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Structure of Pentahydrogendioxygen(1+) Diaquadisulfatomanganate(III), [H₅O₂]⁺[Mn(H₂O)₂(SO₄)₂][−]

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Abstract. $M_r = 320.12$, orthorhombic, $Pnma$, $a = 9.630$ (4), $b = 18.171$ (8), $c = 5.481$ (3) Å, $V = 959.1$ (8) Å³, $Z = 4$, $D_x = 2.23$ Mg m^{−3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 15.9$ cm^{−1}, $F(000) = 648$, $T = 298$ K, $R = 5.1\%$ for 1136 reflections. Manganese exhibits Jahn–Teller distorted octahedral coordination; the MnO₆ groups are connected by SO₄ tetrahedra *via* vertices forming sheets of composition [Mn(H₂O)₂(SO₄)_{4/2}][−] which are separated by layers of [H₅O₂]⁺.

Introduction. Repeatedly, preparative investigations on manganese(III) sulfates Mn₂(SO₄)₃ (Franke, 1887; Domange, 1939) and Mn₂(SO₄)₃·H₂SO₄· n H₂O with $n = 4–8$ (Ubbelohde, 1935; Kharabadze, 1963) have been reported. Until now, however, no structural information on this class of compounds has been available. In the course of systematic investigations on the action of sulfuric acid on Ba(MnO₄)₂ we prepared the title compound as single crystals and report in this paper its crystal structure.

Experimental. 160 mg Ba(MnO₄)₂ added to 5 ml conc. H₂SO₄, BaSO₄ precipitated, solution decanted and left standing in a watchglass in the atmosphere; solution slowly evolved oxygen and absorbed moisture from the air, forming red-brown crystals which were washed repeatedly with CCl₄ and dried; reaction products were coarsely crystalline transparent red-brown tablets. Rhombic-shaped crystal, 0.4 × 0.2 × 0.1 mm, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, 25 reflections used for measuring lattice parameters, L_p correction, absorption ignored, $2 < \theta < 30^\circ$, $0 \leq h \leq 16$, $-25 \leq k \leq 30$, $0 \leq l \leq 9$, no standard reflections used; 4193 reflections measured, 1136 independent with $I > 3\sigma(I)$, $R_{int} = 0.063$; Patterson methods, two H from difference map, rest in calculated positions, anisotropic full-matrix refinement (except H atoms) on F , $R = 0.051$ (unit weights); max. LS shift = 0.02/e.s.d., $\Delta\rho$ excursions +0.95

to -0.98 e Å^{−3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); *Structure Determination Package* (Enraf–Nonius, 1979) on PDP 11/45.

Discussion. Positional parameters are given in Table 1.* The crystal structure consists of distorted MnO₆ octahedra and SO₄ tetrahedra, which are interconnected by vertices forming a two-dimensional net. The differences within the S–O bond lengths (Table 2) are caused by different functions of these oxygens: two are bridging, while the remaining two are terminal (*cf.* Figs. 1 and 2). The elongation of the octahedra results from the Jahn–Teller effect of the trivalent manganese, the oxidation state of which was confirmed by chemical methods (iodometry) and magnetic susceptibility measurements.† The relative elongation of the axial Mn–O distances (9.4%) is not as pronounced as in the cases of KMnO₂ (18.1%) or NaMnO₂ (25.0%) (Jansen, Chang & Hoppe, 1982; Jansen & Hoppe, 1973). This feature may be explained by the fact that the axial oxygens are terminal ones, which usually leads to reduced bond distances and thus would partly compensate for the influence of the Jahn–Teller effect.

Bond length/bond-strength considerations (Brown, 1981) clearly show that O(1), O(2), O(4), O(6) and O(7) are coordinated by hydrogen or involved in hydrogen bonds. Some of the expected hydrogen atoms have been localized from a difference map. The most probable positions of the remaining hydrogens are given in Fig. 1, which in addition shows a proposal for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38764 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Faraday method, paramagnetic in the temperature range 15–298 K. Curie–Weiss law. $\theta = -3$ K. $\mu = 4.98$ BM (46.18×10^{-24} JT^{−1}).

system of hydrogen bonds interconnecting the [Mn(H₂O)₂(SO₄)₂]⁻ layers mentioned above.

The compound investigated by us seems to be identical with Mn₂(SO₄)₃·H₂SO₄·nH₂O (*n* = 4–8) (Ubbelohde, 1935; Kharabadze, 1963), for which so far only qualitative properties (colour, crystal shape) have been reported.

Table 1. Positional and thermal parameters and their e.s.d.'s

$$B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Mn	0.0000	0.0000	0.0000	0.96 (8)
S	0.2325 (8)	0.0858 (5)	0.2835 (2)	1.06 (1)
O(1)	0.2233 (3)	0.3664 (2)	0.4971 (6)	1.68 (4)
O(2)	0.2788 (3)	0.1254 (2)	0.0681 (6)	1.95 (5)
O(3)	0.0873 (3)	0.0564 (2)	0.2446 (5)	1.59 (4)
O(4)	0.0114 (3)	0.5955 (2)	0.2231 (5)	1.68 (4)
O(5)	0.3199 (3)	0.0208 (2)	0.3328 (5)	1.51 (4)
O(6)	0.1349 (6)	0.2500	0.9451 (14)	3.6 (1)
O(7)	0.3831 (6)	0.2500	0.5665 (20)	5.4 (2)

Table 2. Interatomic distances (Å) and bond angles (°) in the MnO₆, SO₄²⁻ and H₅O₂⁺ groups with e.s.d.'s in parentheses

Mn–O(3)	2 × 1.885 (2)	O(2)–O(3)	1 × 2.431 (3)
Mn–O(4)	2 × 2.126 (2)	O(2)–O(4)	1 × 2.820 (3)
Mn–O(5)	2 × 1.998 (2)	O(2)–O(5)	1 × 2.424 (3)
S–O(1)	1 × 1.460 (2)	O(2)–O(6)	1 × 2.739 (3)
S–O(2)	1 × 1.453 (2)	O(3)–O(4)	1 × 2.825 (3)
S–O(3)	1 × 1.512 (2)	O(3)–O(4)	1 × 2.858 (3)
S–O(5)	1 × 1.475 (1)	O(3)–O(5)	1 × 2.381 (3)
O(1)–O(2)	1 × 2.416 (3)	O(3)–O(5)	1 × 2.689 (3)
O(1)–O(3)	1 × 2.366 (3)	O(3)–O(5)	1 × 2.804 (3)
O(1)–O(4)	1 × 2.818 (3)	O(4)–O(5)	1 × 2.822 (3)
O(1)–O(4)	1 × 2.922 (3)	O(4)–O(7)	2 × 2.426 (6)
O(1)–O(5)	1 × 2.424 (3)	O(6)–H(1)	2 × 0.945
O(1)–O(7)	2 × 2.643 (3)	O(7)–H(2)	2 × 0.907
O(3)–Mn–O(3)	180.00 (16)	O(1)–S–O(2)	112.06 (13)
O(3)–Mn–O(4)	89.33 (9)	O(1)–S–O(3)	105.49 (12)
O(3)–Mn–O(4)	90.67 (9)	O(1)–S–O(5)	111.34 (13)
O(3)–Mn–O(5)	92.40 (8)	O(2)–S–O(3)	110.14 (13)
O(3)–Mn–O(5)	87.60 (8)	O(2)–S–O(5)	111.73 (13)
O(4)–Mn–O(4)	180.00 (6)	O(3)–S–O(5)	105.70 (12)
O(4)–Mn–O(5)	86.30 (8)		
O(4)–Mn–O(5)	93.70 (8)		
O(5)–Mn–O(5)	180.00 (18)		

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The Homologous Series Sb₂S₃·*n*PbS: Structures of Diantimony Dilead Pentasulphide, Pb₂Sb₂S₅, and the Related Phase Diantimony Ditin Pentasulphide, Sn₂Sb₂S₅

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Abstract. Pb₂Sb₂S₅, *M_r* = 818.2, *Pnma*, *a* = 641.2, *Pnma*, *a* = 19.59 (3), *b* = 3.938 (3), *c* = 19.808 (5), *b* = 4.042 (2), *c* = 11.353 (4) Å, *V* = 11.426 (3) Å³, *V* = 881 Å³, *Z* = 4, *F*(000) = 1128; 909.0 Å³, *Z* = 4, *F*(000) = 1384; Sn₂Sb₂S₅, *M_r* = λ(Cu Kα₁) = 1.54056 Å, room temperature. A

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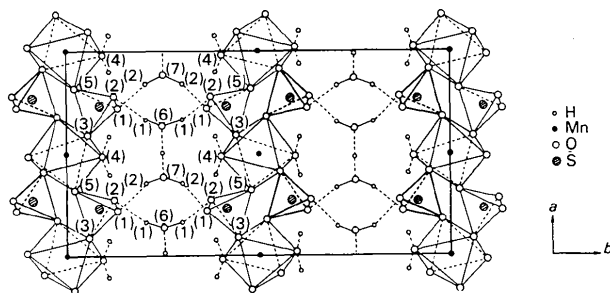


Fig. 1. Projection of the crystal structure of [H₅O₂][Mn(H₂O)₂(SO₄)₂] on (001). The numbering of O and H corresponds to Table 1.

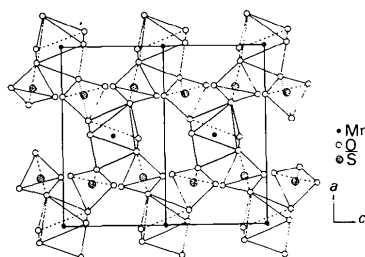


Fig. 2. Sheet of composition [Mn(H₂O)₂(SO₄)₂]⁻ viewed along [010].

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