JOURNAL OF SOLID STATE CHEMISTRY 113, 252–256 (1994)

Crystal Structure of $Mn(II)Mn(III)_2O(SeO_3)_3$

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Received December 13, 1993; accepted February 9, 1994

Crystals of $Mn(II)Mn(III)_2O(SeO_3)_3$ were prepared under low-hydrothermal conditions. The structure was determined by direct and Fourier methods using single-crystal X-ray diffraction data up to $\sin\theta/\lambda = 0.6$ Å^{-1} [monoclinic, space group $C2/m$, $Z = 4$, $a = 15.454(4)$ Å, $b = 6.652(2)$ Å, $c = 9.682(2)$ Å, $\beta = 118.83(1)°$; $R_w = 0.023$ for 698 observed reflections]. The structure of $Mn(II)Mn(III)_2O(SeO_3)_3$ contains three crystallographically different types of MnO_6 octahedra forming $^1_\infty Mn(II)O_4$ chains parallel to [010] and $^2_\infty Mn(III)_2O_7$ net-shaped sheets parallel to (001), which are connected by three types of pyramidal SeO_3 groups as well as by a common oxygen corner. The $Mn(III)O_6$ octahedra exhibit pronounced Jahn–Teller elongations, whereas a similar distortion of the $Mn(II)O_6$ polyhedron is attributed to interpolyhedral connections. The oxo-oxygen is coordinated to three Mn(III) cations within the $Mn(III)_2O_7$ sheets with very short Mn–O bond lengths.

INTRODUCTION

In the course of synthesis experiments in the system MnO_2–SeO_2–H_2O–X_2O (X = Li, Na, K), aiming at the preparation of selenite compounds containing manganese in its tetravalent state, the following new phases have so far been obtained and investigated: the Mn(IV) compound $Mn(SeO_3)_2$ (1, 2), the buetschliite-type compound $K_2Mn(SeO_3)_2$ (3) containing divalent Mn, and the Mn(II)–Mn(III) mixed-valence compounds $KMn(II)_4Mn(III)(SeO_3)_6$ and $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ (4). The present paper reports the synthesis and crystal structure investigation of a further new Mn(II)–Mn(III) selenite obtained in these experiments, $Mn(II)Mn(III)_2O(SeO_3)_3$.

EXPERIMENTAL

Single crystals of $Mn(II)Mn(III)_2O(SeO_3)_3$, forming dark brown-red needles up to 0.04 mm in width and 0.4 mm in length, were prepared under hydrothermal conditions at 220(5)°C (5 days) in closed Teflon-lined steel vessels ($V \approx 40$ cm^3), which were filled with approximately equimolar amounts of MnO_2, SeO_2, and KOH, as well as with some drops of water (filling degree ≈10 vol%). Further products obtained were colorless crystals of a potassium selenite and obviously unreacted MnO_2 powder. Preliminary X-ray work was done by oscillation and Weissenberg photography. Crystals of $Mn(II)Mn(III)_2O(SeO_3)_3$ are elongated along [010], and the predominant forms are {100}, {10$\bar{1}$}, and {010}. The size of the crystal used for the structure investigation is 0.020 × 0.038 × 0.26 mm. Lattice constants (refined from 44 accurate 2θ values in the range $34° < 2\theta < 42°$) and X-ray intensities were measured on a Stoe four-circle diffractometer AED2 with graphite-monochromatized Mo$K\alpha$ radiation [2θ–ω scans; 45 steps/reflection (2 × 7 steps used for background correction), increased for α_1–α_2 splitting; 0.03° and 0.5–1.5 s/step; three standard reflections, each 120 min, intensity variation less than 2%]. Because of the small size of the crystal, only X-ray intensities up to $2\theta = 50°$ were measured. Corrections for Lorentz and polarization effects as well as an absorption correction by ψ scans were applied. Complex neutral atomic scattering functions were taken from the International Tables for X-Ray Crystallography (5). The structure was solved by direct methods and subsequent Fourier summations. All calculations were done with the program system STRUCSY (6). Crystal data and relevant details concerning the full-matrix least-squares refinement are summarized in Table 1, and the final atomic parameters are listed in Table 2.

DISCUSSION

Selected interatomic distances, bond angles, and octahedral distortion parameters Δ_{oct} $\{(1/6)\Sigma[(d_i - d_m)/d_m]^2\}$ and $\sigma^2_{oct}\{(1/11)\Sigma(a_i - 90)^2\}$ for $Mn(II)Mn(III)_2O(SeO_3)_3$ are listed in Table 3 and bond valence calculations according to (7) are summarized in Table 4. The crystal structure of $Mn(II)Mn(III)_2O(SeO_3)_3$ is illustrated in Figs. 1 and 2 in projections onto (010) and (001), respectively. There are three crystallographically different selenium atoms in $Mn(II)Mn(III)_2O(SeO_3)_3$, all occupying sites with point symmetry m. The Se atoms are coordinated to three oxygen atoms in a one-sided pyramidal configuration, a characteristic consequence of the activity of lone-pair electrons of the Se(IV) atoms. Individual and mean

0022-4596/94 $6.00

TABLE 1
Summary of Crystal Data and Details of the Structure Refinement of $Mn(II)Mn(III)_2O(SeO_3)_3$

Space group	$C2/m$
a(Å)	15.454(4)
b(Å)	6.652(2)
c(Å)	9.682(2)
β(°)	118.83(1)
V(Å^3)	871.9
Z	4
ρ_{calc} (g cm^{-3})	4.279
μ(Mo$K\alpha$) (cm^{-1})	163.62
Measured reflections	1628
Unique data set	840
Data with $F_o > 3\sigma(F_o)$	698
Variables	89
Absorption correction	ψ scans
Min/max transmission factors	0.12/0.18
Extinction coefficient g (14)	0.8(2) × 10^{-6}
R	0.030
R_w ($w = 1/[\sigma(F_o)]^2$)	0.023

Se–O bond lengths and O–Se–O angles are in accordance with the geometries found in many other selenite compounds or with average values cited in the literature (e.g., 8, 9). The different bond lengths within the $Se(1)O_3$ and $Se(2)O_3$ groups are obviously correlated with the further coordination of the oxygen atoms. O(1) and O(2), with shorter distances to the Se atoms, are further coordinated to only one Mn atom, namely O(1) to the divalent Mn(1) atom and O(2) to the trivalent Mn(3) atom (see below for discussion of the oxidation state of the manganese atoms). On the other hand, the oxygen atoms O(4) and O(5), which complete the coordination of Se(1) and Se(2), respectively, are further bound to two Mn atoms. In comparison, the $Se(3)O_3$ groups are nearly regularly shaped.

The manganese atoms in $Mn(II)Mn(III)_2O(SeO_3)_3$ occupy three crystallographically different positions with point symmetries $\bar{1}$ [Mn(1), Mn(3)] and m [Mn(2)]. The assignment of these positions to Mn(II) or Mn(III) ions is based on crystal chemical considerations. First, significantly different mean Mn–O distances are expected for $Mn(II)O_6$ and $Mn(III)O_6$ polyhedra: 2.205 Å (*10*) and 2.023 Å (11) are given in the literature as average Mn–O distances for divalent and trivalent manganese, respectively. Second, due to the d^4 electron configuration of Mn(III) atoms, $Mn(III)O_6$ polyhedra are subject to Jahn–Teller distortions of octahedral environments to (mostly elongated) dipyramids, whereas no Jahn–Teller distortions are predicted for the d^5 ion Mn(II). The mean Mn(1)–O distance of 2.192 Å undoubtedly reveals the divalent state of Mn(I). In accordance, the bond valence sum for Mn(1) is 2.12 vu (valence units). The rather strong [4 + 2] distortion of the $Mn(1)O_6$ octahedron (Δ_{oct} = 0.00282) resembles a Jahn–Teller distortion expected for Mn(III), but must be attributed to interpolyhedral connections (see below). Furthermore, rather strong distortions of $Mn(II)O_6$ octahedra are quite commonly reported in the literature (12). Mean Mn–O bond lengths of 2.045 and 2.027 Å as well as the type and extent of the polyhedral distortions clearly indicate the trivalent state of Mn(2) and Mn(3). The respective bond valence sums are 2.99 and 3.32 vu. The distortion of the $Mn(2)O_6$ octahedron, Δ_{oct} = 0.00503, is in the usual range for Mn(III) ions [compare (11)], whereas the elongation of the $Mn(3)O_6$ octahedron, Δ_{oct} = 0.00969, is unusually strong. Distortions of a similar magnitude are only rarely found for Mn(III) ions; examples among selenites are the

TABLE 2
Structure Parameters of $Mn(II)Mn(III)_2O(SeO_3)_3$ (e.s.d.'s in Parentheses)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	½	½	½	0.0182(8)	0.0142(8)	0.0184(8)	−0.0017(6)	0.0074(6)	−0.0020(6)
Mn(2)	0.61603(10)	0	0.08537(15)	0.0117(7)	0.0107(7)	0.0165(7)	0	0.0082(6)	0
Mn(3)	½	½	0	0.0167(8)	0.0091(7)	0.0160(7)	0.0019(6)	0.0076(6)	−0.0015(5)
Se(1)	0.52496(7)	0	0.33256(10)	0.0169(5)	0.0142(5)	0.0158(5)	0	0.0096(4)	0
Se(2)	0.86367(7)	0	0.32727(10)	0.0150(5)	0.0128(5)	0.0131(4)	0	0.0059(4)	0
Se(3)	0.89082(7)	0	0.82937(10)	0.0146(5)	0.0100(4)	0.0154(5)	0	0.0080(4)	0
O(1)	0.5984(3)	0.1989(7)	0.4092(5)	0.014(3)	0.019(3)	0.028(3)	−0.005(2)	0.006(2)	−0.008(2)
O(2)	0.8513(3)	0.1999(6)	0.2126(5)	0.022(3)	0.014(3)	0.022(3)	−0.002(2)	0.009(2)	0.006(2)
O(3)	0.8669(3)	0.1958(7)	0.9208(5)	0.019(3)	0.019(3)	0.019(2)	0.002(2)	0.010(2)	−0.005(2)
O(4)	0.5152(5)	0	0.1432(7)	0.023(4)	0.015(3)	0.022(4)	0	0.014(3)	0
O(5)	0.2488(5)	0	0.6715(7)	0.026(4)	0.010(3)	0.023(3)	0	0.019(3)	0
O(6)	0.7855(4)	0	0.6548(7)	0.015(4)	0.019(4)	0.014(3)	0	0.002(3)	0
O(7)	0.6939(4)	0	0.9882(6)	0.015(4)	0.010(3)	0.016(3)	0	0.011(3)	0

Note. The anisotropic displacement parameter is defined as $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$.

TABLE 3

Interatomic Distances (Å), Bond Angles (°), and Octahedral Distortion Parameters Δ_{oct} $\{=(1/6)\Sigma[(d_i - d_m)/d_m]^2\}$ and $\sigma^2_{oct}\{=(1/11)\Sigma(a_i - 90)^2\}$ in $Mn(II)Mn(III)_2O(SeO_3)_3$

Mn(1)	O(1)	O(1)	O(5)	O(5)	O(6)	O(6)
O(1)	2.095(4)		3.117(8)	3.188(7)	2.947(7)	3.022(8)
O(1)	180	2.095(4)	3.188(7)	3.117(8)	3.022(8)	2.947(7)
O(5)	88.7(2)	91.3(2)	2.356(5)		3.391(2)	2.940(9)
O(5)	91.3(2)	88.7(2)	180	2.356(5)	2.940(9)	3.391(2)
O(6)	88.6(2)	91.4(2)	98.2(2)	81.8(2)	2.126(4)	
O(6)	91.4(2)	88.6(2)	81.8(2)	98.2(2)	180	2.126(4)

⟨Mn(1)–O⟩ = 2.192; Δ_{oct} = 0.00282, σ^2_{oct} = 25.8

Mn(2)	O(3)	O(3)	O(4)	O(4)	O(5)	O(7)
O(3)	2.045(4)		2.981(7)	3.037(7)	3.001(7)	2.561(6)
O(3)	163.3(6)	2.045(4)	2.981(7)	3.037(7)	3.001(7)	2.561(6)
O(4)	98.3(2)	98.3(2)	1.893(7)	2.580(12)	3.196(10)	
O(4)	92.3(2)	92.3(2)	78.7(4)	2.163(6)		2.845(10)
O(5)	87.9(2)	87.9(2)	99.8(3)	178.5(9)	2.272(7)	2.971(9)
O(7)	82.0(2)	82.0(2)	168.6(8)	89.9(3)	91.6(3)	1.851(6)

⟨Mn(2)–O⟩ = 2.045; Δ_{oct} = 0.00503, σ^2_{oct} = 46.7

Mn(3)	O(2)	O(2)	O(3)	O(3)	O(7)	O(7)
O(2)	1.921(4)		2.950(7)	3.053(7)	2.635(6)	2.703(7)
O(2)	180	1.921(4)	3.053(7)	2.950(7)	2.703(7)	2.635(6)
O(3)	88.0(2)	92.0(2)	2.306(5)		2.561(6)	3.309(8)
O(3)	92.0(2)	88.0(2)	180	2.306(5)	3.309(8)	2.561(6)
O(7)	88.5(2)	91.5(2)	75.1(2)	104.9(2)	1.853(2)	
O(7)	91.5(2)	88.5(2)	104.9(2)	75.1(2)	180	1.853(2)

⟨Mn(3)–O⟩ = 2.027; Δ_{oct} = 0.00969, σ^2_{oct} = 82.9

Se(1)	O(1)	O(1)	O(4)
O(1)	1.667(4)	2.647(9)	2.617(8)
O(1)	105.1(3)	1.667(4)	2.617(8)
O(4)	99.3(2)	99.3(2)	1.766(6)

⟨Se(1)–O⟩ = 1.700, ⟨O–Se(1)–O⟩ = 101.2

Se(2)	O(2)	O(2)	O(5)
O(2)	1.683(4)	2.659(8)	2.663(8)
O(2)	104.4(3)	1.683(4)	2.663(8)
O(5)	102.0(2)	102.0(2)	1.744(7)

⟨Se(2)–O⟩ = 1.703, ⟨O–Se(2)–O⟩ = 102.8

Se(3)	O(3)	O(3)	O(6)
O(3)	1.712(4)	2.604(9)	2.605(7)
O(3)	99.0(3)	1.712(4)	2.605(7)
O(6)	100.0(2)	100.0(2)	1.689(6)

⟨Se(3)–O⟩ = 1.704, ⟨O–Se(3)–O⟩ = 99.7

$Mn(III)O_6$ polyhedron in $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ (4) with Δ_{oct} = 0.00920 or a $Mn(III)O_6$ polyhedron in $Mn_2(SeO_3)_3 \cdot 3H_2O$ (13) with Δ_{oct} = 0.00999.

The coordination polyhedra in $Mn(II)Mn(III)_2O(SeO_3)_3$ are linked to a three-dimensional framework (Fig. 1). Considering polyhedral edge connections, $^1_\infty Mn(1)O_4$ chains parallel to [010] and $^2_\infty Mn(2)Mn(3)O_7$ net-shaped sheets parallel to (001) (Fig. 2) can be distinguished. The common edges between the $Mn(II)O_6$ polyhedra in the $Mn(1)O_4$ chains are O(5)–O(6), 2.940 Å long. Common edges between $Mn(III)O_6$ polyhedra within the $Mn(2, 3)_2O_7$ sheets measure only 2.580 Å [O(4)–O(4) edge shared by two $Mn(2)O_6$ octahedra] and 2.561 Å [O(3)–O(7) common edges between $Mn(2)O_6$ and $Mn(3)O_6$ octahedra]. Linkage between chains and sheets is achieved by a shared corner, O(5), thus resulting in particularly elongated Mn(1)–O(5) and Mn(2)–O(5) distances, as well as by the selenite groups (Fig. 1). The $Se(1)O_3$ pyramid shares two O(1) corners with a $Mn(1)O_4$ chain and O(4) with two $Mn(2)O_6$ polyhedra in the sheet, while Se(3) has two O(3) corners in common with a sheet and O(6) in common with a chain. The $Se(2)O_3$ pyramids can be described as being located within the sheets (Fig. 2), but O(5) is in addition shared with the $Mn(1)O_4$ chain. The apparent free space remaining between parallel chains (Fig. 1) and within the net-shaped sheets (Fig. 2) is obviously claimed by the lone-pair electrons of the Se(IV) atoms.

The oxygen atoms in $Mn(II)Mn(III)_2O(SeO_3)_3$ are coordinated to two, three, or four cations (see Table 4). The angles around the two-coordinated O(1) and O(2) atoms are 134.4° [Se(1)–O(1)–Mn(1)] and 128.2° [Se(2)–O(2)–Mn(3)]. The oxygen atoms O(3), O(4), O(6), and O(7) are coordinated to three cations. The coordination figures of O(3) and O(4) are approximately or exactly planar, respectively, whereas O(6) and O(7) are coordinated in slightly pyramidal configurations (respective bond angle sums of 343.2° and 350.8°). O(7) is an oxo-oxygen, which is coordinated with very short bond lengths to three Mn(III) atoms, namely to one Mn(2) (1.851 Å) and two Mn(3) atoms (1.853 Å), thus contributing to the distortions of the corresponding manganese polyhedra. The four-coordinated O(5) atom occupies a distorted tetrahedron (mean bond angle, 109.1°) with comparatively long bond lengths to Se(2), Mn(2), and two Mn(1). Bond valence sums (Table 4) for the oxygens O(1) to O(6) range from 1.89 to 2.19 vu, whereas the bond valence sum for the oxo-oxygen O(7) is 2.34 vu. The latter indicates an overestimation of the bond strengths for the extremely short Mn(III)–O bond lengths.

ACKNOWLEDGMENT

The author thanks Prof. Dr. E. Tillmanns and Doz. Dr. H. Effenberger for discussions and helpful comments.

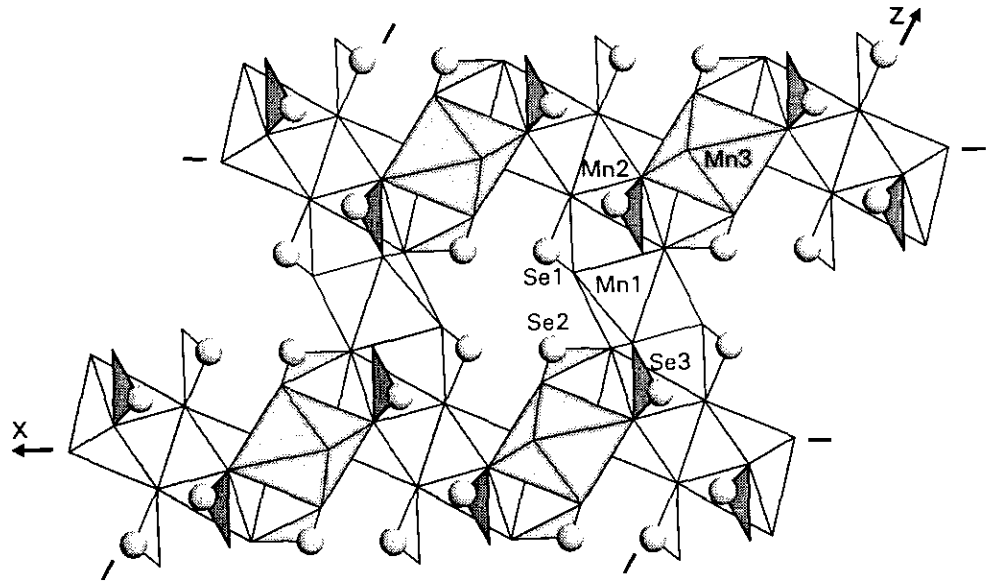

FIG. 1. Crystal structure of $Mn(II)Mn(III)_2O(SeO_3)_3$ in a projection along [010].

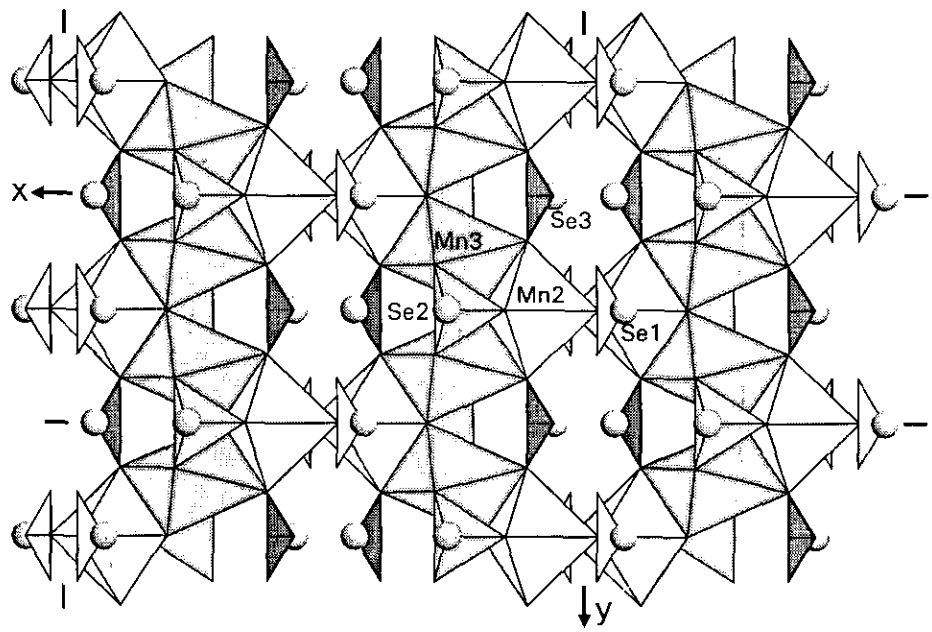

FIG. 2. Projection of the crystal structure of $Mn(II)Mn(III)_2O(SeO_3)_3$ onto (001), showing a $^2_\infty Mn(2)Mn(3)O_7$ net-shaped sheet with adjacent SeO_3 groups.

TABLE 4
Bond Valences ν (in Valence Units vu) in $Mn(II)Mn(III)_2O(SeO_3)_3$, Calculated According to (7)

	Mn(1)	*Mn(2)*	*Mn(3)*	*Se(1)*	*Se(2)*	*Se(3)*	Σ
O(1)	$0.44^{\downarrow\rightarrow}$			$1.48^{\downarrow\rightarrow}$			1.92
O(2)			$0.65^{\downarrow\rightarrow}$		$1.41^{\downarrow\rightarrow}$		2.06
O(3)		$0.46^{\downarrow\rightarrow}$	$0.23^{\downarrow\rightarrow}$			$1.31^{\downarrow\rightarrow}$	2.00
O(4)		$0.70^{\downarrow\rightarrow}$ $0.34^{\downarrow\rightarrow}$		$1.13^{\downarrow\rightarrow}$			2.17
O(5)	$0.22^{\downarrow\rightarrow}$	$0.25^{\downarrow\rightarrow}$			$1.20^{\downarrow\rightarrow}$		1.89
O(6)	$0.40^{\downarrow\rightarrow}$					$1.39^{\downarrow\rightarrow}$	2.19
O(7)		$0.78^{\downarrow\rightarrow}$	$0.78^{\downarrow\rightarrow}$				2.34
Σ	2.12	2.99	3.32	4.09	4.02	4.01	

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