

Manganese(II) sulfate tetrahydrate (ilesite)

Peter Held* and Ladislav Bohatý

Institut für Kristallographie, Universität zu Köln,
Zùlpicher Str. 49b, D-50674 Köln, GermanyCorrespondence e-mail:
peter.held@uni-koeln.de

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(S-O) = 0.002 \text{ \AA}$

R factor = 0.027

wR factor = 0.073

Data-to-parameter ratio = 16.3

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $Mn(SO_4) \cdot 4H_2O$, contains centrosymmetric bis(μ -sulfato-*O:O'*)bis[tetraaquamanganese(II)] dimers, with two *cis*-located bridging sulfate anions and two coordination octahedra around manganese(II) forming eight-membered rings. The manganese cations are surrounded by six O atoms of four water molecules and two sulfate groups, forming a slightly distorted octahedron. The $[Mn(H_2O)_4(SO_4)]_2$ rings are linked by hydrogen bonds of weak to medium strength.

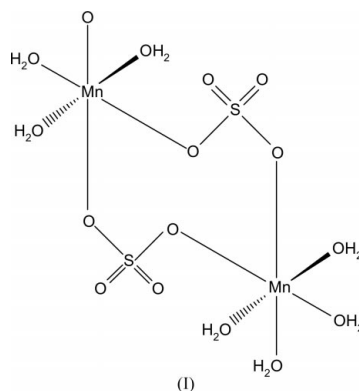
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Comment

The tetrahydrates of the sulfates of the divalent cations, Mg, Mn and Fe, were synthesized and morphologically described by the middle of the 19th century (for a summary, see Groth, 1908). The first X-ray single-crystal structure determination of the Mg and Fe compounds was achieved by Baur (1962), followed by a detailed neutron diffraction structure analysis of a single crystal of the Mg compound (Baur, 1964). About 30 years later, the structure of the Co member was determined (Kellersohn, 1992) and recently the structure of $Zn(SO_4) \cdot 4H_2O$ was published (Blake *et al.*, 2001; annotated by Baur, 2002). All the tetrahydrates mentioned above are isostructural. In this paper we present the structure of $MnSO_4 \cdot 4H_2O$, (I), whose isostructurality was predicted by Baur (2002). The manganese compound exists also in nature with the mineralogical name ilesite, and belongs to the starkeyite group (Strunz & Nickel, 2001). The authors mentioned above emphasize that tetrahydrates are unstable in air, but can easily be stored for months in inert liquids such as paraffin oil without decomposition. We observed that, after the decomposition has started on the crystal surface, the dehydration cannot be stopped without taking steps against it, such as controlled humidity or passivation.



The crystallization of $MnSO_4 \cdot 4H_2O$ from an aqueous solution of sulfuric acid, manganese sulfate monohydrate and ethylenediamine in the molar ratio 1:1:1 was not expected (in

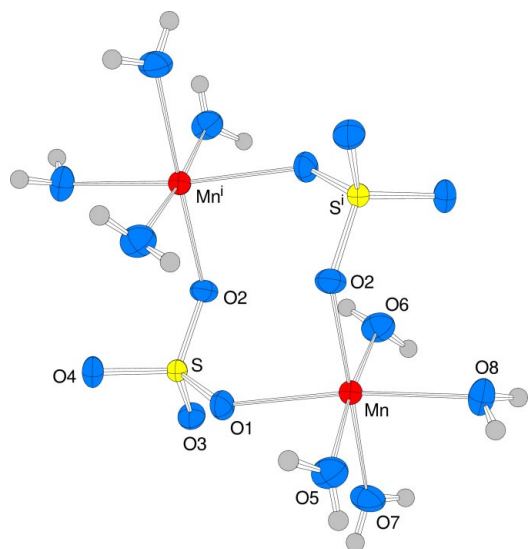


Figure 1
ORTEP projection, parallel to (100), of the title compound, with the atom-numbering scheme. Non-H atoms are shown as 50% probability ellipsoids. [Symmetry code: (i): $-x, -y, -z$.]

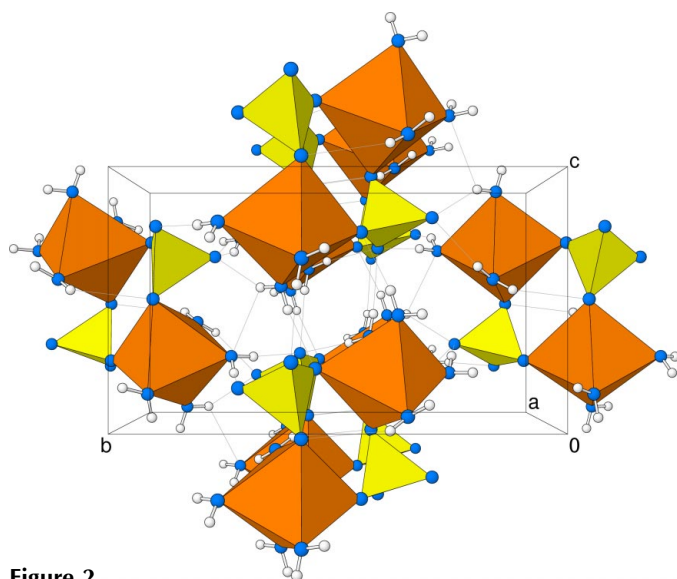


Figure 2
Foreshortened (100) projection of the title compound, showing $[\text{SO}_4]$ tetrahedra (yellow), $[\text{Mn}(\text{H}_2\text{O})_4\text{O}_2]$ octahedra (orange), oxygen (blue) and hydrogen (light grey) atoms. Hydrogen bonds (grey lines) interlink different dimers.

our search for double sulfates of ethylenediammonium and divalent cations). Heating, to 340 K, of the solution involved in the neutralization reaction of sulfuric acid and ethylenediamine is the key to the synthesis of the title compound. The crystal consists of dimers containing two $[\text{Mn}(\text{H}_2\text{O})_4(\text{SO}_4)]$ units related by a centre of symmetry and forming an eight-membered ring (Fig. 1). The manganese cations are surrounded by six O atoms of four water molecules and two sulfate groups, in the form of an almost ideal octahedron. The obvious deviation from ideal geometry is revealed in the enlargement of the Mn—O5 distance, accompanied by a

decrease in the Mn—O6 distance. In the dimer, the manganese cations are separated by a distance of 4.5464 (7) Å. The tetrahedral configuration of the sulfate atoms is almost ideal, although two O atoms (O3, O4) do not take part in the dimer formation. The bis(μ -sulfato- $O:O'$)bis[tetraaquamanganese(II)] rings are interconnected *via* hydrogen bonds of medium strength in the range 2.740 (2)–2.857 (3) Å (with the exception of the intramolecular O6—H62 \cdots O2), forming a three-dimensional body-centred framework (Fig. 2). An analogous hydrogen bonding system was found in the Mg, Fe and Co sulfate tetrahydrates (for schematic presentation see Baur, 1964), whereas the hydrogen-bonding data reported for the Zn compound are not convincing, because the hydrogen-bond length was constrained in the refinement calculation. The existence of the O6—H62 \cdots O2 hydrogen bond was discussed in detail in early works. Baur (1962, 1964) disputes the formation because of unfavourable geometric parameters, in combination with a large displacement vibration amplitude of H62. We agree with Kellersohn (1992) in the inclusion of H62 in the hydrogen-bonding scheme, because of bond-valence considerations and his published calculations. Moreover, it is not possible to decide whether one or both bifurcating hydrogen bonds to two symmetrically equivalent O2 atoms exist. The first reinforces ring construction as an intradimer bond, while the second interconnects two different dimers. Owing to the abundance of examples, we are inclined to extend the geometric criteria for the existence of a hydrogen bond, but, in the end, this has to be confirmed in combination with vibrational spectroscopic studies.

Experimental

Crystal data

$\text{Mn}(\text{SO}_4)\cdot 4\text{H}_2\text{O}$
 $M_r = 223.06$
 Monoclinic, $P2_1/n$
 $a = 5.9783$ (6) Å
 $b = 13.809$ (1) Å
 $c = 8.0481$ (7) Å
 $\beta = 90.80$ (1)°
 $V = 664.4$ (1) Å³
 $Z = 4$

$D_x = 2.230$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.6$ – 18.5°
 $\mu = 2.30$ mm⁻¹
 $T = 293$ (2) K
 Parallelepiped, pale red
 $0.19 \times 0.18 \times 0.16$ mm

Data collection

Nonius MACH3 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 MolEN (Fair, 1990)
 $T_{\min} = 0.644$, $T_{\max} = 0.692$
 6258 measured reflections
 2026 independent reflections
 1425 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

$\theta_{\max} = 30.4^\circ$
 $h = -8 \rightarrow 8$
 $k = -19 \rightarrow 19$
 $l = -11 \rightarrow 11$
 3 standard reflections
 every 100 reflections
 frequency: 60 min
 intensity decay: 0.7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.05$
 2026 reflections
 124 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.1046P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.52$ e Å⁻³
 $\Delta\rho_{\min} = -0.50$ e Å⁻³
 Extinction correction: SHELXL
 Extinction coefficient: 0.041 (2)

Table 1

Selected geometric parameters (Å).

Mn—O5	2.1585 (18)	Mn—O6 ^{iv}	2.1949 (19)
Mn—O2 ⁱⁱ	2.1713 (16)	S—O4	1.4650 (16)
Mn—O1 ⁱⁱⁱ	2.1721 (16)	S—O2	1.4799 (15)
Mn—O8	2.1721 (17)	S—O3	1.4811 (16)
Mn—O7 ^{iv}	2.1799 (19)	S—O1	1.4847 (16)

Symmetry codes: (ii) $x, y, z - 1$; (iii) $-x, -y, 1 - z$; (iv) $x - 1, y, z$.**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H51 [·] ··O3	0.74 (4)	2.16 (4)	2.891 (2)	172 (4)
O5—H52 [·] ··O3 ^v	0.88 (4)	1.91 (4)	2.771 (3)	166 (3)
O6—H61 [·] ··O4 ^{vi}	0.85 (4)	2.10 (4)	2.857 (3)	148 (4)
O6—H62 [·] ··O2 ^v	0.79 (4)	2.55 (4)	3.094 (3)	127 (4)
O6—H62 [·] ··O2 ⁱⁱ	0.79 (4)	2.57 (4)	3.208 (3)	140 (4)
O7—H71 [·] ··O4 ^{vi}	0.77 (3)	2.16 (3)	2.854 (3)	149 (3)
O7—H72 [·] ··O1 ^{vii}	0.77 (4)	2.05 (4)	2.813 (2)	169 (4)
O8—H81 [·] ··O4 ^{vi}	0.76 (4)	2.18 (4)	2.850 (3)	147 (4)
O8—H82 [·] ··O3 ^{viii}	0.85 (4)	1.89 (4)	2.740 (2)	175 (3)

Symmetry codes: (ii) $x, y, z - 1$; (v) $1 - x, -y, 1 - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $1 + x, y, z$; (viii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.Data collection: *MACH3 Server Software* (Nonius, 1993); cell refinement: *MACH3 Server Software*; data reduction: *MolEN* (Fair,1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002) and *ORTEPIII* (Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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