

# Crystal Structure of Manganese(III) Hydrogen Selenite Diselenite, $\text{MnH}(\text{SeO}_3)(\text{Se}_2\text{O}_5)$

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The crystal structure of manganese(III) hydrogen selenite diselenite,  $\text{MnH}(\text{SeO}_3)(\text{Se}_2\text{O}_5)$ , has been determined by X-ray methods. The compound is monoclinic, and belongs to the space group  $P2_1/n$  with  $Z=4$ . The cell dimensions are  $a=7.451(2)$  Å,  $b=12.583(4)$  Å,  $c=7.575(2)$  Å and  $\beta=92.82(2)^\circ$ . The structure was solved by direct methods, and refined to  $R=0.035$ .

The  $\text{MnO}_6$ -octahedron is distorted by Jahn-Teller forces, with Mn—O bonds ranging from 1.916 Å to 2.179 Å. The compound contains both selenite and diselenite groups, which act as bridging ligands between two and three Mn atoms, respectively. The Se—O bonds range between 1.662 and 1.776 Å in the selenite and between 1.664 and 1.803 Å in the diselenite group.

The structural features of Mn(III) compounds are of interest because of the high spin  $d^4$ -configuration leading to Jahn-Teller distortions of the coordination polyhedron around the central atom. As a part of our studies on the manganese selenites we described the preparation and structure of  $\text{Mn}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ , a compound having tetragonally elongated  $\text{MnO}_6$ -octahedra.<sup>1</sup> Recently it was found that a praseodymium compound with both a selenite and a diselenite group as a ligand could be prepared.<sup>2</sup> We report now the preparation and structure of  $\text{MnH}(\text{SeO}_3)(\text{Se}_2\text{O}_5)$ .

## EXPERIMENTAL

Manganese(III) hydrogen selenite diselenite,  $\text{MnH}(\text{SeO}_3)(\text{Se}_2\text{O}_5)$ , was prepared in two stages. First, freshly precipitated, hydrated manganese dioxide and a concentrated solution (1 mol/dm<sup>3</sup>) of selenous acid were placed in a steel reactor with Teflon lining, and the

suspension was held at 140 °C for 1–3 weeks. A red, amorphous manganese selenite precipitation was obtained. This was filtered off and placed a second time in the reactor at 140 °C, with an excess of 1 mol/dm<sup>3</sup> selenous acid. The tightness of the sealing of the reactor was so adjusted that all the water was able to escape within 2–3 days and thus the  $\text{SeO}_2$  concentration was gradually increased. When the resulting white mass consisting mainly of  $\text{SeO}_2$  was extracted with water, the dark-red, lustrous, well-developed prisms of  $\text{MnH}(\text{SeO}_3)(\text{Se}_2\text{O}_5)$  remained in the residue.

The intensities of 1366 reflections with  $I > 3\sigma$  ( $I$ ) were measured between  $5^\circ < 2\theta < 55^\circ$  in a  $\theta$ – $2\theta$  scan, using a Syntex  $P2_1$  (fortran version) automatic four-circle diffractometer and graphite monochromatized  $\text{MoK}\alpha$ -radiation. The scan speed was 2°/min. The size of the crystal was approximately  $0.2 \times 0.2 \times 0.2$  mm<sup>3</sup>. The unit cell dimensions were obtained by measuring 25 independent reflections from the random-orientation rotation photograph and centering their positional parameters with the diffractometer. The unit cell dimensions for the selected set of axes are, after least-squares treatment  $a=7.451(2)$  Å,  $b=12.583(4)$  Å,  $c=7.575(2)$  Å and  $\beta=92.82(2)^\circ$  and the unit cell belongs to the space group  $P2_1/n$  according to the systematic absences  $h0l$  with  $h+l=2n+1$  and  $0k0$  with  $k=2n+1$ . Calculated density for the crystals was 3.94 g/cm<sup>3</sup>. There are four formula units in the unit cell. Lorentz, polarization and empirical absorption corrections (from the  $\phi$ -scan data,  $\mu=170.5$  cm<sup>-1</sup>) were applied to the data.

Neutral atoms were presumed in the solving and refinement of the structure and the values for their scattering factors were obtained from the International Tables.<sup>3</sup> All the calculations were performed on a Univac 1108 computer using the X-Ray 1976 program package.<sup>4</sup> The structure was solved by direct methods with 208  $E$ -values bigger than 1.4. The  $E$ -map gave the sites of the Se and Mn atoms. These were then refined to an  $R$  of 17.9 %, and the subse-

Table 1. Atomic coordinates and anisotropic temperature coefficients with their estimated standard deviations. The temperature coefficients are of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ , and have been multiplied by 10<sup>4</sup>.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Mn	.4387(2)	.6792(1)	.3055(2)	80(6)	53(6)	68(6)	6(5)	15(5)	5(5)
Se1	.0520(1)	.7988(1)	.3869(1)	107(4)	84(4)	90(4)	18(3)	27(3)	10(3)
Se2	.0668(1)	.6330(1)	.0677(1)	109(4)	85(4)	94(4)	-13(3)	5(3)	-1(3)
Se3	.7258(1)	.5148(1)	.4281(1)	109(1)	78(4)	128(4)	11(3)	16(3)	7(3)
O1	.5337(9)	.7647(6)	.0780(8)	187(36)	128(34)	95(31)	-53(28)	48(26)	-25(26)
O2	.2742(9)	.7930(6)	.3440(9)	121(32)	107(32)	189(34)	-8(27)	47(26)	-19(28)
O3	.2667(9)	.5970(6)	.1577(10)	139(34)	117(33)	204(36)	27(27)	-11(28)	8(28)
O4	.6222(9)	.7603(6)	.4510(9)	115(32)	181(35)	97(31)	48(27)	15(25)	42(27)
O5	.8891(10)	.0720(6)	.2466(9)	178(35)	165(36)	87(31)	-59(29)	47(26)	21(27)
O6	.6099(10)	.4040(6)	.4583(9)	198(36)	107(33)	143(33)	34(28)	54(27)	79(27)
O7	.6001(11)	.9606(6)	.1963(11)	247(42)	155(38)	328(45)	-57(32)	148(35)	-82(33)
O8	.5384(10)	.1930(6)	.2511(9)	158(34)	268(42)	129(33)	50(31)	67(27)	46(31)

Table 2. Selected bond distances (Å) and angles (°). The estimated standard deviations are in parentheses.

Mn-O1	2.179(7)	Se1-O1	1.664(7)	O1-Se1-O2	105.5(3)
Mn-O2	1.916(7)	Se1-O2	1.705(7)	O1-Se1-O8	96.1(3)
Mn-O3	1.956(7)	Se1-O8	1.803(8)	O2-Se1-O8	101.3(3)
Mn-O4	1.994(7)	Se2-O8	1.781(8)	O8-Se2-O3	102.6(3)
Mn-O5	1.916(7)	Se2-O3	1.670(7)	O8-Se2-O4	101.4(4)
Mn-O6	2.119(7)	Se2-O4	1.671(7)	O3-Se2-O4	101.3(3)
				Se1-O8-Se2	126.4(4)
O1-Mn-O6	170.8(3)	Se3-O5	1.700(7)		
O2-Mn-O5	175.7(3)	Se3-O6	1.662(7)	O5-Se3-O6	102.5(3)
O3-Mn-O4	177.7(3)	Se3-O7	1.776(8)	O5-Se3-O7	95.9(4)
O1-Mn-O3	92.2(3)			O6-Se3-O7	98.6(4)
O4-Mn-O5	91.5(3)				
O2-Mn-O6	95.9(3)				

quent difference Fourier map revealed the sites of all the O atoms. After refinement with isotropic temperature factors the value of *R* was 4.3 %, and with anisotropic temperature factors, after block-diagonal refinement, 3.5 %.

The  $|F_o|$  and  $|F_c|$  listing is available from the authors upon request.

## DISCUSSION

The atomic coordinates and anisotropic temperature coefficients are given in Table 1. The seleniums Se1 and Se2 belong to a diselenite ion and Se3 to a selenite ion. In Table 2 some characteristic bond lengths and angles are given.

The compound contains both selenite and diselenite groups. One of the Se-O bonds in the selenite group is significantly longer, 1.776(8)

Å, than the other two, suggesting a hydrogen bridge. Similar stretching was detected in PrH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>(Se<sub>2</sub>O<sub>7</sub>), in which the Se-O bonds of the two non-equivalent selenite groups lie in the range 1.624(14)-1.656(16) Å and 1.766(16)-1.805(18) Å for Se-O and Se-OH bonds, respectively.<sup>3</sup> The selenite group acts as a bridging ligand between two Mn atoms, and the Se links the apical oxygen of one octahedron to the equatorial oxygen of another.

The geometry of the diselenite group is like that of several other diselenite compounds. However, the bonds to the oxygen bridging the two Se atoms are slightly shorter than usual: 1.781(8) and 1.803(8) Å, compared with 1.835 and 1.847 Å in PrH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>(Se<sub>2</sub>O<sub>7</sub>), 1.831 Å in MnSe<sub>2</sub>O<sub>6</sub>, 1.831 Å in CuSe<sub>2</sub>O<sub>6</sub>, 1.768 and 1.822 Å in VSe<sub>2</sub>O<sub>6</sub> and 1.827 Å in

$\text{ZnSe}_2\text{O}_6^{2-}$ .<sup>5-8</sup> The ion is also less bent than usual. The angle  $\text{Se1}-\text{O8}-\text{Se2}$  is  $126.4(4)^\circ$ , which may well be a consequence of the short  $\text{Se}-\text{O}$  bond lengths: if the angle were  $120^\circ$ , the  $\text{Se}-\text{O}$  bonds would be of the order  $1.84 \text{ \AA}$ , with a fixed  $\text{Se1}-\text{Se2}$  distance. In the other diselenites the corresponding bond angles range between  $119.6$  and  $123.8^\circ$ . Four of the oxygens in the  $\text{Se}_2\text{O}_6^{2-}$ -ion are within bonding distance of three  $\text{Mn}$  atoms, and the ion acts as a bridging ligand between them (*cf.* Fig. 1). Two of the oxygens are coordinated to the same  $\text{Mn}$ , and are on the equatorial plane of the octahedron. The third oxygen,  $\text{O2}$ , is on the equatorial plane of another  $\text{MnO}_6$ -octahedron, and the fourth one,  $\text{O1}$ , forms the apical oxygen of yet another  $\text{MnO}_6$ -octahedron. Thus, the two apical oxygens of the octahedron are from different groups, one being contributed by the diselenite group and the other by the selenite group. One of the equatorial oxygens,  $\text{O5}$ , is also different from the others: it belongs to a selenite group, while the other three belong to diselenite groups. These differences are reflected in the  $\text{Mn}-\text{O}$  distances.

The coordination polyhedron around  $\text{Mn}$  is distorted as expected. Two of the  $\text{Mn}-\text{O}$  bond distances are noticeably larger than the

other four. Since the difference between the extreme values within the four shorter bond distances is more than 11 times the corresponding estimated standard deviation, they are not statistically of equal length. The bonds can be arranged into pairs of like magnitude ( $\text{O1}$  and  $\text{O6}$ ,  $\text{O3}$  and  $\text{O4}$ ,  $\text{O2}$  and  $\text{O5}$ ) with the bonds of each pair situated on opposite sides of the central atoms. The distorted polyhedron thus approximates an orthorhombically distorted octahedron.

The distorted  $\text{MnO}_6$ -octahedra in  $\text{Mn}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$  offer an interesting comparison. One of the three non-equivalent octahedra is tetragonally elongated and two are orthorhombically distorted. The range of bond lengths in the equatorial plane is  $1.891(9)-1.938(9) \text{ \AA}$  and in the axial direction, when the apical oxygens are contributed by water molecules,  $2.248(10)-2.346(10) \text{ \AA}$ .<sup>9</sup> It is most interesting to note that the one apical oxygen belonging to a selenite group has a shorter  $\text{Mn}-\text{O}$  bond length of  $2.140(9) \text{ \AA}$ , a value quite compatible with those obtained in the present work ( $2.119(7)-2.179(7) \text{ \AA}$ ). Thus, in  $\text{Mn}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ , hydrogen bond formation stretches the  $\text{Mn}-\text{O}$  bonds in the axial direction markedly.

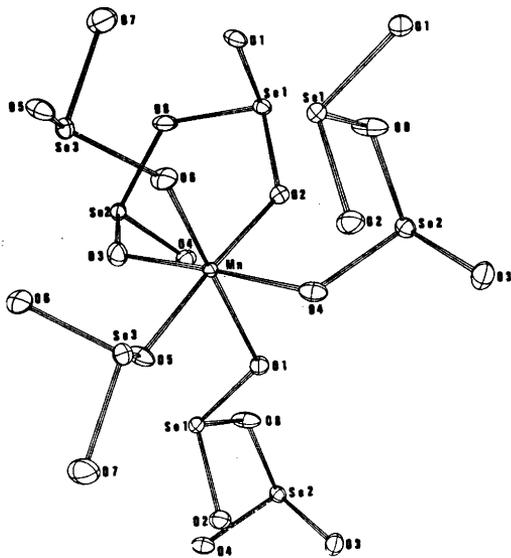


Fig. 1. Bonding scheme of selenite and diselenite groups in  $\text{MnH}(\text{SeO}_3)$  ( $\text{Se}_2\text{O}_6$ ).

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