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Hydrothermal Synthesis and Crystal Structure of $Mn(SeO_3)_2$

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Crystals of $Mn(SeO_3)_2$ were prepared by hydrothermal synthesis; the crystal structure was determined by direct and Fourier methods using single crystal X-ray data up to $\sin \theta/\lambda = 0.9$ Å^{-1} [monoclinic, space group $P2_1/n$ (C^5_{2h}, No. 14) $Z = 2$, $a = 5.061(1)$ Å, $b = 6.660(1)$ Å, $c = 7.255(1)$ Å, $\beta = 91.01(1)°$; $R = 0.021$ for 1458 reflections]. Isolated $Mn(IV)O_6$ octahedra (mean Mn–O: 1.891 Å) are connected via $Se(IV)O_3$ pyramids (mean Se–O: 1.716 Å) to a framework structure. © 1991 Academic Press, Inc.

Introduction

$Mn(SeO_3)_2$ has been described previously, for a survey on the properties including methods of preparation cf. (*1*) and literature cited therein. $Mn(SeO_3)_2$ seems to be the only compound known to contain Mn(IV) and Se(IV), whereas Mn(II) and Mn(III) form several compounds with selenium(IV) anions (*1–4*).

Crystal structures of hydrogen-free oxosalts of Mn(IV) are not known, the minerals jouravskite $Ca_3Mn(IV)(SO_4)(CO_3)(OH)_6 \cdot 12H_2O$ (*5*) and despujolsite $Ca_3Mn(IV)(SO_4)_2(OH)_6 \cdot 3H_2O$ (*6*) contain $Mn(IV)(OH)_6$ octahedra. Most information on the geometry of Mn(IV) polyhedra is based on structural work of Mn(IV) oxides and related compounds: the mean Mn(IV)–O bond length for octahedral coordination was found to be 1.90 Å (*7*). For comparison it seemed interesting to determine the crystal structure of the oxosalt $Mn(SeO_3)_2$.

Experimental

$Mn(SeO_3)_2$ was synthesized under hydrothermal conditions in Teflon-lined vessels of ≈50 cm^3 capacity: 0.5 g of $Mn(CH_3COO)_2 \cdot 4H_2O$ and 1 ml each of H_2O and H_2SeO_4 were heated to 500 K and kept at this temperature for 1 week. After cooling to room temperature, crystals of $Mn(IV)(SeO_3)_2$ had formed. The compounds used for synthesis contain Mn(II) and Se(VI), therefore an oxidation of Mn(II) → Mn(IV) directly combined with the reaction Se(VI) → Se(IV) is indicated. The crystals, obtained in sizes up to 3 mm, are elongated parallel to [100] with the predominant forms {011} and {110}. They are dark red colored without clear pleochroic behavior and show semimetallic luster.

A crystal 0.4 × 0.1 × 0.1 mm in size was used for X-ray investigations. Lattice parameters (derived by least-squares methods from 40 accurate 2θ values in the range $30° < 2\theta < 43°$) and X-ray intensities were measured at 295 K on a four-circle diffractometer. A summary of crystal data, details of X-ray data collection and the structure refinement is given in Table I. The intensities were corrected for Lorentz and polarization effects as well as for absorption ac-

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TABLE I

SUMMARY OF CRYSTAL DATA, X-RAY MEASUREMENTS AND STRUCTURE REFINEMENTS OF $Mn(SeO_3)_2$

Space group	$P2_1/n$ (C^5_{2h}, No. 14)
a (Å)	5.061(1)
b (Å)	6.660(1)
c (Å)	7.255(1)
β (°)	91.01(1)
V (Å^3)	244.49
Formula units per cell	2
Calculated density ρcalc (g cm^{-3})	4.196
Absorption coefficient μ(Mo$K\alpha$) (cm^{-1})	170.5

Stoe four circle diffractometer AED2; graphite monochromatized Mo$K\alpha$ radiation; program system STRUCSY [Stoe & Cie, Darmstadt, FRG (*8*)].

$2\theta - \omega$ scans; 40 steps/reflection, increased for α_1–α_2 splitting; step width 0.03°, 0.5–1.5 sec/step; 2*6 steps for background measurement; three standard reflections each 120 min, variation of $I \leq 1.6\%$; 2θ max = 80°

Extinction coefficient, g	$3.8(1) \cdot 10^{-5}$
Total measured reflections ($\pm h$ $\pm k$ $+l$)	3197
Unique data set	1510
Reflections with $F_0 > 3\sigma(F_0)$ (refinement)	1458
Number of variables	44
Reliability index R	0.021
R_w ($w = 1/[\sigma(F_0)]^2$)	0.024

cording to the shape of the crystal. The Gaussian integration gave transmission factors from 5.7 to 12.4%. The crystal structure of $Mn(SeO_3)_2$ was solved by direct methods and subsequent Fourier summations. Final structural parameters (Table II) were obtained by full-matrix least-squares techniques. Complex scattering curves for neutral atoms (*9*) were used and a secondary isotropic extinction correction (*10*) was applied.

Nonpolarized IR absorption spectra of

TABLE II

STRUCTURAL PARAMETERS OF $Mn(SeO_3)_2$, e.s.d.'s IN PARENTHESES

Atom	Mn	Se	O(1)	O(2)	O(3)
x/a	0.5	0.98458(3)	0.1961(2)	0.6997(2)	0.0528(2)
y/b	0.5	0.67723(2)	0.6635(2)	0.7243(2)	0.9212(2)
z/c	0.5	0.30435(2)	0.4935(2)	0.4198(2)	0.2479(1)
U_{11}	116(1)	134(1)	142(4)	137(4)	200(5)
U_{22}	121(1)	134(1)	172(4)	142(4)	157(4)
U_{33}	110(1)	125(1)	144(4)	205(4)	132(4)
U_{12}	1(1)	−1(0)	30(3)	0(3)	−40(3)
U_{13}	0(1)	1(0)	−15(3)	26(3)	−14(3)
U_{23}	−2(1)	8(0)	4(3)	21(3)	29(3)

Note. U_{ij} are given in pm^2. ATF = $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij} h_i h_j a^* ia^* j]$.

TABLE III

Interatomic Distances (Å), Bond Angles [°], and Bond Valences ν [v.u.] (*11*) in $Mn(SeO_3)_2$ with e.s.d.'s in Parentheses

			ν
Mn-O1	2×	1.884(1)	0.70
Mn-O2	2×	1.901(1)	0.67
Mn-O3	2×	1.888(1)	0.69
⟨Mn-O⟩		1.891	Σ 4.12
O1-Mn-O2	2×	88.63(5)	[2.644(2)]
O1-Mn-O2′	2×	91.37(5)	[2.708(2)]
O1-Mn-O3	2×	91.99(5)	[2.713(2)]
O1-Mn-O3′	2×	88.01(5)	[2.621(2)]
O2-Mn-O3	2×	89.65(5)	[2.671(2)]
O2-Mn-O3′	2×	90.35(5)	[2.687(2)]
			ν
Se-O1		1.728(1)	1.27
Se-O2		1.709(1)	1.34
Se-O3		1.712(1)	1.33
⟨Se-O⟩		1.716	Σ 3.94
O1-Se-O2		97.87(5)	[2.591(2)]
O1-Se-O3		96.62(5)	[2.569(1)]
O2-Se-O3		96.80(5)	[2.559(2)]
⟨O-Se-O⟩		97.10	[2.573]

Note. For the bond strength calculation of Se(IV) the improved data given by Hawthorne *et al.* (*12*) were used. Intrapolyhedral O-O distances are given in brackets.

crystal plates were measured between 4000 and 2000 cm^{-1} with an IR spectrophotometer Perkin-Elmer 580 B.

Discussion

Selected interatomic distances, bond angles, and bond strengths (*11*, *12*) are listed in Table III. Figures 1 and 2 illustrate the atomic arrangement of $Mn(SeO_3)_2$. The Mn atom (site symmetry $\bar{1}$) is coordinated to six oxygen atoms forming a nearly regular octahedron: the Mn-O bond lengths deviate 0.01 Å at most from the mean value 1.981 Å, the variations of the O-Mn-O angles from 90° do not exceed 2°. These MnO_6 octahedra are isolated from each other and share corners only with six selenite groups to build a framework structure (see Figs. 1 and 2). The Se atoms are one-sided pyramidal coordinated to three oxygen atoms. The average bond angle O-Se-O (97.1°) is significantly smaller than mean values given in literature [e.g. Hawthorne *et al.* (*12*): 100.2° or Fischer and Zemann (*13*): 101°], whereas the mean Se-O distance (1.716 Å) is slightly longer compared to the average value of 1.709 Å

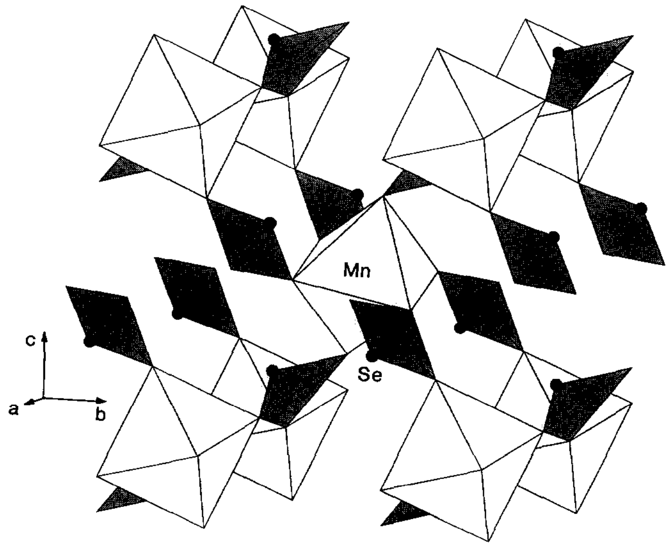

Fig. 1. A projection of the crystal structure of $Mn(SeO_3)_2$ seen in a direction slightly inclined to [100].

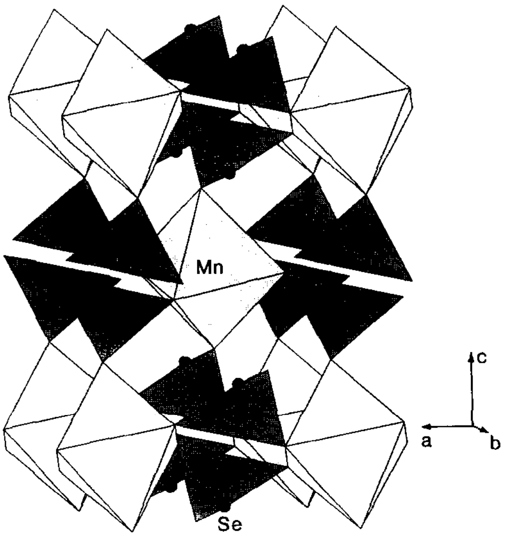

FIG. 2. A projection of the crystal structure of $Mn(SeO_3)_2$ seen in a direction slightly inclined to [010].

(*12*). The oxygen atoms O1, O2, and O3 are 2-coordinated to one Se(IV) and one Mn(IV) atom. The bond angles Mn–O–Se are 123.00°, 117.61°, and 117.75°.

As the coexistence of Mn(IV) and Se(IV) in a compound is unusual, special attention was paid to the valence states in $Mn(SeO_3)_2$. The one-sided pyramidal coordination around the Se atom is characteristic of the activity of lone-pair electrons and leaves no doubt about its tetravalent oxidation state. Deduced from the chemical formula, the Mn atom has to be tetravalent, too. This is confirmed by crystal chemical considerations. Divalent manganese in an octahedral environment would cause larger Mn–O distances. $Mn(III)O_6$ "octahedra" are known to be Jahn–Teller distorted with a mean Mn(III)–O bond length of 2.023 Å, or considering the extent of the distortion Δ [$\Delta = 1/6\Sigma((R_i - R)/R)^2$]: 1.994 Å + 7.08$\Delta$ Å (*14*). On the contrary, the regular geometry of the MnO_6 octahedron and the bond lengths in $Mn(SeO_3)_2$ are in good agreement with the data for $Mn(IV)O_6$ polyhedra given in literature (*7*). Furthermore, an at least partial substitution of Mn(IV) by Mn(II) or Mn(III) would necessitate a balance of charges, most likely realized by H atoms. However, bond valences are well balanced for all the oxygen atoms (ν = 1.97, 2.01 and 2.02 v.u., respectively) and a final difference Fourier map did not show any suitable peaks. In order to exclude the presence of even minor OH amouns, IR spectroscopic investigations were performed. In the measured sensitive region between 4000 and 2000 cm^{-1} the spectra showed low extinction and no absorption bands, confirming the absence of OH and H_2O contents in the crystal structure.

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