

seven sulphur atoms forming a monocapped trigonal prism, with the prism axes parallel to *b*. The five metal atoms that lie in the boundary between blocks have the same coordination polyhedron as *M*(1)–*M*(10), but in the case of *M*(12) and *M*(15) the prism axis lies parallel to the mirror plane. Because of the similar atomic scattering factors for Sn and Sb no attempt has been made to assign these species to particular *M* sites.

Confirmation of the structure presented above for $\text{Sn}_3\text{Sb}_2\text{S}_6$ comes from two lines of evidence. Firstly, the powder X-ray diffraction pattern computed for the model agrees well with that obtained experimentally (Table 1). The 2θ range covered by the data in Table 1 includes 556 allowed reflections; of these only 39 have $(I/I_o)_{\text{calc}} > 10\%$ and all such reflections were observed. Secondly, a calculated HRTEM image gives a good match with the experimental image (inset, Fig. 2). The simulated image was computed by the Cowley–Moodie multislice method (Cowley & Moodie, 1957; Goodman & Moodie, 1974). For 1001 diffracted beams and 50 slices (each 2 Å thick) the multislice program uses 25 min of CPU time on a Univac 1100/82 computer; this clearly places a restriction on the use of image calculation as a means of refining structures having a large unit cell.

The structure determination described in this paper provides a good example of the use of HRTEM in a case where, owing to the size of the unit cell and the difficulty of growing good crystals, single-crystal X-ray data may be difficult to obtain and to interpret. The atom positions derived in this study are considered to be correct to within approximately 0.5 Å; a neutron powder diffraction refinement will be attempted at a later date.

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Neutron Diffraction Refinement of Magnesium Sulfite Hexahydrate, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$

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Abstract. $M_r = 212.5$, rhombohedral, $R\bar{3}$, $a = 5.933(2)$ Å, $\alpha = 96.28(2)^\circ$, $V = 204.8(2)$ Å³, $Z = 1$, $D_x = 1.72$ g cm⁻³, $\lambda = 1.21$ Å, $\mu(\text{estimated}) = 2.0$ cm⁻¹, $T = 293$ K, $R = 0.036$ for 1049 observed neutron reflections. The structure was solved previously from X-ray data but the hydrogen atoms were not located [Flack (1973). *Acta Cryst.* **B29**, 656–658]. The refined dimensions of the

The recognition of $\text{Sn}_3\text{Sb}_2\text{S}_6$ as a block structure based on a simpler substructure suggests that its range of composition may result from disorder in the dimensions of the block; further work is in progress to investigate this possibility.

The image computation program was written and developed by P. L. Fejes, A. J. Skarnulis and M. A. O'Keefe. X-ray powder diffraction patterns were calculated by means of the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977), kindly provided by E. Parthé.

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SO_3^{2-} ion are S–O = 1.528(2) Å and O–S–O = 104.3(1)°. The O–H distances in the water molecules are in the range 0.957(4)–0.980(3) Å.

Introduction. To evaluate the structure and properties of the lone pair of electrons on S in SO_3^{2-} SCF calculations have been carried out (Strömberg, Gropen, Wahlgren & Lindqvist, 1983). The series

MgXO₃·6H₂O, X = S, Se and Te, is so far the only known case of isomorphism between structures containing SO₃²⁻, SeO₃²⁻ and TeO₃²⁻. Previous structural information on the series comprises X-ray diffraction studies of MgSO₃·6H₂O (Flack, 1973) and MgSeO₃·6H₂O (Weiss, Wendling & Grandjean, 1966).

The present work deals with a neutron diffraction refinement of the hydrogen-bond structure in MgSO₃·6H₂O, which is needed for a correct description of the potential field in the crystals. The accompanying paper describes structure determinations and refinements of MgSeO₃·6H₂O and MgTeO₃·6H₂O from X-ray data (Andersen, Lindqvist & Moret, 1984).

Experimental. Cell dimensions refined from a Guinier powder photograph (Lindqvist & Wengelin, 1967); large colorless crystals of MgSO₃·6H₂O grown from aqueous solution; irregular prism of approximate dimensions 2.6 × 2.2 × 1.9 mm mounted in a glass capillary to avoid decomposition due to oxidation in air; Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy reactor R2 at Studsvik was used, doubly Cu(200) monochromated neutron beam at λ = 1.21 Å (Stedman, Almquist, Raunio & Nilsson, 1969); 1120 reflections* measured (ω/2θ scan; 2θ < 110°; 0 ≤ h ≤ 8, -8 ≤ k ≤ 8, -8 ≤ l ≤ 8) and evaluated by profile analysis according to Lehmann & Larsen (1974) (program *LELA*; Lindqvist & Ljungström, 1979) giving 1049 (325 unique) intensities with I ≥ 3σ(I); standard reflections 410, 042 and 232, stable, Lorentz correction, absorption correction with Gaussian grids of 6 × 6 × 6, transmission factor 0.638–0.704, secondary-extinction refinement (g = 0.633 × 10⁻⁴; Coppens & Hamilton, 1970), hydrogen atoms located from Fourier maps (program *XTL*; Syntex, 1973), anisotropic full-matrix refinement of the 1049 non-averaged reflections (Busing, Martin & Levy, 1962; Coppens & Hamilton, 1970), minimizing $\sum w(|F_o| - |F_c|)^2$, wR = 0.049, S = 0.16, w = (7.0 + F_o + 0.00001F_o²)⁻¹ giving satisfactory weight analysis, Δ/σ < 0.5%, scattering lengths from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic coordinates with equivalent isotropic temperature factors are given in Table 1. There are no significant differences between the non-hydrogen atomic coordinates in the present neutron diffraction study compared to those obtained in the previous X-ray work (Flack, 1973). Distances and angles within the SO₃²⁻ ion and the Mg(H₂O)₆²⁺ octahedron are given in Table 2.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39128 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors (Å²) according to Hamilton (1959)*

W denotes an oxygen atom in a water molecule.

	x	y	z	B _{eq}
Mg*	0.0	0.0	0.0	1.49 (1)
S	0.5021 (6)	0.5021 (6)	0.5021 (6)	2.18 (2)
O	0.5598 (3)	0.4826 (3)	0.2565 (3)	2.12 (2)
W(1)	-0.3165 (3)	-0.1254 (3)	0.0765 (4)	2.45 (3)
W(2)	0.3288 (3)	0.1464 (3)	-0.0496 (3)	1.98 (2)
H(1)	-0.4523 (5)	-0.0624 (5)	0.0258 (6)	3.87 (6)
H(2)	-0.3632 (5)	-0.2635 (5)	0.1408 (6)	3.32 (5)
H(3)	0.4036 (5)	0.2737 (5)	0.0651 (5)	2.84 (4)
H(4)	0.3672 (5)	0.1930 (5)	-0.1956 (5)	2.91 (4)

* Fixed to define the origin.

Table 2. *Distances (Å) and angles (°) in MgSO₃·6H₂O*

I = this work, II = Flack (1973).*

	I	II
Mg–W(1)	2.059 (2)	2.071 (5)
Mg–W(2)	2.112 (2)	2.093 (3)
S–O	1.528 (2)	1.536 (5)
W(1)–Mg–W(1)	93.8 (1)	92.9 (2)
W(1)–Mg–W(2)	174.9 (1)	175.8 (2)
W(2)–Mg–W(2)	86.6 (1)	87.3 (1)
O–S–O(1)	104.3 (2)	104.2 (3)

Symmetry code (I): (i) z, x, y.

* Flack (1973) described the structure in R3, hexagonal setting, as did Weiss *et al.* (1966) for MgSeO₃·6H₂O. However, their coordinate systems have been chosen with different orientations. Flack seems to have used erroneous cell dimensions (a = 5.895 Å, α = 96.0°, rhombohedral setting) in his calculation of distances and angles. With his hexagonal cell (corresponding to a = 5.928 Å, α = 96.3°) the above values were obtained, which are in better agreement with the present results.

The S–O bond distance in MgSO₃·6H₂O is slightly but significantly shorter than in α-FeSO₃·3H₂O (Johansson & Lindqvist, 1979) and in β-MnSO₃ (Magnusson, Johansson & Lindqvist, 1981) having average S–O distances of 1.536 (1) and 1.539 (3) Å, respectively. Of other previously determined SO₃²⁻ ions with trigonal symmetry, the isomorphous NiSO₃·6H₂O has a comparable distance of 1.536 (7) Å (Baggio & Becka, 1969), while Na₂SO₃ has a shorter value of 1.504 (3) Å (Larsson & Kierkegaard, 1969). It has been proposed by Kierkegaard, Larsson & Nyberg (1972) that covalent metal interactions or hydrogen bonds to the sulfite oxygen atoms would cause the S–O bond distance to increase. SCF Hartree–Fock calculations on MgSO₃·6H₂O gave an SO₃²⁻ geometry in close agreement with the present experimental result (Andersen, Lindqvist, Strömberg & Strömberg, 1984).

Details of the hydrogen-bond system in MgSO₃·6H₂O are shown in Fig. 1 and Table 3. The hydrogen bonds of W(1) are oriented so that the Mg atom lies in the H(1)–W(1)–H(2) plane, which explains why the Mg–W(1) interaction is stronger than that of Mg–W(2). The H(3)–W(2)–H(4) water

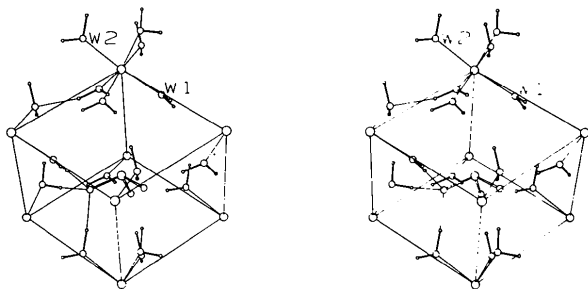


Fig. 1. A stereoscopic view of the $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ unit cell.

Table 3. Hydrogen-bonding distances (Å) and angles (°)

A	B	C	$d(A-C)$	$d(A-B)$	$d(B \cdots C)$	$\angle(A-B \cdots C)$
$W(1)-H(1) \cdots W(2^{II})$			2.872 (3)	0.958 (4)	1.941 (4)	163.6 (3)
$W(1)-H(2) \cdots O^{(III)}$			2.726 (3)	0.967 (4)	1.759 (3)	178.3 (4)
$W(2)-H(3) \cdots O$			2.687 (3)	0.989 (3)	1.701 (3)	173.8 (3)
$W(2)-H(4) \cdots O^{(IV)}$			2.701 (3)	0.980 (3)	1.731 (3)	169.4 (3)
$H(1)-W(1)-H(2)$			1.551 (4)	—	—	107.4 (3)
$H(3)-W(2)-H(4)$			1.553 (4)	—	—	104.1 (3)

Symmetry codes: (ii) $x - 1, y, z$; (iii) $x, y - 1, z$; (iv) $y, z, x - 1$.

molecule is distorted from this favorable orientation owing to the strong hydrogen bonds between $W(2)$ and the SO_3^{2-} ion. The SO_3^{2-} ion takes part in nine of the twelve hydrogen bonds in the cell, each sulfite oxygen being bonded in the oxygen plane through $W(1)-H(2) \cdots O$ and $W(2)-H(4) \cdots O$ and perpendicular to it through $W(2)-H(3) \cdots O$ (cf. Fig. 1). The other three hydrogen bonds are between water molecules in different $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ units.

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The Structures of Magnesium Tellurate(IV) Hexahydrate, $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$, and Magnesium Selenate(IV) Hexahydrate, $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$

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Abstract. $\text{MgTeO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ isomorphous, $M_r = 307.9, 259.4$, rhombohedral, $R3$, $a = 6.011 (3), 5.965 (2) \text{ \AA}$, $\alpha = 97.36 (4), 97.28 (2)^\circ$, $V = 211.3 (1), 206.7 (1) \text{ \AA}^3$, $Z = 1$, $D_x = 2.42 (1)$,

The authors wish to thank Dr Jaques Moret for providing the crystals.

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$2.08 (1) \text{ g cm}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.71069 \text{ \AA}$, $\mu = 37.4, 49.8 \text{ cm}^{-1}$, $F(000) = 148, 130$, $T = 293 \text{ K}$, 819, 695 diffractometer reflections, $R = 0.029, 0.021$. The structures are isomorphous with $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. The dimen-