The Crystal Structure of Manganese(II) Selenite Monodeuterate

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The crystal structure of manganese(II) selenite monodeuterate, $MnSeO_3.D_2O$, has been determined by X-ray methods. The compound is orthorhombic with crystal axes $a = 13.179(6)$ Å. $b = 5.826(4)$ Å and $c = 4.933(3)$ Å. It has four formula units in the unit cell, and belongs to the space group $Pnma$ (No. 62).

The structure consists of layers of distorted MnO_6-octahedra with four shared vertices. The $Mn-O$ distances range from 2.135 to 2.310 Å. The selenium atoms are situated in the cavities within the network, and the bonding scheme of the selenium is the main reason for the distortion of the octahedra. Each octahedron is tilted at an angle of 119.8° with respect to the four neighbouring octahedra.

Several compounds of the system $MnO - SeO_2 - H_2O$ are known. Recently the compounds $MnSeO_3$, $MnSeO_3.2H_2O$ and $MnSe_2O_5$ have been prepared and described.[1-3] In all of these the manganese atom is octahedrally coordinated, and in the case of $MnSeO_3$ and $MnSeO_3$.-$2H_2O$ the coordination polyhedron is considerably distorted. This is somewhat unexpected since the $t_{2g}^3 e_g^2$ configuration of the Mn^{2+} ion implies a spherically distributed d-electron density around the metal ion, which in turn would favour regular octahedra in the solid state.

The structure of $MnSeO_3$ can be described in terms of MnO_6-octahedra with shared vertices and selenium(IV) ions in the cavities thus formed. In $MnSeO_3.2H_2O$, on the other hand, the MnO_6-polyhedra are joined by the selenium (IV) ions into a three-dimensional network. In connection with our studies on manganese selenites we have now prepared the monodeuterate, $MnSeO_3.D_2O$, and have undertaken its structural characterization to throw more light on the coordination of divalent manganese in selenite compounds.

EXPERIMENTAL

A solution of 1 mol/dm³ potassium selenite was added dropwise to a solution of 1 mol/dm³ manganese sulfate until the precipitation of manganese as a selenite hydrate was complete. After this, selenous acid (1 mol/dm³) was added slowly with vigorous stirring until the precipitate just dissolved at $pH = 4.2 \pm 0.2$. The solution was then kept at $80 - 95 °C$ for $16 - 24$ h. Flat, needle-shaped crystals with a pink tint were formed. All the preparations were made in heavy water, since the crystals thus obtained were larger. The crystals showed a great tendency to split into sheets if gently touched under microscopic investigation.

For recording of the X-ray data, a Syntex $P2_1$ (Fortran-version) automatic diffractometer and graphite monochromatized $MoK\alpha$-radiation were used. Unit cell dimensions were obtained by measuring 14 independent reflections with the diffractometer after which they were refined by least-squares methods. The axes were $a = 13.179(6)$ Å, $b = 5.826(4)$ Å and $c = 4.933(3)$ Å. The space group was deduced from the original intensity data to be $Pnma$ (No. 62). There are four formula units in the cell, and calculated and measured (flotation) densities were 3.51 and 3.5 g cm⁻³, respectively.

Intensity data for 560 independent reflections were collected at the interval $5° < 2\theta < 60°$ using the $\theta - 2\theta$ scanning technique and 1°/min scan speed. Of these reflections, 500 were taken as observed with the criterion of $I > 2\sigma(I)$. Lorentz, polarization and empirical absorption corrections were applied ($\mu = 127.4$ cm⁻¹). The size of the crystal was 0.1 × 0.1 × 0.15 mm.

The scattering factors for all the atoms were taken from the International Tables.[4] The positions of Se and Mn were obtained by direct methods with the computer program package X-Ray 1976, which was used also in the refinement of the structure.[5] In the final cycles of block-diagonal refinement, anisotropic temperature coefficents were used, and the value of R was reduced to 0.066. The F_0 and F_c listing is available from the authors upon request.

Table 1. Atomic coordinates and thermal parameters with estimated standard deviations for the atoms. The anisotropic temperature coefficients are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. The values of U_{ij} are multiplied by 10^4.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.7683(2)	0.2500	0.3985(5)	219(11)	161(10)	86(10)	0	−6(9)	0
Se	0.4018(1)	0.7500	0.0247(3)	148(6)	179(6)	89(6)	0	7(6)	0
O1	0.3632(9)	0.7500	0.3489(22)	261(57)	194(53)	81(47)	0	46(45)	0
O2	0.1671(6)	0.0303(14)	0.3824(15)	231(34)	155(36)	115(33)	23(33)	23(30)	26(30)
O3	0.8908(9)	0.2500	0.0918(24)	253(59)	204(55)	209(61)	0	31(51)	0

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations.[a]

Mn−O1	2.135(12)	Se−O1	1.678(11)
Mn−O2^{i,iii}	2.135(8) (2×)	Se−O2^{i,iii}	1.720(8) (2×)
Mn−O2^{ii,iv}	2.310(8) (2×)		
Mn−O3	2.212(13)	O1−Se−O2^{i,iii}	103.2(4) (2×)
		O2−Se−O2^{i,iii}	96.2(4)

[a] The superscripts denote the following symmetry operations:

  i x,y,z
  ii $1/2-x,1/2+y,1/2+z$
  iii $x,1/2-y,z$
  iv $1/2-x,-y,1/2+z$

DISCUSSION

The atomic coordinates and anisotropic temperature factors are given in Table 1. As can be seen, the manganese, selenium and two of the three oxygens are located in special positions. The oxygen labelled O3 belongs to the water molecule.

The structure consists of MnO$_6$-octahedra joined by four shared equatorial vertices into a layer network (*cf.* Fig. 1). The equatorial oxygens (O2) are three-coordinated, with bond lengths to the selenium and two manganese atoms of 1.720(8), 2.135(8) and 2.310(8) Å, respectively. These values coincide well with those in other manganese selenites (*cf.* Table 3). The bond arrangement of the oxygens is pyramidal, and the bond angles are 119.8(4), 125.0(4) and 97.9(4)° for the angles Mn−O2−Mn', Mn−O2−Se and Se−O2−Mn', respectively.

Each MnO$_6$-octahedron is tilted with respect to the four neighbouring ones. The tilt angle is extraordinarily large, the angle Mn−O2−Mn' deviating from 180° by 60.2°. In this respect the structure of MnSeO$_3$.D$_2$O is similar to

anhydrous manganese(II) selenite, which can also be described in terms of MnO$_6$-octahedra.[1] The number of shared vertices in this case is six, but the octahedra are tilted, and there are two different tilt angles of 121.7 and 127.6°.
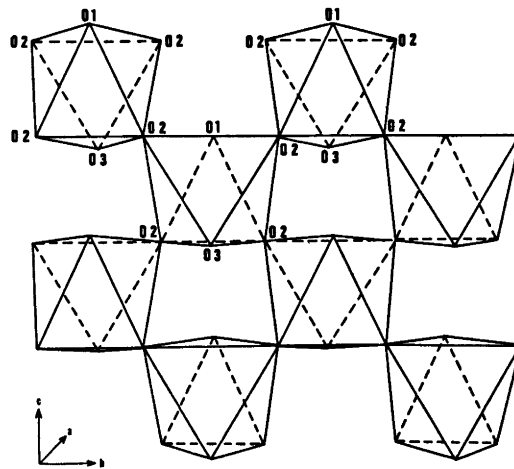

Fig. 1. A layer of tilted MnO$_6$-octahedra in MnSeO$_3$.D$_2$O.

Table 3. Manganese-oxygen and selenium-oxygen bond lengths (Å) selenium-oxygen bond angles (°) with standard deviations in manganese(II) selenites.

Compound	Range of Mn−O bond lengths	Range of Se−O bond lengths	Range of O−Se−O bond angles	Ref.
$MnSeO_3$	2.172−2.281	1.710−1.716	95.3−103.5	1
$MnSeO_3.D_2O$	2.135(12)−2.310(8)	1.678(11)−1.710(8)	96.2(4)−103.2(4)	Present work
$MnSeO_3.2H_2O$	2.189(2)−2.278(2)	1.692(2)−1.713(2)	100.4(1)−101.7(1)	2
$MnSe_2O_5$	2.179(14)−2.206(16)	1.644(14)−1.831(9)	95.9(6)−102.8(6)	3

In regular octahedra, if the edge length of the octahedron is accepted as the minimum value for the distance between the caps of two octahedra with a shared vertex, the maximum value for the deviation from 180° is, for geometric reasons, 48.2°.[6] The fact that the tilt angle in the present case exceeds this by 12° reflects the significant distortion of the coordination polyhedron. The variations of the edge lengths of the octahedron (*cf.* Fig. 2) clearly express this distortion. The irregularity of the distortion is striking, and it cannot be solely identified as one or the other of the two common forms of distortion encountered in octahedral coordination (tetragonal/trigonal elongation or contraction). The irregularity is mainly caused by one markedly shorter edge length (2.560 Å) as compared with the others in the octahedron (2.954−3.313 Å, *cf.* Fig. 2) It is worthwhile to note that this edge length appears between the two equatorial oxygens O2 which are bonded to the same selenium atom. The Mn−O bond lengths are also stretched, to 2.310(8) Å in both cases. It can be concluded that the main reason for these

anomalies is the tendency of the selenite group to maintain its geometry in the compound.

The selenium atoms are bonded to two equatorial oxygens (O2) of one and the cap oxygen (O1) of another octahedron (*cf.* Fig. 2). The bond lengths are normal as compared with the values observed in other manganese selenites (*cf.* Table 3). The bond angles in the selenite group agree with those of the anhydrous $MnSeO_3$.

The contribution of the water molecule to the distortion is somewhat difficult to judge. In $MnSeO_3$ no water molecules are present and in $MnSeO_3.D_2O$ the distance Mn−O3 (which could be assumed to stretch due to hydrogen bonds) is 2.212(13) Å, representing almost the mean of the shortest and longest Mn−O bond lengths in the compound. However, in $MnSeO_3.2H_2O$, which also has a distorted MnO_6-octahedron, the longest bonds are found between the divalent manganese and the two water oxygens. The most regular octahedron seems to be found in the diselenite compound.
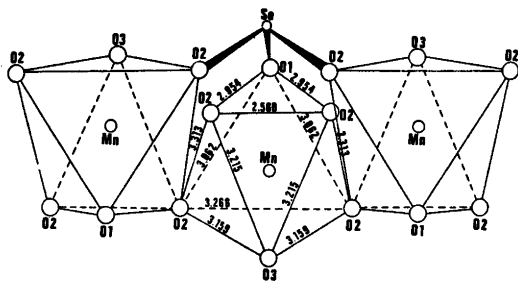

Fig. 2. The pyramidal bond arrangement of selenium(IV) and the distorted MnO_6-octahedron with edge lengths. The *a*-axis is vertical, the *b*-axis horizontal and the *c*-axis perpendicular to the figure plane.

REFERENCES

1. Kohn, K., Inove, K., Florie, O. and Akimoto, S.-I. *J. Solid State Chem. 18* (1976) 27.
2. Koskenlinna, M., Niinistö, L. and Valkonen, J. *Cryst. Struct. Commun. 5* (1976) 663.
3. Koskenlinna, M., Niinistö, L. and Valkonen, J. *Acta Chem. Scand. A 30* (1976) 836.
4. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4, p. 72.
5. Stewart, J. M., Ed., *The X-Ray System, Version of 1976,* Technical Report TR-466 of the Computer Science Center, University of Maryland, College Park.
6. Wells, A. F. *Structural Inorganic Chemistry,* Clarendon Press, Oxford 1975, p. 157.