

The Structure of Loseyite

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(Received 8 July 1980; accepted 14 January 1981)

Abstract

Loseyite, $\text{Mn}_{3.48}\text{Zn}_{2.99}\text{Mg}_{0.53}(\text{CO}_3)_2(\text{OH})_{10}$, from Franklin, New Jersey, crystallizes in space group $A2/a$ with $a = 16.408$ (7), $b = 5.540$ (3), $c = 15.150$ (4) Å, $\beta = 95.48$ (3)°, and $Z = 4$. The crystal structure has been determined by direct and Fourier methods from 956 equi-inclination counter data recorded with Ni-filtered Cu $K\alpha$ radiation and refined by least-squares methods to an R_w value of 0.050. The fundamental building unit of the structure is a regularly stepped sheet of edge- and corner-sharing manganese octahedra, with ideal composition $[\text{Mn}_4\Box_1\text{O}_2(\text{OH})_{10}]^{6-}$, oriented parallel to (001). The vacant octahedral site, \Box , in this sheet unit shares its upper and lower faces with tetrahedral $[\text{ZnO}(\text{OH})_3]^{3-}$ groups. The two O atoms are each shared with a carbonate group on opposite sides of, and oriented normal to, the layers. Two of the ten hydroxyl groups do not participate in edge- or corner-sharing within the layer, but both are corner-shared with a zinc tetrahedron possessing twofold symmetry with the composition $[\text{ZnO}_2(\text{OH})_2]^{4-}$. Connectivity between the sheets is achieved directly through corner-sharing with this latter zinc tetrahedron, and also indirectly through corner-sharing between the carbonate group and both kinds of tetrahedron. Site-population analyses carried out during refinement indicate that the Mn and asymmetric Zn sites contain between 6 and 9% Mg, and the twofold Zn site 33% Mg (all within $\pm 1\%$). A set of H atom positions has been proposed, based on considerations of O atom electroneutrality and hybridization state, which suggest a simple hydrogen-bonding scheme between the carbonate group and both zinc tetrahedra.

Introduction

The rare mineral loseyite occurs as transparent, white lath-like crystals elongated parallel to [010] and flattened normal to [100] in cavities and small veinlets in massive ore at Franklin, Sussex County, New Jersey (Bauer & Berman, 1929). Associated phases include altered pyrochroite, sussexite, chlorophoenicite and calcite. The crystal class and cell dimensions were determined by Wolfe & Frondel from X-ray photo-

graphs (private communication in Palache, Berman & Frondel, 1951). The only analysis reported by Bauer & Berman (1929) corresponds to the formula $\text{Mn}_{3.52}\text{Zn}_{2.88}\text{Mg}_{0.60}(\text{CO}_3)_2(\text{OH})_{10}$, with Mn:Zn:Mg \approx 1.0:0.82:0.17.

Experimental

Several fragments of loseyite were analysed with a JXA50A electron microprobe using the MK7 version of the computer program *NPL-IC-BM* (Frost, 1977) for data reduction and Mn metal, ZnS (Zn) and MgAl_2O_4 (Mg) as standards. The accelerating voltage and sample current were maintained at 20 kV and 20 nA respectively and the electron beam was expanded to an area 20 μm in diameter to minimize thermal decomposition of the sample during the analysis. The mean ratio of Mn:Zn:Mg determined from seven spot analyses was 1.0:0.862:0.151, close to the ratio determined by Bauer & Berman (1929), and corresponding to the formula $\text{Mn}_{3.48}\text{Zn}_{2.99}\text{Mg}_{0.53}(\text{CO}_3)_2(\text{OH})_{10}$. However, individual elemental concentrations in different loseyite crystallites were observed to vary by as much as 10% and it is clear that the structure can accommodate a limited range of cation substitutions. No evidence was found for the presence of Fe or other elements in significant amounts.

The crystal selected for data collection was a transparent platelet with well-developed (100) cleavage faces, and dimensions 0.075 \times 0.075 \times 0.033 mm. Preliminary X-ray precession and Weissenberg photographs showed that reflections hkl and $h0l$ were absent for $k + l \neq 2n$ and $h \neq 2n$ respectively, and suggested the possible space groups Aa or $A2/a$. The specimen was mounted on a Stoe automatic Weissenberg diffractometer and the unit-cell parameters were refined by a least-squares technique from the observed 2θ values of 35 manually centred reflections in the range $2\theta = 12$ – 87° , measured at 295K with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54180$ Å). The resultant cell dimensions (see *Abstract*) are in reasonable agreement with those determined by Wolfe & Frondel (in Palache *et al.*, 1951).

The intensities of 2187 reflections of the type $\pm h, k, \pm l$ with $k = 0$ – 4 and $k + l = 2n$ were collected with the

ω -scan technique to a maximum 2θ value of 130° using a step width of 0.01° in ω and a step counting time of 0.7 s (equivalent to $0.86^\circ \text{ min}^{-1}$). Backgrounds were determined from 10 s stationary counts at both ends of each dispersion-corrected [$\Delta\omega = 2.0 + 0.6(|\sin \mu/\tan Y|)$] scan range. Standard reflections monitored at regular intervals for each reciprocal-lattice layer showed no significant variation in either intensity or position. These data were then corrected for background, Lorentz, polarization and absorption effects using a linear absorption coefficient of 32.2 mm^{-1} (the transmission factors ranged from 0.108 to 0.406). Multiply measured and symmetry-equivalent reflections consistent with point group $2/m$ were then averaged to yield a set of 956 unique structure factors, F_o , each with a standard deviation estimated from the equation $\sigma_{F_o} = [\sigma_I^2 + (0.03 I)^2]^{0.5}/2I^{0.5}$, where I is the corrected raw intensity (reset to 1.0 when measured as zero or negative) and σ_I is derived from counting and averaging statistics.* The overall agreement factor between averaged intensities was 0.054, but only those observations with $F_o > 3\sigma_{F_o}$ or $F_o < F_c$ (816 in the final cycles) were included in the subsequent least-squares analysis (agreement factor = 0.046).

Structure determination and refinement

Due to the presence of a high degree of pseudo-symmetry the Mn and Zn atom positions were determined from \mathcal{E}_2 relationships (Hauptman & Karle, 1953) in space group $F2/a$, and the O and C atoms from successive partially phased Fourier syntheses in Aa . The coordinates and isotropic temperature factors of these atoms were then refined by least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_{F_o}^2$, to yield a conventional R_w value of 0.100 but the temperature factors of chemically equivalent atoms were variable and several bond lengths were unreasonably short. Refinement was then continued in $A2/a$ with the population parameters of the metal atoms also released in a crude attempt to account for the possible random substitution of magnesium over these sites ($R_w = 0.070$). Conversion to anisotropic temperature factors,† incorporating the symmetry restrictions of Levy (1956) and the inclusion of an isotropic extinction parameter as defined by Larson (1967), then reduced R_w to 0.051.

* Lists of structure factors, anisotropic thermal parameters and r.m.s. displacements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36004 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The anisotropic ellipsoids have the following form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Calculation of a Fourier difference synthesis using only those data with $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$ failed to show significant peaks of residual electron density in the vicinity of any of the five O atoms assumed to be hydrogen-bond donors on the basis of electrostatic bond-strength sums (Brown & Wu, 1976). Possible proton positions were therefore determined from considerations of the observed donor-acceptor distances $O_a \cdots O_a$, and likely O_a and O_a hybridization states based on the spatial distribution of their coordinating cations.

The five H atoms were positioned 0.96 Å from their respective O_a , assigned isotropic temperature factors $U = 0.05 \text{ \AA}^2$ and included, but not refined, in the subsequent least-squares analysis. Refinement then proceeded smoothly, and with little change, to convergence (parameter shifts in the final cycle were less than one tenth of the appropriate e.s.d.) at R and R_w values of 0.069 and 0.051 respectively. The final value for the extinction parameter was $4.5(4) \times 10^{-3}$ and the error in an observation of unit weight was 3.698. Atomic coordinates and equivalent isotropic thermal parameters along with their standard deviations estimated from the inverted full matrix are given in Table 1. The anisotropic temperature factor coefficients, together with the r.m.s. components of thermal displacement and thermal ellipsoid orientations have been deposited.

Table 1. Fractional atomic coordinates, equivalent isotropic thermal parameters, and site populations

Figures in parentheses here and in all subsequent tables represent the e.s.d. in terms of the least significant figure to the left. B_{eq} is defined as $8\pi^2$ (mean square radial displacement)/3. Occupancy factors: Mn(1) 0.907 (10)Mn, 0.093 Mg; Mn(2) 0.935 (11)Mn, 0.065 Mg; Zn(1) 0.937 (10)Zn, 0.063 Mg; Zn(2) 0.669 (11)Zn, 0.331 Mg.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Mn(1)	0.40984 (14)	0.2525 (9)	0.28147 (15)	2.00 (8)
Mn(2)	0.18432 (14)	0.2594 (8)	0.19606 (14)	1.87 (7)
Zn(1)	0.03923 (11)	0.2462 (6)	0.36370 (12)	1.83 (6)
Zn(2)	0.25	0.2816 (12)	0.0	1.78 (14)
C	0.3723 (9)	0.4133 (34)	0.4758 (10)	1.9 (5)
O(1)	0.0762 (6)	0.2547 (30)	0.4941 (6)	2.8 (2)
O(2)	0.4733 (6)	0.0897 (22)	0.1752 (6)	2.3 (3)
O(3)	0.1182 (6)	0.0806 (21)	0.2960 (6)	1.9 (3)
O(4)	0.0654 (6)	0.4340 (20)	0.1413 (6)	1.7 (3)
O(5)	0.2447 (6)	0.4649 (24)	0.1022 (7)	2.9 (3)
O(6)	0.3436 (6)	0.0708 (22)	0.0302 (6)	2.6 (3)
O(7)	0.3496 (6)	0.4334 (23)	0.3932 (6)	2.3 (3)
O(8)	0.3009 (6)	0.0732 (20)	0.2235 (6)	1.7 (3)
H(26)	0.440	0.160	0.126	4.0
H(35)	0.164	0.060	0.342	4.0
H(41)	0.070	0.472	0.078	4.0
H(57)	0.285	0.112	0.410	4.0
H(86)	0.313	0.048	0.162	4.0

Scattering factors for Mn, Zn, Mg, C and O (neutral atoms) were obtained from *International Tables for X-ray Crystallography* (1974) and were corrected for both real and imaginary anomalous-dispersion components. For H, the spherical scattering factor suggested by Stewart, Davidson & Simpson (1965) was used. Structure solution, refinement and geometry calculations were all performed with the XRAY 76 system of programs (Stewart, 1976).

Discussion of the structure

Loseyite crystallizes with the topology displayed in Figs. 1 and 2, and the bonding dimensions summarized in Table 2. In summary, the structure consists of regularly stepped sheets of edge- and corner-sharing Mn octahedra oriented parallel to (001) and connected to each other by sharing corners with isolated Zn tetrahedra and carbonate groups.

The repeating unit within the layers is a ring of six edge-sharing octahedra with overall ideal composition $[\text{Mn}_4\Box_1\text{O}_2(\text{OH})_{10}]^{6-}$, where \Box denotes a vacant octahedral site at the centre (of symmetry) of the ring. These ring units merge together in the *b* direction to produce infinite edge-sharing octahedral ribbons (Fig. 2), therein accounting for the elongate [010] habit exhibited by the mineral. The ribbons in turn share alternate upper and lower outer corners, O(8), with each other in the *a* direction to produce a faulted sheet with a shallow saw-tooth-like cross section (Fig. 1) in

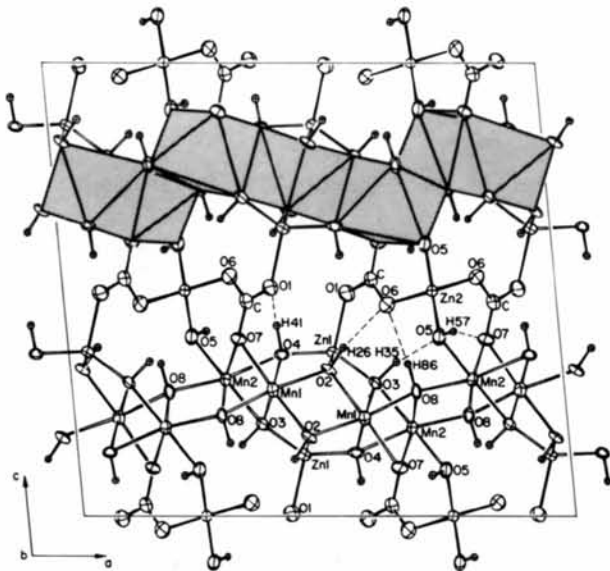


Fig. 1. Unit-cell diagram of the loseyite crystal structure viewed down the *b* axis. Thermal ellipsoids for all atoms (*B* for hydrogen set to 0.5 \AA^2) represent 50% probability surfaces. The Zn(2) tetrahedra and carbonate groups in the interlayer region have been indicated by filled conical bonds, and the hydrogen bonds by dashed lines. One sheet of Mn octahedra has been represented by opaque polyhedra.

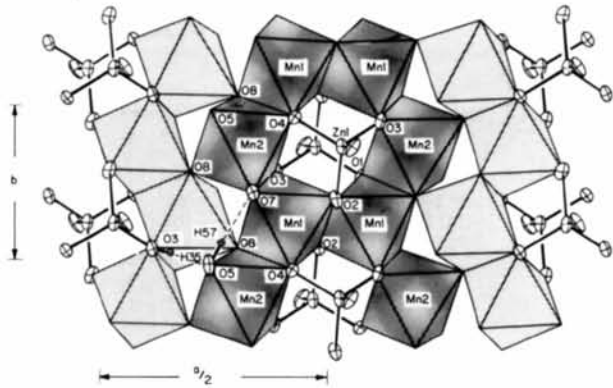


Fig. 2. Diagram of the Mn octahedron sheet at $z = 0.25$ in the loseyite unit cell. The octahedra have been represented as opaque polyhedra and the pairs of Zn(1) tetrahedra above and below the vacant sites in this sheet as filled conical bonds. Hydrogen bonds and thermal ellipsoids are as in Fig. 1.

which the individual ribbons are inclined at an angle of 16° to (001). [In fact, this sheet is identical to a $(0,1,10)_c$ slice of the corundum-type structure.] The two outer corners, O(5) and O(7), of the repeat unit not shared with adjacent ribbons are instead shared with a Zn tetrahedron and a carbonate group, respectively, in the interlayer region. Both of these groups, together with a second kind of Zn tetrahedron lying above and below the vacant octahedral site in the sheet repeat unit, serve to connect the layers in the *c* direction.

The loseyite structure type appears to be unique, although it has structural elements in common with several other compounds, including $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (hydrozincite; Ghose, 1964), $\text{Mg}_9\text{Zn}_4\text{Mn}_2(\text{SO}_4)_2(\text{OH})_{26} \cdot 8\text{H}_2\text{O}$ (mooreite; Hill, 1980), $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Stählin & Oswald, 1970), $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Allmann, 1968), and $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ (chalcophanite; Wadsley, 1955). The structures of all six of these compounds are summarized in Table 3. Each consists of sheets of edge-sharing octahedra containing a variable number of vacant metal-atom sites sharing their upper and lower faces with a $[\text{ZnX}(\text{OH})_3]^{n-}$ tetrahedron, where $X = \text{O}, \text{OH}, \text{H}_2\text{O}$ or Cl , or in the case of chalcophanite, a $[\text{ZnO}_3(\text{H}_2\text{O})_3]^-$ octahedron. Loseyite differs from the other five compounds in that the ratio of octahedral sites (metal plus vacancies) to anions in the repeat unit is not 1:2 and the sheet is therefore not of the CdI_2 type.

Moreover, for the last three structures in Table 3 the layers are held together only by hydrogen bonding between the 'free' nitrate groups or water molecules in the interlayer region and the O atoms or hydroxyl groups in the sheets, whereas for the other three structures one or more of the interlayer groups share corners with the octahedra in the sheets (mooreite, however, also has 'free' sulphate groups between the layers).

Table 2. *Interatomic distances (Å) and angles (°)*

Mn(1) octahedron				Mn(2) octahedron					
Mn(1)—O(4)	2.135 (11)	O(4)—O(2)	3.108 (16)	92.9 (4)	Mn(2)—O(8)	2.124 (11)	O(8)—O(5)	2.876 (14)	84.9 (4)
O(2)	2.153 (10)	O(8) _s	2.959 (13)	87.1 (4)	O(5)	2.140 (12)	O(8)'	3.371 (11)	103.2 (2)
O(8)	2.158 (10)	O(2)	3.036 (13)	88.1 (4)	O(8)'	2.180 (10)	O(3)	3.061 (15)	90.6 (4)
O(2)'	2.189 (12)	O(7)	3.164 (16)	91.7 (4)	O(3)	2.183 (10)	O(4) _s	2.959 (13)	84.7 (4)
O(3)	2.193 (11)	O(2)—O(2)'	2.947 (20)	85.4 (4)	O(4)	2.264 (10)	O(5)—O(8)	2.934 (16)	85.7 (4)
O(7)	2.272 (11)	O(3)	3.011 (13)	87.8 (4)	O(7)	2.293 (12)	O(4)	3.061 (15)	88.1 (4)
Average	2.183	O(7)	3.179 (14)	91.8 (4)	Average	2.197	O(7)	3.331 (18)	97.4 (4)
		O(8)—O(2)'	2.991 (14)	86.8 (4)			O(8)'	3.289 (14)	97.9 (4)
		O(3)	3.135 (15)	92.3 (4)			O(7)	2.993 (14)	84.2 (4)
		O(7)	3.293 (14)	96.0 (4)			O(3)—O(4)	3.113 (14)	88.9 (4)
		O(2)'	3.157 (16)	92.2 (4)			O(7) _s	3.078 (14)	86.7 (4)
		O(3)—O(7) _s	3.074 (14)	87.1 (4)			O(4)—O(7)	3.170 (16)	88.2 (4)
Zn(1) tetrahedron				Zn(2) tetrahedron					
Zn(1)—O(3)	1.956 (10)	O(3)—O(4)	3.245 (14)	111.0 (5)	Zn(2)—O(5) × 2	1.861 (12)	O(5)—O(5)'	3.119 (21)	113.9 (8)
O(4)	1.981 (10)	O(2)	3.244 (16)	110.3 (4)	O(6) × 2	1.949 (12)	O(6) × 2	2.988 (17)	103.3 (4)
O(2)	1.997 (12)	O(1)	3.288 (14)	111.9 (4)	Average	1.905	O(6) × 2	3.216 (16)	115.1 (5)
O(1)	2.012 (9)	O(4)—O(2)	3.334 (16)	113.9 (4)			O(6)—O(6)'	3.121 (19)	106.4 (7)
Average	1.987	O(1)	3.129 (14)	103.2 (4)					
		O(2)—O(1)	3.207 (16)	106.3 (6)					
					Carbonate group				
					C—O(7)	1.273 (21)	O(7)—O(1)	2.231 (15)	122.2 (15)
					O(1)	1.275 (17)	O(6)	2.223 (14)	117.9 (14)
					O(6)	1.318 (20)	O(1)—O(6)	2.242 (18)	119.8 (13)
					Average	1.289			

Shared edges between occupied octahedra are indicated by *s*.

Hydrogen bonds

O _a	H	O _a	O _a —H	H...O _a	O _a '...O _a	∠O _a —H...O _a	∠M—O _a —H
O(2)	H(26)	O(6)	0.963	2.101	2.910 (13)	140.6	97.0, 119.7, 97.3
O(3)	H(35)	O(5)	0.981	1.730	2.680 (14)	161.9	100.5, 98.5, 113.0
O(4)	H(41)	O(1)	0.991	2.026	2.869 (16)	141.6	102.5, 109.0, 107.6
O(5)	H(57)	O(7)	0.959	2.100	3.026 (17)	161.9	111.5, 108.8
O(8)	H(86)	O(6)	0.981	2.108	3.075 (14)	168.2	114.0, 102.5, 98.1

Table 3. *Summary of the structural details of loseyite and related compounds*

Compound	Octahedral sheet formula normalized to one vacancy	Interlayer separation (Å)	Group coordinated to vacant octahedral site	Zn...Zn separation across vacant site (Å)	Interlayer groups	References
Loseyite	[Mn ₄ □ ₁ O ₂ (OH) ₁₀] ⁶⁻	7.54	[ZnO(OH) ₃] ³⁻	3.561	[ZnO ₂ (OH) ₂] ⁴⁻ , [CO ₃] ²⁻	This study
Hydrozincite	[Zn ₃ □ ₁ O ₂ (OH) ₆] ⁴⁻	6.77	[ZnO(OH) ₃] ³⁻	3.496	[CO ₃] ²⁻	Ghose (1964)
Mooreite	[Mg _{4.5} □ ₁ (OH) ₁₁] ²⁻	10.17	[Zn(OH) ₄] ²⁻	3.526	[Mn(OH) ₂ (H ₂ O) ₄], [SO ₄] _{free} ²⁻	Hill (1980)
Zn ₅ (OH) ₈ (NO ₃) ₂ ·2H ₂ O	[Zn ₃ □ ₁ (OH) ₈] ²⁻	9.72	[Zn(H ₂ O)(OH) ₃] ⁻	3.421	[NO ₃] _{free}	Stählin & Oswald (1970)
Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O	[Zn ₃ □ ₁ (OH) ₈] ²⁻	7.88	[ZnCl(OH) ₃] ²⁻	3.395	[H ₂ O] _{free}	Allmann (1968)
Chalcophanite	[Mn ₆ □ ₁ O ₁₄] ⁴⁻	7.12	[ZnO ₃ (H ₂ O) ₃] ⁻	4.245	—	Wadsley (1955)

The manganese octahedron layer

Mean bond lengths within the two nonequivalent Mn octahedra (Table 1) are close to the value 2.20 Å expected for a divalent Mn atom in the high-spin state (Shannon, 1976; Table 4). The greater angular distortion observed for the Mn(2) polyhedron is clearly a function of the fact that it lies in a highly asymmetric environment on the periphery of the octahedron ribbon whereas the Mn(1) octahedron is closer to the centre (Figs. 1 and 2). For both polyhedra, however, the shorter edge lengths and narrower valence angles are associated with the edges shared between octahedra

(marked with an *s* in Table 2), while the larger edges and angles are associated with the unshared edges on the top and bottom of the ribbon: mean values of 3.00 Å, 86.2°, and 3.12 Å, 91.0° respectively for the shared and unshared edges.

The mean distance between the centre of the vacant octahedron (at 0, $\frac{1}{4}$, $\frac{1}{4}$) and its surrounding O atoms is 2.238 Å. This value is larger (by 0.04 Å) than the average Mn—O bond length in the occupied octahedra, but can be readily understood in terms of the relatively larger electrostatic repulsion between O atoms in the absence of a central cation. In Fig. 3 a plot has been made of vacant octahedron mean 'bond' lengths *versus*

Table 4. *Brown & Wu (1976) bond-strength sums, p (v.u.)*

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	p
Mn(1)		0.35, 0.33	0.32	0.37			0.27	0.35	1.99
Mn(2)			0.33	0.27	0.37		0.25	0.34, 0.38	1.94
Zn(1)	0.42	0.43	0.50	0.46					1.81
Zn(2)					0.63 × 2	0.49 × 2			2.24
C	1.37					1.18	1.37		3.92
H(26)		0.80				0.14			0.94
H(35)			0.77		0.22				0.99
H(41)	0.15			0.75					0.90
H(57)					0.80		0.14		0.94
H(86)						0.14		0.77	0.91
p	1.94	1.91	1.92	1.85	2.02	1.95	2.03	1.84	

mean occupied octahedron bond lengths for the six compounds listed in Table 3, together with the related dioctahedral layer structures gibbsite [γ -Al(OH)₃; Saalfeld & Wedde, 1974], bayerite [α -Al(OH)₃; Zigan, Joswig & Burger, 1978] and margarite [CaAl₂(Al₂Si₂)O₁₀(OH)₂; Guggenheim & Bailey, 1978], and several precisely refined zinc spinels (gahnite, ZnAl₂O₄; franklinite, ZnFe₂O₄; ZnGa₂O₄; ZnV₂O₄; Hill, Craig & Gibbs, 1979). All these compounds consist of sheets of edge-sharing octahedra containing a variable number of vacant sites, and all but the three dioctahedral structures have a tetrahedrally coordinated Zn atom bonded to the upper and lower faces of the vacant site [chalcophanite is excluded from the discussion since the atomic coordinates of Wadsley (1955) represent an idealized geometry and the vacant site is constrained to

have the same size as the occupied sites]. As might be anticipated, there is a strong linear relationship ($r = 0.85$) between the 'sizes' of the vacant and occupied octahedra, with the degree of disparity between the two decreasing as the occupied octahedron increases in mean bond length. The two polyhedra become equal in size at a mean sheet bond length of about 2.31 Å, at which point it can be argued that the vacant site has attained its most stable volume (about 16.4 Å³).

The zinc tetrahedra

As discussed above, the vacant octahedral site in the layer repeat unit shares its upper and lower faces with two equivalent Zn(1)O(OH)₃ tetrahedra. The area of the base of a regular tetrahedron with bond length 1.99 Å is 4.57 Å², only slightly larger than the mean area of the upper and lower faces of the occupied octahedron in the sheet (4.29 Å²). As a result the Zn(1) tetrahedron suffers relatively little distortion in articulating to the octahedron sheet. Indeed, the maximum variation in bond lengths is only 0.056 Å, and the range of valence angles (103 to 114°) is typical for Zn in this coordination. The Zn...Zn separation across the vacant site (3.561 Å) is close to the corresponding distances across the vacant sites in the other compounds listed in Table 3, and all are greater than, or near, the upper ends of the ranges of cation separations observed between *corner*-sharing ZnO₄ tetrahedra (3.02 to 3.58 Å; Hill, in preparation) and between *edge*-sharing ZnO₆ octahedra (2.00 to 3.45 Å; Hill, 1979). It is, therefore, unlikely that there are strong Zn...Zn repulsive interactions across the sheets which would represent a significant destabilizing influence on the atomic arrangement.

The second kind of Zn tetrahedron in the loseyite asymmetric unit has the composition ZnO₂(OH)₂ with the Zn atom, Zn(2), lying on the twofold axis at ($\frac{1}{4}$, y , 0). The two Zn(2)—O bonds are both shorter than any of those in the Zn(1) tetrahedron, and themselves differ by nearly 0.09 Å, probably in response to steric constraints imposed by direct articulation between adjacent octahedron sheets, and also to the markedly

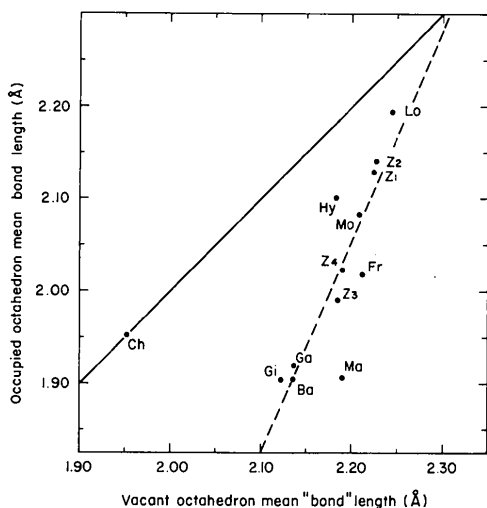


Fig. 3. Plot of occupied octahedron mean bond length versus vacant octahedron mean 'bond' length in the octahedral edge-sharing sheets of loseyite (Lo), hydrozincite (Hy), mooreite (Mo), Zn₅(OH)₈(NO₃)₂·2H₂O (Z₁), Zn₅(OH)₈Cl₂·H₂O (Z₂), chalcophanite (Ch), gibbsite (Gi), bayerite (Ba), margarite (Ma), gahnite (Ga), franklinite (Fr), ZnGa₂O₄ (Z₃), and ZnV₂O₄ (Z₄). The solid line represents a 1:1 relationship between the two quantities, and the dashed line is the estimated regression line fitted to all the data points except Ch.

different environments of O(5) and O(6). Even allowing for the presence of 33% Mg in the Zn(2) site (Table 1), the Zn(2)–O(5) bond is among the shortest observed for zinc in tetrahedral coordination. In fact, of more than 300 Zn–O bond lengths examined by the author, only 11 are less than 1.90 Å long and only one of these is shorter than the Zn–O(5) bond in loseyite: 1.85 (4) Å in hydrozincite (Ghose, 1964). The reason for the shortness of the bond is not entirely obvious since O(5) is not significantly underbonded when the contributions from H(57) and H(35) are included in the bond-strength sum (Table 4). However, O(5) has by far the largest U_{22} coefficient of any atom in the structure (table deposited) and the bond length does increase marginally to 1.888 (12) Å when a correction for anisotropic thermal motion is made under the independent approximation (Busing & Levy, 1964).

The carbonate group

Unlike the carbonate group in hydrozincite, all three O atoms bonded to C in loseyite are also bonded to Zn or Mn and the group has essentially regular geometry (Table 2). Indeed, all bonds and angles are close to ideal values and the C atom lies only 0.021 (18) Å out of the plane of the three O atoms.

Hydrogen bonding

Although the H atom coordinates given in Table 1 represent tentative positions based on considerations of O atom electroneutrality (Table 4) and hybridization states, all distance and angle parameters describing the five hydroxyl groups and their associated hydrogen bonds (Table 2) are consistent with the corresponding mean values measured in other crystalline hydroxides and hydrates by neutron diffraction (Ferraris & Franchini-Angela, 1972).

Of the five hydrogen bonds, indicated by dashed lines in Figs. 1 and 2, three are directed away from the octahedron sheet towards the carbonate O atoms O(1) and O(6), and two are between the O atoms O(3), O(5) and O(7) in the sheet itself.

Cation ordering

The metal-atom site populations obtained during least-squares refinement (Table 1) indicate that between 6 and 9 (± 1)% of the Mn and Zn(1) sites, along with 33 (± 1)% of the Zn(2) site, are randomly occupied by Mg atoms. Although limited by the closeness of the scattering abilities of Mn and Zn and the fact that only two elements could be made to occupy the same site during refinement, the resultant Mn:Zn:Mg ratio of 1.0:0.69:0.21 is in reasonable agreement with the value obtained from the microprobe analysis. If anything, the results suggest that a small amount of Zn

may also be present in the Mn sites. For all four metal-atom sites, however, either the small level of substitution, or the close similarity of the ionic radii (Shannon, 1976), has produced little change from the bond lengths expected for chemically pure sites.

It is a pleasure to acknowledge the support of a Queen Elizabeth II Fellowship for the duration of this study. I am especially grateful to Dr C. A. Francis of the Harvard Mineralogical Museum for making loseyite-type material available for study (specimen number HU 92776), to Dr W. G. Mumme for assistance during data collection, to Dr I. E. Grey for numerous helpful suggestions during structure solution and refinement, and to Mr I. R. Harrowfield for the microprobe analysis. Calculations were performed on the CSIRO Cyber 76 computer.

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