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Synthesis and Crystal Structures of the New Alkaline–Mn(II)–Mn(III) Selenites $KMn(II)_4Mn(III)(SeO_3)_6$ and $Li_5Mn(II)_4Mn(III)(SeO_3)_8$

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Crystals of $KMn(II)_4Mn(III)(SeO_3)_6$ and $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ were synthesized under hydrothermal conditions and their structures were determined by single-crystal X-ray diffraction data ($KMn(II)_4Mn(III)(SeO_3)_6$: monoclinic, space group $C2/c$, $Z = 4$, $a = 17.660(3)$ Å, $b = 10.240(1)$ Å, $c = 9.582(1)$ Å, $\beta = 91.32(1)°$, $R_w = 0.038$ for 2557 reflections up to $2\Theta = 65°$; $Li_5Mn(II)_4Mn(III)(SeO_3)_8$: triclinic, space group $P\bar{1}$, $Z = 1$, $a = 7.505(2)$ Å, $b = 8.350(2)$ Å, $c = 10.413(2)$ Å, $\alpha = 73.84(1)°$, $\beta = 88.24(1)°$, $\gamma = 64.24(1)°$, $R_w = 0.028$ for 4318 reflections up to $2\Theta = 70°$). In $KMn(II)_4Mn(III)(SeO_3)_6$, the coordination octahedra of the Mn(II), Mn(III), and K atoms form pseudotrigonal layers which are connected by pyramidal SeO_3 groups. The structure of $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ is composed of SeO_3 pyramids, $Mn(II)O_6$ and $Mn(III)O_6$ octahedra, LiO_4 tetrahedra, and a trigonal prismatic coordination polyhedron in which the central position is occupied statistically by Mn(II) and Li atoms in the proportion 1 : 1. In both compounds, the coordination octahedra of Mn(III) atoms exhibit pronounced Jahn–Teller distortions.

Introduction

Recently, the Mn(IV) compound $Mn(SeO_3)_2$ was obtained by hydrothermal synthesis and the crystal structure was determined by means of single-crystal X-ray diffraction methods (*1*). As the knowledge on the crystal chemistry of tetravalent manganese is poor, further syntheses were undertaken in the system MnO_2–SeO_2–H_2O–X_2O (X = Li, Na, K), but so far no other Mn(IV) selenites have been obtained. In the course of these experiments, single crystals of $K_2Mn(SeO_3)_2$ (*2*) $Mn(Se_2O_5)$ (*3*) (containing divalent Mn), and three unknown Mn(II)–Mn(III) compounds $Mn(II)Mn(III)_2O(SeO_3)_3$ (*4*), $KMn(II)_4Mn(III)(SeO_3)_6$, and $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ (this work) were synthesized.

Experimental

Crystals of the title compounds were synthesized under the following conditions: Teflon-lined steel vessels ($V \approx 40$ cm^3) were filled with approximately equimolar amounts of MnO_2, SeO_2, and KOH or MnO_2, SeO_2, and $LiOH \cdot H_2O$. In both cases, some drops of water were added. The closed vessels were heated to ≈ 495 K and kept at this temperature for 4 days. Crystals of $KMn(II)_4Mn(III)(SeO_3)_6$ were obtained up to a diameter of 1 mm; the dark brown crystals are pseudohexagonal prismatic with (monoclinic) forms {100}, {1$\bar{1}$0}, and {001}. $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ was obtained in brown triclinic crystals up to diameters of 0.6 mm with predominant forms {100}, {010}, {10$\bar{1}$}, {01$\bar{1}$}, and {$\bar{1}$12}, sometimes also {110} and {011}.

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Preliminary X-ray investigations were done by oscillation and Weissenberg photography. Unit-cell dimensions (refined from 36/38 accurate 2Θ values in the range $38° < 2\Theta < 42°$) and X-ray intensities were measured on a Stoe AED2 four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation (2Θ–ω scans with 32/40 steps/reflection, increased for α_1–α_2 splitting; 0.03° and 0.5–1.5s/step; 2 × 5/6 steps each side for background measurement; 3 standard reflections each 120 min). The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction by ψ-scans was applied. Complex scattering curves for neutral atoms were taken from (*5*). Crystal data and additional information about the refinements are given in Table I. The structures olved by direct methods and subsequent Fourier summations; final structural parameters, listed in Tables II and III, were obtained by full-matrix least-squares refinements. All calculations were done with the program system STRUCSY (*6*).

In the course of the structure solution of $Li_5Mn(II)_4Mn(III)(SeO_3)_8$, Fourier syntheses revealed that one of the coordination polyhedra, namely the trigonal prism, is not fully occupied by Mn(II), as was assumed in the first steps of structure solution. Applying the scattering curves of Mn, the refinement converged with an occupancy factor of ≈ 55% for this site. In this case—assuming a divalent state of the Mn atom—nearly one positive charge is missing in the formula unit. This charge could be equalized by filling half of the site with Mn(II) atoms, the other half with Li atoms. In order to verify this assumption, the Li content of the compound was determined by means of AAS; the analysis yielded a

TABLE I

SUMMARY OF CRYSTAL DATA AND STRUCTURE REFINEMENTS OF $KMn(II)_4Mn(III)(SeO_3)_6$ AND $Li_5Mn(II)_4Mn(III)(SeO_3)_8$

	$KMn(II)_4Mn(III)(SeO_3)_6$	$Li_5Mn(II)_4Mn(III)(SeO_3)_8$
Space group	$C2/c$	$P\bar{1}$
a [Å]	17.660(3)	7.505(2)
b [Å]	10.240(1)	8.350(2)
c [Å]	9.582(1)	10.413(2)
α [°]		73.84(1)
β [°]	91.32(1)	88.24(1)
γ [°]		64.24(1)
V [Å^3]	1732.4	561.4
ρ_{calc} [g cm^{-3}]	4.124	3.919
μ(Mo$K\alpha$) [cm^{-1}]	160.17	153.70
Crystal dimensions [mm]	0.11 × 0.13 × 0.16	0.08 × 0.21 × 0.26
Extinction coefficient g (*17*)	1.2(1) × 10^{-6}	4.9(2) × 10^{-6}
$2\Theta_{max}$ [°]	65	70
Measured reflections	6619	9940
Unique data set	3162	4970
Data with $F_o > 3\sigma(F_o)$	2557	4318
Variables	138	194
Absorption correction	ψ scans	ψ scans
Min/max transmission factors	0.048/0.128	0.015/0.085
R	0.043	0.031
R_w ($w = 1/[\sigma(F_o)]^2$)	0.038	0.028

TABLE II

STRUCTURE PARAMETERS OF $KMn(II)_4Mn(III)(SeO_3)_6$, 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}
K	0	.00113(20)	¾	.0263(11)	.0278(9)	.0524(14)	0	−.0006(9)	0
Mn(1)	.66917(5)	.00026(7)	.16195(8)	.0169(4)	.0166(3)	.0179(4)	.0000(3)	−.0031(3)	−.0001(3)
Mn(2)	.31459(5)	.68748(7)	.25137(9)	.0177(4)	.0172(3)	.0139(4)	−.0006(3)	−.0017(3)	−.0003(2)
Mn(3)	0	.38456(10)	¾	.0154(5)	.0176(5)	.0127(5)	0	−.0022(4)	0
Se(1)	.19213(3)	.11541(5)	.58464(5)	.0167(2)	.0163(2)	.0136(2)	.0013(2)	−.0022(2)	−.0003(2)
Se(2)	.03519(3)	.64949(5)	.91515(5)	.0161(2)	.0170(2)	.0128(2)	.0008(2)	−.0023(2)	−.0004(2)
Se(3)	.34961(3)	.26337(5)	.09084(5)	.0170(3)	.0156(2)	.0142(2)	.0000(2)	−.0005(2)	−.0007(2)
O(1)	.2283(2)	.6220(3)	.8129(4)	.0171(19)	.0191(17)	.0219(19)	.0017(14)	−.0085(15)	−.0006(13)
O(2)	.1470(2)	.0199(4)	.1375(4)	.0176(20)	.0193(17)	.0272(22)	.0021(14)	.0023(15)	−.0032(14)
O(3)	.7710(2)	.9257(4)	.5723(4)	.0228(21)	.0237(18)	.0166(19)	.0065(15)	.0040(15)	.0001(13)
O(4)	.9294(2)	.4766(4)	.1859(4)	.0182(20)	.0203(17)	.0202(19)	−.0013(14)	.0011(14)	−.0044(13)
O(5)	.9236(2)	.6098(3)	.4290(4)	.0195(20)	.0238(17)	.0145(17)	−.0041(15)	−.0030(14)	−.0020(13)
O(6)	.0826(2)	.2207(3)	.3570(4)	.0244(21)	.0187(17)	.0200(19)	−.0024(15)	−.0003(15)	−.0037(13)
O(7)	.3027(2)	.1543(3)	.1881(4)	.0236(22)	.0207(17)	.0178(18)	.0038(15)	.0045(15)	.0061(13)
O(8)	.3492(3)	.8105(4)	.4326(4)	.0294(23)	.0186(16)	.0153(18)	−.0017(15)	−.0059(16)	.0039(13)
O(9)	.9414(2)	.2483(4)	.6527(4)	.0202(21)	.0239(18)	.0208(19)	.0051(15)	−.0022(15)	.0009(14)

Note. ATF = $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$.

TABLE III

STRUCTURE PARAMETERS OF $Li_5Mn(II)_4Mn(III)(SeO_3)_8$, 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}
Li(1)	.6500(9)	.4550(7)	.4176(6)	.0262(29)	.0195(21)	.0323(28)	−.0062(21)	.0042(24)	−.0077(19)
Li(2)	.2524(10)	.5452(8)	.0749(7)	.0274(31)	.0317(27)	.0400(33)	−.0145(24)	−.0148(26)	.0086(23)
Mn/Li*	.93890(13)	.38093(10)	.66313(8)	.0226(4)	.0199(3)	.0235(4)	−.0108(8)	.0058(3)	−.0076(3)
Mn(1)	0	0	½	.0217(3)	.0202(2)	.0193(2)	−.0110(2)	.0015(2)	−.0041(2)
Mn(2)	.06175(7)	.28590(6)	.22048(5)	.0224(2)	.0233(2)	.0217(2)	−.0122(2)	.0020(2)	−.0046(1)
Mn(3)	0	0	0	.0154(3)	.0179(2)	.0164(2)	−.0064(2)	−.0005(2)	−.0030(2)
Se(1)	.32565(4)	.74246(4)	.79563(3)	.0172(1)	.0210(1)	.0192(1)	−.0094(1)	.0028(1)	−.0063(1)
Se(2)	.68205(4)	.17832(4)	.73701(3)	.0146(1)	.0203(1)	.0170(1)	−.0071(1)	.0019(1)	−.0038(1)
Se(3)	.26557(4)	.24281(4)	.93144(3)	.0180(1)	.0207(1)	.0195(1)	−.0087(1)	.0052(1)	−.0055(1)
Se(4)	.29040(5)	.21217(4)	.52333(3)	.0173(1)	.0219(1)	.0224(1)	−.0077(1)	.0008(1)	−.0054(1)
O(1)	.8559(3)	.2450(3)	.0952(2)	.0170(10)	.0241(9)	.0186(8)	−.0084(8)	.0056(8)	−.0071(7)
O(2)	.1947(3)	.7409(3)	.6629(2)	.0218(11)	.0232(9)	.0196(8)	−.0081(8)	.0010(8)	−.0071(7)
O(3)	.5145(3)	.4809(3)	.1501(2)	.0207(11)	.0253(9)	.0330(12)	−.0063(8)	−.0002(9)	−.0097(8)
O(4)	.7983(3)	.0075(3)	.6636(2)	.0232(11)	.0210(8)	.0228(9)	−.0088(8)	.0029(8)	−.0059(7)
O(5)	.8774(3)	.1749(3)	.8252(2)	.0201(10)	.0251(9)	.0188(8)	−.0108(8)	−.0013(8)	−.0041(7)
O(6)	.3543(3)	.6321(3)	.3896(2)	.0235(11)	.0214(9)	.0188(8)	−.0070(8)	.0006(8)	−.0011(7)
O(7)	.0410(3)	.4094(3)	.8518(2)	.0246(11)	.0200(8)	.0217(9)	−.0082(8)	.0023(8)	−.0052(7)
O(8)	.2692(3)	.2880(3)	.0783(2)	.0258(11)	.0294(10)	.0212(9)	−.0145(9)	.0035(9)	−.0096(8)
O(9)	.7716(3)	.9541(3)	.0219(2)	.0165(10)	.0201(8)	.0299(10)	−.0075(8)	.0000(8)	−.0038(7)
O(10)	.9003(4)	.8404(3)	.4273(2)	.0292(12)	.0299(10)	.0309(11)	−.0194(9)	.0105(9)	−.0141(8)
O(11)	.2194(4)	.3358(3)	.3599(2)	.0345(13)	.0299(10)	.0193(9)	−.0185(10)	.0013(9)	−.0058(8)
O(12)	.7723(4)	.6171(4)	.4044(3)	.0449(16)	.0510(14)	.0400(14)	−.0345(13)	.0195(12)	−.0302(12)

Note. *Occupancy: ½Mn + ½Li. ATF = $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$.

content of 2.74(15)% Li. The theoretical value for this model (5 Li atoms in the formula unit) is 2.62% Li; for a model with an occupation of solely ½Mn (which then has to be trivalent), it is 2.11% Li (4 Li atoms in the formula unit). Refining Mn and Li together on this site led to occupancy factors of 0.517(2) for Mn and 0.483(2) for Li. A symmetry reduction to $P1$ indicated no cation ordering of Mn and Li on the two related sites, and rotation and Weissenberg photographs showed no indications of superlattice reflections. Therefore, the final refinement was done in $P\bar{1}$ and the occupancies of Mn and Li were fixed at the ideal value of 0.5. Crystal-chemical considerations concerning this problem as well as the Mn(II)–Mn(III) cation distribution are stated in detail in the discussion.

Discussion

$KMn(II)_4Mn(III)(SeO_3)_6$

Important interatomic distances, angles, and distortion parameters Δ_{oct} {= (1/6) $\Sigma[(d_i - d_m)/d_m]^2$} and σ^2_{oct} {= (1/11)$\Sigma(a_i - 90)^2$} (for octahedral environments) in $KMn(II)_4Mn(III)(SeO_3)_6$ are listed in Table IV. The coordination polyhedra are clear-cut in this compound. The Se atoms are one-sided pyramidally coordinated to three oxygen atoms. Individual and mean Se–O bond lengths coincide with data given in the literature (*7*), whereas all three crystallographically different SeO_3 pyramids are slightly flattened (mean angles 103.4°, 102.5°, and 103.6°) compared to the reported average O–Se–O angles of 100.2° (*7*) or 101° (*8*).

All other cations are coordinated by oxygen atoms in more or less distorted octahedral configurations. Mean bond lengths within the $Mn(1)O_6$ and $Mn(2)O_6$ polyhedra are comparable with average Mn–O distances known for divalent Mn atoms: e.g., Baur (*9*) gives 2.205 Å as mean Mn(II)–O distance, and nearly the same value (2.20 Å) is given in (*10*). Bond valences of 2.07 vu (valence units) and 2.13 vu, respectively, were obtained from bond-valence calculations according to (*11*); thus Mn(1) and Mn(2) are Mn(II) atoms. The distortion of these polyhedra is moderate and irregular. On the contrary, the $Mn(3)O_6$ octahedron (point symmetry 2) exhibits a pronounced distortion. There are four meridional oxygens at ≈1.970 Å and two apical oxygen atoms at 2.208 Å, forming an elongated tetragonal dipyramid. This distortion of the coordination octahedron is typical for the $3d^4$ electronic configuration of Mn(III) atoms (Jahn–Teller effect). The bond valence of 2.86 vu and the mean Mn(3)–O distance of 2.049 Å also indicate the trivalent state of the Mn(3) atoms: Shannon *et al.* (*12*) derived 2.023 Å or—considering the extent of the distortion—1.994 Å + 7.08Δ as mean Mn(III)–O distance.

The K atom (point symmetry 2) is surrounded by six O atoms forming an octahedron, which is strongly flattened parallel (001). The mean K–O distance of 2.866 Å is rather long considering an effective ionic radius of 1.38 Å for K^+ in sixfold coordination (*13*); individual K–O distances hardly deviate from the mean value.

The interpolyhedral connections in $KMn(II)_4Mn(III)(SeO_3)_6$ result in the formation of pseudo-trigonal $(KMn(II)_4Mn(III)O_{18})^{24-}$-sheets parallel (001) (Fig. 1). Each KO_6 polyhedron shares three short edges with MnO_6 octahedra; the shortest one, O(9)–O(9) = 2.753(8) Å, is in common with Mn(3), and two edges O(2)–O(6) = 3.171(5) Å are shared with $Mn(2)O_6$ polyhedra. This configuration causes strong flattening of the KO_6 polyhedron parallel (001) and explains the anisotropic thermal motion of the K atom with r.m.s. amplitudes of 0.23 Å perpendicular to (001) and 0.16 Å within the sheet. $Mn(2)O_6$ and $Mn(3)O_6$ each share two short edges with $Mn(1)O_6$ (Mn(2): O(1)–O(8) = 2.781(6) Å, O(3)–O(7) = 2.788(6) Å; Mn(3): 2 × O(4)–O(5) = 2.703(5) Å), which complete a $(KMn(II)_4Mn(III)O_{18})^{24-}$ sheet.

TABLE IV

INTERATOMIC DISTANCES [Å], BOND ANGLES [°], AND DISTORTION PARAMETERS Δ_{oct} AND σ^2_{oct} (FOR OCTAHEDRAL ENVIRONMENTS) IN $KMn(II)_4Mn(III)(SeO_3)_6$

K	O(2)	O(2)	O(6)	O(6)	O(9)	O(9)
O(2)	2.842(3)		3.171(5)	4.548(6)	3.765(6)	4.558(6)
O(2)	171.3(9)	2.842(3)	4.548(6)	3.171(5)	4.558(6)	3.765(6)
O(6)	67.4(1)	105.4(1)	2.876(4)	3.527(8)	4.822(5)	
O(6)	105.4(1)	67.4(1)	75.7(2)	2.876(4)		4.822(5)
O(9)	82.3(1)	105.6(1)	113.8(1)	169.9(4)	2.881(4)	2.753(8)
O(9)	105.6(1)	82.3(1)	169.9(4)	113.8(1)	57.1(2)	2.881(4)

$\langle K–O \rangle$ = 2.866; Δ_{oct} = 0.00004, σ^2_{oct} = 411.0

Mn(1)	O(1)	O(3)	O(4)	O(5)	O(7)	O(8)
O(1)	2.163(3)	3.163(6)	2.962(6)		2.881(5)	2.781(6)
O(3)	94.4(2)	2.149(4)		3.455(6)	2.788(6)	3.435(6)
O(4)	82.9(2)	160.0(4)	2.308(4)	2.703(5)	2.884(6)	3.262(5)
O(5)	157.4(4)	106.9(2)	74.5(2)	2.153(3)	3.141(6)	3.335(5)
O(7)	83.1(2)	80.1(2)	79.8(2)	92.8(2)	2.183(3)	
O(8)	80.0(2)	105.5(2)	93.6(2)	101.1(2)	162.4(5)	2.165(3)

$\langle Mn(1)–O \rangle$ = 2.187; Δ_{oct} = 0.00064, σ^2_{oct} = 120.9

Mn(2)	O(1)	O(2)	O(3)	O(6)	O(7)	O(8)
O(1)	2.177(3)		3.299(5)	3.073(6)	2.912(5)	2.781(6)
O(2)	166.3(5)	2.122(3)	3.155(6)	3.171(5)	3.102(6)	3.051(5)
O(3)	98.0(2)	93.9(2)	2.196(4)	3.051(6)	2.788(6)	
O(6)	90.8(2)	96.2(2)	89.5(2)	2.139(4)		3.186(6)
O(7)	83.6(2)	92.0(2)	78.9(2)	166.3(5)	2.191(4)	3.309(6)
O(8)	78.5(2)	89.3(2)	175.1(7)	93.9(2)	97.2(2)	2.220(3)

$\langle Mn(2)–O \rangle$ = 2.174; Δ_{oct} = 0.00024, σ^2_{oct} = 44.2

Mn(3)	O(4)	O(4)	O(5)	O(5)	O(9)	O(9)
O(4)	1.980(3)	2.755(8)	2.703(5)	3.155(6)		2.844(5)
O(4)	88.2(2)	1.980(3)	3.155(6)	2.703(5)	2.844(5)	
O(5)	80.2(2)	97.6(2)	2.208(3)		2.914(6)	3.043(5)
O(5)	97.6(2)	80.2(2)	177.0(8)	2.208(3)	3.043(5)	2.914(6)
O(9)	168.7(7)	92.4(2)	88.5(2)	93.6(2)	1.960(4)	2.753(8)
O(9)	92.4(2)	168.7(7)	93.6(2)	88.5(2)	89.2(2)	1.960(4)

$\langle Mn(3)–O \rangle$ = 2.049; Δ_{oct} = 0.00301, σ^2_{oct} = 32.1

Se(1)	O(1)	O(2)	O(3)
O(1)	1.697(4)	2.671(5)	2.626(6)
O(2)	104.5(2)	1.683(3)	2.684(6)
O(3)	101.1(2)	104.8(2)	1.705(4)

$\langle Se(1)–O \rangle$ = 1.695, $\langle O–Se(1)–O \rangle$ = 103.4

Se(2)	O(4)	O(5)	O(6)
O(4)	1.739(3)	2.616(5)	2.660(5)
O(5)	99.2(2)	1.696(3)	2.691(5)
O(6)	102.4(2)	106.0(2)	1.674(3)

$\langle Se(2)–O \rangle$ = 1.703, $\langle O–Se(2)–O \rangle$ = 102.5

Se(3)	O(7)	O(8)	O(9)
O(7)	1.685(3)	2.625(6)	2.674(6)
O(8)	101.9(2)	1.694(3)	2.711(6)
O(9)	103.6(2)	105.2(2)	1.718(4)

$\langle Se(3)–O \rangle$ = 1.699, $\langle O–Se(3)–O \rangle$ = 103.6

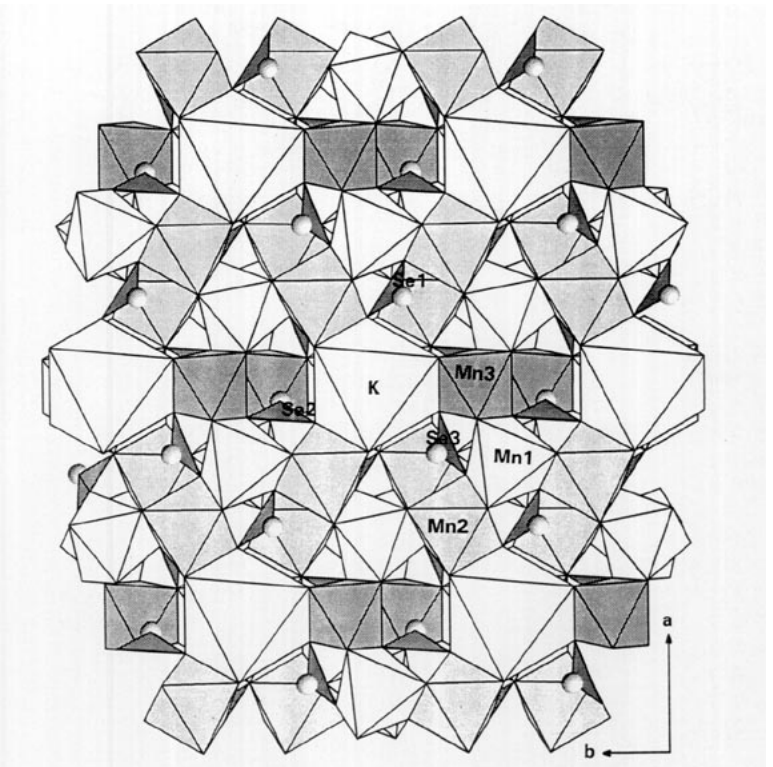

FIG. 1. The crystal structure of $KMn(II)_4Mn(III)(SeO_3)_6$ projected along [001].

The sheets are linked by interlayed SeO_3 pyramids (Fig. 2), sharing each of their corners with two cation octahedra. The planes defined by the oxygen ligands of the three different selenite groups are nearly parallel [001]. All oxygen atoms are coordinated by three cations in nearly planar arrangements, and their bond-valence sums are between 1.97 and 2.09 vu.

$Li_5Mn(II)_4Mn(III)(SeO_3)_8$

Selected interatomic distances, bond angles, and distortion parameters Δ_{oct}, σ^2_{oct} (for octahedra), Δ_{pris} (for the trigonal

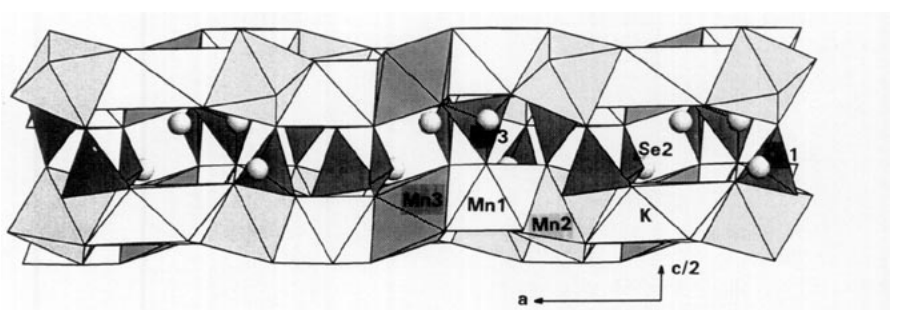

FIG. 2. Projection of the structure of $KMn(II)_4Mn(III)(SeO_3)_6$ along [010].

TABLE V

INTERATOMIC DISTANCES [Å] BOND ANGLES [°] AND DISTORTION PARAMETERS Δ_{oct}, σ^2_{oct} (FOR OCTAHEDRAL ENVIRONMENTS), Δ_{pris} (FOR THE TRIGONAL PRISM), BLD, AND ELD (FOR TETRAHEDRAL ENVIRONMENTS) IN $Li_5Mn(II)_4Mn(III)(SeO_3)_8$

Li(1)	O(2)	O(6)	O(6)	O(12)
O(2)	1.945(6)	3.624(3)	3.263(3)	3.163(4)
O(6)	131.1(2)	2.036(6)	2.869(5)	3.092(4)
O(6)	114.2(2)	92.3(4)	1.941(6)	2.991(4)
O(12)	110.1(3)	103.0(2)	101.8(3)	1.914(6)

⟨Li(1)–O⟩ = 1.959, ⟨O–Li(1)–O⟩ = 108.7; BLD = 1.97, ELD = 5.82

Li(2)	O(1)	O(3)	O(7)	O(8)
O(1)	1.998(7)	3.338(3)	3.122(3)	3.515(3)
O(3)	116.5(3)	1.928(7)	3.859(4)	3.142(4)
O(7)	95.5(3)	137.3(3)	2.215(7)	2.853(3)
O(8)	118.8(3)	103.0(3)	83.1(3)	2.086(7)

⟨Li(2)–O⟩ = 2.057, ⟨O–Li(2)–O⟩ = 109.0; BLD = 4.56, ELD = 8.04

Mn/Li	O(5)	O(6)	O(7)	O(10)	O(11)	O(12)
O(5)	2.246(2)	2.534(3)[a]	2.797(3)[b]	3.073(3)[a]		
O(6)	67.1(1)	2.339(2)		3.152(4)[a]	3.142(4)[b]	
O(7)	77.2(1)	129.0(1)	2.239(2)		2.692(3)[a]	2.993(4)[a]
O(10)	88.1(1)	88.6(1)	126.3(1)	2.172(2)		2.505(4)[b]
O(11)	120.1(1)	90.4(1)	77.0(1)	148.6(2)	2.079(2)	3.264(4)[a]
O(12)	131.6(1)	147.7(2)	83.3(1)	68.7(1)	97.3(1)	2.263(3)

⟨Mn/Li–O⟩ = 2.223; Δ_{pris} = 0.00132

Mn(1)	O(2)	O(2)	O(4)	O(4)	O(10)	O(10)
O(2)	2.249(2)		2.839(3)	3.477(3)	3.032(3)	3.108(3)
O(2)	180	2.249(2)	3.477(3)	2.839(3)	3.108(3)	3.032(3)
O(4)	78.5(1)	101.5(1)	2.240(2)		3.075(3)	3.053(4)
O(4)	101.5(1)	78.5(1)	180	2.240(2)	3.053(4)	3.075(3)
O(10)	88.6(1)	91.4(1)	90.4(1)	89.6(1)	2.091(2)	
O(10)	91.4(1)	88.6(1)	89.6(1)	90.4(1)	180	2.091(2)

⟨Mn(1)–O⟩ = 2.193; Δ_{oct} = 0.00109, σ^2_{oct} = 48.9

Mn(2)	O(1)	O(2)	O(4)	O(7)	O(8)	O(11)
O(1)	2.245(2)	2.563(3)	3.192(3)	3.477(3)	3.269(3)	
O(2)	68.6(1)	2.304(2)	2.839(3)	3.531(3)		3.462(4)
O(4)	92.3(1)	78.5(1)	2.181(1)		3.298(3)	3.003(3)
O(7)	102.5(1)	102.8(1)	164.6(2)	2.214(2)	2.853(3)	2.692(3)
O(8)	97.0(1)	165.4(3)	100.2(1)	82.4(1)	2.117(2)	3.057(3)
O(11)	170.7(4)	102.5(1)	88.2(1)	76.5(1)	92.0(1)	2.133(2)

⟨Mn(2)–O⟩ = 2.199; Δ_{oct} = 0.00085, σ^2_{oct} = 134.1

Mn(3)	O(1)	O(1)	O(5)	O(5)	O(9)	O(9)
O(1)	2.340(2)		3.013(3)	3.061(3)	3.046(3)	2.991(3)
O(1)	180	2.340(2)	3.061(3)	3.013(3)	2.991(3)	3.046(3)
O(5)	89.1(1)	90.9(1)	1.936(2)		2.702(3)	2.734(3)
O(5)	90.9(1)	89.1(1)	180	1.936(2)	2.734(3)	2.702(3)
O(9)	91.1(1)	88.9(1)	89.3(1)	90.7(1)	1.907(2)	
O(9)	88.9(1)	91.1(1)	90.7(1)	89.3(1)	180	1.907(2)

⟨Mn(3)–O⟩ = 2.061; Δ_{oct} = 0.00920, σ^2_{oct} = 0.9

TABLE V—*Continued*

Se(1)	O(1)	O(2)	O(3)
O(1)	1.734(2)	2.563(3)	2.631(3)
O(2)	95.6(1)	1.726(2)	2.593(3)
O(3)	101.7(1)	100.0(1)	1.657(2)
⟨Se(1)–O⟩ = 1.706, ⟨O–Se(1)–O⟩ = 99.1			
Se(2)	O(4)	O(5)	O(6)
O(4)	1.692(2)	2.688(3)	2.605(3)
O(5)	103.1(1)	1.739(2)	2.534(3)
O(6)	101.4(1)	95.8(1)	1.674(2)
⟨Se(2)–O⟩ = 1.702, ⟨O–Se(2)–O⟩ = 100.1			
Se(3)	O(7)	O(8)	O(9)
O(7)	1.694(2)	2.634(3)	2.665(3)
O(8)	102.7(1)	1.678(2)	2.646(3)
O(9)	102.6(1)	102.2(1)	1.721(2)
⟨Se(3)–O⟩ = 1.698, ⟨O–Se(3)–O⟩ = 102.5			
Se(4)	O(10)	O(11)	O(12)
O(10)	1.697(2)	2.663(4)	2.505(4)
O(11)	103.8(1)	1.687(2)	2.598(4)
O(12)	95.9(1)	101.1(1)	1.677(3)
⟨Se(4)–O⟩ = 1.687, ⟨O–Se(4)–O⟩ = 100.3			

[a] Edge within a triangle of the trigonal prism.
[b] Edge between triangles.

prism, defined as for Δ_{oct}), BLD {$= (100/4)\Sigma(|d_i - d_m|/d_m)$} and ELD {$= (100/4)\Sigma(|e_i - e_m|/e_m)$} (for tetrahedral environments) in $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ are given in Table V. The shapes of the SeO_3 groups in this compound comply also with crystal chemical experience, except that the mean Se(4)–O distance is rather short considering the literature data (*7*).

The Mn(1) atoms (point symmetry $\bar{1}$) are [2 + 4]-coordinated: four coplanar O atoms have 2.245 Å as mean Mn(1)–O distance, and two oxygens with Mn(1)–O = 2.091 Å complete the compressed octahedron. Although this kind of distortion might theoretically be caused by the electron configuration of Mn(III) ions (in most cases, an elongation of the $Mn(III)O_6$ octahedra is observed), the average Mn(1)–O bond length of 2.193 Å [compare (*9, 10*)] and a calculated bond valence (*11*) of 2.06 vu show the divalent state of Mn(1). The same considerations concerning the valence state can be applied to Mn(2) with a mean Mn(2)–O distance of 2.199 Å and 2.02 vu. The calculated bond valence of 3.00 vu clearly shows the trivalent state of Mn(3). The extent of the octahedral elongation with $\Delta_{oct} = 0.00920$ is uncommon even for the Jahn–Teller distorted Mn(III) ion: Shannon et al. (*12*) found $Mn(III)O_6$ polyhedra up to $\Delta_{oct} = 0.0071$. Their relationship, $\bar{R} = 1.994 + 7.08\,\Delta$, gives 2.059 Å for a Δ_{oct} value of 0.0092 and therefore closely agrees with the mean Mn(3)–O distance of 2.061 Å. As it is common for centric Jahn–Teller elongated $Mn(III)O_6$ or $Cu(II)O_6$ polyhedra, the bond-angle distortion within the $Mn(3)O_6$ polyhedron is very small.

The atom labeled Mn/Li is coordinated to six O atoms forming a trigonal prism with a mean cation–oxygen distance of 2.223 Å (a further O atom occurs at 2.796(3) Å). It is assumed that this site is

equally occupied by Mn(II) and Li atoms (compare also the experimental section). Unfortunately, there are only few data available on the crystal chemistry of Mn or Li in trigonal prismatic coordination by oxygens. However, bond lengths are comparable with these data as well as with data for Mn(II) atoms or Li atoms in octahedral coordination: e.g., trigonal prismatic coordination of Mn(II) atoms by oxygens is found in $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$ (*14*). There, the mean Mn–O distance is 2.242 Å. In the high-pressure form of Mn_2GeO_4 (*15*), the Mn(II)–O distance within the trigonal prism is 2.19 Å. In a comprehensive paper on the crystal chemistry of lithium by Wenger and Armbruster (*16*), no case of Li in trigonal prismatic coordination by oxygens is reported. The overall mean $Li^{[6]}$–O distance was found to be 2.15 Å and individual average bond lengths of 32 LiO_6 octahedra vary between 2.1 and 2.3 Å. Thus, available literature data comply rather well with the assumed occupation of the trigonal prism in $Li_5Mn(II)_4Mn(III)(SeO_3)_8$. This is further supported by the calculated bond valence sum of 1.35 vu, whereas occupancy by $\frac{1}{2}$ Mn(III) gives 0.88 vu only.

The lithium atoms Li(1) and Li(2) are coordinated to four oxygen atoms in strongly distorted tetrahedral configurations. The average $Li(1)^{[4]}$–O distance (a fifth O atom occurs at 2.913(6) Å) and the bond-length distortion agree well with data from the literature (*16*), whereas the edge-length distortion ELD = 5.82 is comparatively strong. The ELD value of the $Li(2)O_4$ tetrahedron is even higher (ELD = 8.04); a BLD of 4.56 is also uncommon for LiO_4 tetrahedra (*16*). The mean $Li(2)^{[4]}$–O distance (2.057 Å) is also very large, but the next-nearest oxygens are at 2.609(7) and 2.881(7) Å, confirming the four coordination.

The crystal structure of $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ (Figs. 3, 4) consists of sheets parallel (100). Within the sheets, structural linkage occurs through common corners and edges, explaining the strong bond-angle or edge-length distortions of the $Mn(2)O_6$,

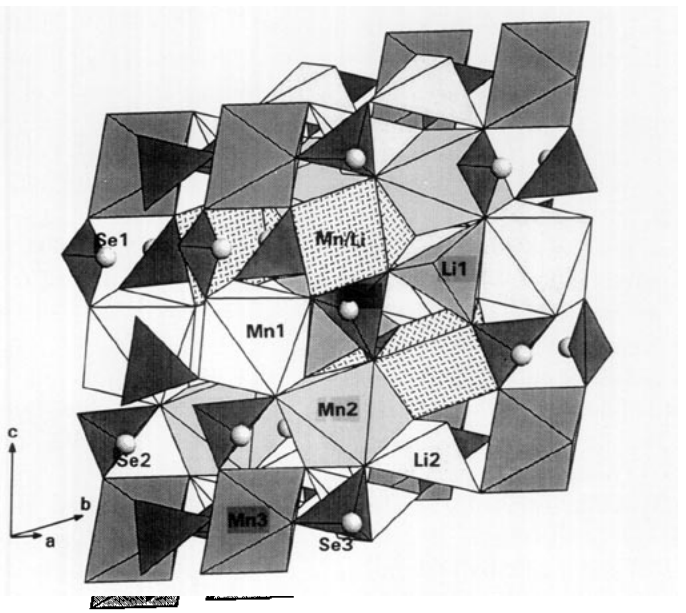

FIG. 3. Projection of the crystal structure of $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ on (100).

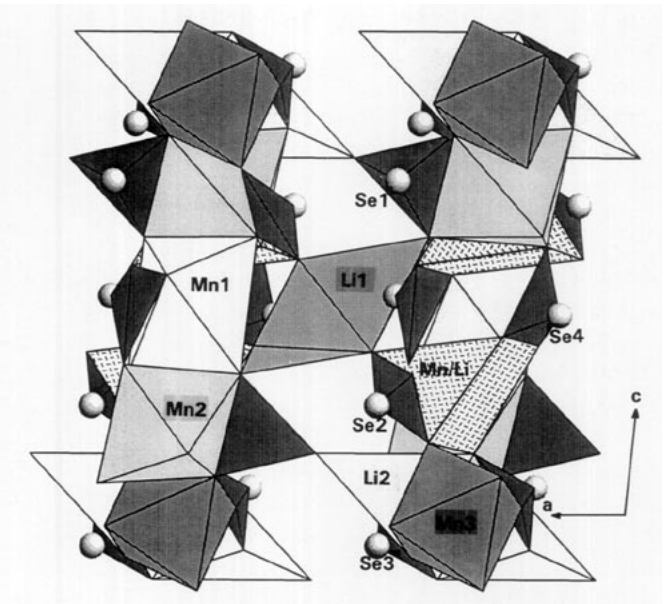

FIG. 4. The crystal structure of $Li_5Mn(II)_4Mn(III)(SeO_3)_8$ as seen along [010].

$(Mn/Li)O_6$, and $Li(2)O_4$ polyhedra; conversely, $Se(3)O_3$ and $Mn(3)O_6$ have no common edges with other polyhedra. Li(2) shares one short edge (O(7)–O(8) = 2.853(3) Å) with a $Mn(2)O_6$ octahedron, and $Mn(1)O_6$ has two common edges with $Mn(2)O_6$ polyhedra (O(2)–O(4) = 2.839(3) Å 2×). The trigonal prism $(Mn/Li)O_6$ shares two of its edges with SeO_3 groups (O(5)–O(6) = 2.534(3) Å and O(10)–O(12) = 2.505(4) Å) and a further edge with a $Mn(2)O_6$ group (O(7)–O(11) = 2.692(3) Å). The $Mn(2)O_6$ polyhedron shares four of its edges with the coordination polyhedra of Li(2), Mn(1), and Mn/Li, and the O(1)–O(2) edge (2.563(3) Å) with a $Se(1)O_3$ pyramid. The sheets are connected by a short common edge (O(6)–O(6) = 2.869(5) Å) between two $Li(1)O_4$ tetrahedra (O(6) is further bound to Se(2) and Mn/Li) and via O(3), which is shared by Se(1) and Li(2). The oxygen atoms O(4), O(5), O(8), O(10), O(11), and O(12) are coordinated to three cations in nearly planar to pyramidal configurations (bond angle sums from 339.3° to 359.3°); O(1), O(2), O(6), and O(7) are fourfold coordinated (strongly distorted tetrahedra), whereas O(3) and O(9) have the coordination number two (Se(1)–O(3)–Li(2) = 118.0°, Se(3)–O(9)–Mn(3) = 134.7°). Bond-valence calculations for the oxygen atoms give sums from 1.80 vu for O(3) to 2.12 vu for O(11).

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References

1. G. GIESTER AND M. WILDNER, *J. Solid State Chem.* **91**, 370 (1991).
2. M. WILDNER, *Acta Crystallogr. Sect. C* **48**, 595 (1992).
3. M. KOSKENLINNA, L. NIINISTÖ, AND J. VALKONEN, *Acta Chem. Scand. Ser. A* **30**, 836 (1976).
4. M. WILDNER, in preparation.
5. "International Tables for X-ray Crystallography," Vol. IV, Kynoch, Birmingham (1974).
6. STOE & CIE, "STRUCSY," Structure system program package, Stoe & Cie, Darmstadt (1984).
7. F. C. HAWTHORNE, L. A. GROAT, AND T. S. ERCIT, *Acta Crystallogr. Sect. C* **43**, 2042 (1987).

8. R. FISCHER AND J. ZEMANN, "Handbook of Geochemistry," Vol. II3, p. 34A, Springer-Verlag, Berlin/Heidelberg/New York (1974).
9. W. H. BAUR, "Structure and Bonding in Crystals," Vol. II, p. 31–52, Academic Press, New York (1981).
10. N. V. BELOV, L. P. OTROSHCHENKO, AND V. I. SIMONOV, *Sov. Phys. Crystallogr.* **29,** 24 (1984).
11. I. D. BROWN AND D. ALTERMATT, *Acta Crystallogr. Sect. B* **41,** 244 (1985).
12. R. D. SHANNON, P. S. GUMERMAN, AND J. CHENAVAS, *Amer. Mineral.* **60,** 714 (1975).
13. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
14. G. ENGEL, J. PRETZSCH, V. GRAMLICH, AND W. H. BAUR, *Acta Crystallogr. Sect. B* **31,** 1854 (1975).
15. A. D. WADSLEY, A. F. REID, AND A. E. RINGWOOD, *Acta Crystallogr. Sect. B* **24,** 740 (1968).
16. M. WENGER AND T. ARMBRUSTER, *Eur. J. Mineral.* **3,** 387 (1991).
17. W. H. ZACHARIASEN, *Acta Crystallogr.* **23,** 558 (1967).