) ₂ SO ₃ H ₂ O]ClO ₄ · H ₂ O	S	monodentate	1.462	110.1	Maslen, Raston, White & Yandell (1975)
Pd(NH ₃) ₃ SO ₃	S	monodentate	1.490	108.6	Spinnler & Becka (1967)
<i>trans</i> Pd(NH ₃) ₂ (SO ₃) ₂	S	monodentate	1.483	108.7	Capparelli & Becka (1969)
(NH ₄) ₉ [Fe(SO ₃) ₆]	O	monodentate	1.551	103.8	Larsson & Niinistö (1973)
			1.500	105.7	
Cu ₂ SO ₃ · CuSO ₃ · 2H ₂ O	S, O	polydentate	1.509	106.9	Kierkegaard & Nyberg (1965)
Ag ₂ SO ₃	S, O	polydentate	1.516	104.6	Larsson (1969)
AgNaSO ₃ · 2H ₂ O	S, O	polydentate	1.542	105.3	Niinistö & Larsson (1973)
			1.512	108.2	
NH ₄ CuSO ₃	S, O	polydentate	1.514	105.3	Nyberg & Kierkegaard (1968)
ZnSO ₃ · 2H ₂ O	O	polydentate	1.552	104.0	Quiñones & Baggio (1972)
			1.512	103.2	
Tl ₂ [Cu(SO ₃) ₂]	O	polydentate	1.550	103.5	Hjerten & Nyberg (1973)
			1.516	105.0	
MnSO ₃ · 3H ₂ O	O	polydentate	1.525	104.5	This work

sulphite geometry, it is important to define the parameters for the free anion. So far three ionic sulphite compounds have been studied. Results for $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ (Baggio & Becka, 1969*b*) and $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (Battelle & Trueblood, 1965) are quite consistent, giving S–O mean distances of 1.524 and 1.536 Å, respectively. These compounds, unlike Na_2SO_3 , where the S–O bond length is 1.504 Å, are hydrates, and show strong evidence of hydrogen bonding.

Kierkegaard, Larsson & Nyberg (1972), in a paper about structure and bonding in metal sulphites, suggested that the true S–O bond length in ionic sulphite must be the one found in Na_2SO_3 , and the lengthening in $\text{NiSO}_3 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ ought to be attributed to hydrogen bonding. In $\text{ZnSO}_3 \cdot 2\text{H}_2\text{O}$ and in $\text{Ti}_2[\text{Cu}(\text{SO}_3)_2]$ the SO_3^{2-} group also coordinates through its three oxygen atoms. In this case, however, the metal–O bonds are not equivalent and this is reflected in S–O bonds. When SO_3^{2-} uses only one oxygen in bonding, as in $(\text{NH}_4)_9[\text{Fe}(\text{SO}_3)_6]$, a significant difference is observed among different S–O bonds (Table 4) although those oxygen atoms not involved in coordination participate in hydrogen bonding. We think that if hydrogen bonding affected S–O distances so greatly, as claimed by Kierkegaard *et al.* (1972) in their explanation of the different S–O values obtained in Na_2SO_3 and nickel and ammonium sulphites, the variations observed in $(\text{NH}_4)_9[\text{Fe}(\text{SO}_3)_6]$ should not be so pronounced.

From an inspection of Table 4 and the discussion reported here, it seems rather difficult to decide which are the most representative values for the S–O bond length in non-coordinated sulphites. On the other hand, it is clear that coordination by sulphur produces a shortening of the S–O bond length when compared with the free anion, since they are the shortest distances reported in sulphite compounds. When coordination occurs through one or more oxygen atoms this conclusion is not so evident. Although a lengthening of the S–O bond length should be expected, in some cases as in $\text{MnSO}_3 \cdot 2\text{H}_2\text{O}$, the S–O bond lengths are even shorter than those reported in some sulphite compounds where oxygen atoms only participate in hydrogen bonding (Battelle & Trueblood, 1965; Baggio & Becka, 1969).

Distances between non-bonded oxygen atoms of the sulphite group in manganese sulphite have a mean value of 2.415 Å which is practically identical with those reported in other sulphites, sulphates and thiosulphates. The constancy of the O...O distances provides

additional support for the idea that the variation in the O–S–O angle can be explained satisfactorily by the predominance of non-bonded repulsion effects, as discussed by Cruickshank & McDonald (1967).

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