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THE ATOMIC ARRANGEMENT OF BRACKEBUSCHITE, REDEFINED AS $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$, AND COMMENTS ON Mn^{3+} OCTAHEDRA

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ABSTRACT

The atomic arrangement of brackebuschite has been refined in space group $P2_1/m$ from three-dimensional X-ray data using as model the isostructural phase gamagarite. The formula is redefined as $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$. The fundamental building block is a $[Mn^{3+}{}_2O_2(V^{5+}O_4)_4]$ chain of edge-linked $Mn^{3+}O_6$ octahedra that is decorated with orthovanadate tetrahedra. The chain in brackebuschite is a component of the fundamental building block of many $(M^{3+}O_6)$-bearing minerals, including spinel, chloritoid, lawsonite, and pumpellyite. In those phases, chains similar to that in brackebuschite link laterally, yielding a 6 × 9 Å sheet that is common to many phases that contain $M^{3+}O_6$ octahedra. The crystal chemistry of the d^4 Mn^{3+} ion in oxygen-based minerals is reviewed. In essentially all such minerals, Mn^{3+} is coordinated in $Mn^{3+}(O,OH)_6$ octahedra. The octahedra suffer distortions due to the Jahn–Teller effect, but in virtually all cases, the distortion suggests that the d_{z^2} orbital is the lone e_g orbital that is occupied, yielding prolate distortions of the octahedra.

Keywords: brackebuschite, crystal structure, Mn^{3+}, Jahn–Teller distortion.

SOMMAIRE

Nous avons affiné l'agencement des atomes de la brackebuschite dans le groupe spatial $P2_1/m$ à partir de données diffractométriques tridimensionnelles et de l'agencement dans la gamagarite, phase isostructurale. Nous en redéfinissons la formule chimique: $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$. Il s'agit d'une chaîne de stoechiométrie $[Mn^{3+}{}_2O_2(V^{5+}O_4)_4]$ d'octaèdres $M^{3+}O_6$ à arêtes partagées, décorée avec tétraèdres d'orthovanadate. La chaîne dans la brackebuschite est une composante du bloc structural fondamental de plusieurs minéraux à $M^{3+}O_6$, par exemple spinel, chloritoïde, lawsonite, et pumpellyite. Dans ces phases, les chaînes, semblables à celle de la brackebuschite, sont liées latéralement, ce qui donne une feuillet mesurant 6 × 9 Å, commun à toutes les phases qui contiennent des octaèdres $M^{3+}O_6$. Nous passons sous revue la chimie cristalline de l'ion d^4 Mn^{3+} dans les minéraux à base d'oxygène. Dans la plupart des cas, le Mn^{3+} se présente sous forme d'octaèdres $Mn^{3+}(O,OH)_6$. Ceux-ci sont difformes à cause de l'effet de Jahn et Teller, mais en général, la distorsion semble indiquer que l'orbite d_{z^2} se trouve à être le seul à caractère e_g qui est occupé, ce qui mène à une distorsion prolate de l'octaèdre.

(Traduit par la Rédaction)

Keywords: brackebuschite, structure cristalline, Mn^{3+}, distorsion de Jahn–Teller.

INTRODUCTION

The formula of brackebuschite has undergone an evolution that belies its simple chemistry. Donaldson & Barnes (1955) recounted the history of attempts to classify the mineral on the basis of chemistry, and offered a provisional solution to the crystal structure undertaken using film methods of determining structure-factors. Although they noted that uncertainties still remained in the structure determination, their work suggested as formula $Pb_2(Mn^{2+},Fe^{2+})(VO_4)_2{\bullet}H_2O$. That formula has persisted, even with the solution of the atomic arrangement of arsenbrackebuschite [$Pb_2(Fe^{3+},Zn)(AsO_4)_2(OH,H_2O)$: Abraham *et al.* 1978, Hofmeister & Tillmanns 1976] and gamagarite [$Ba_2(Fe^{3+},Mn^{3+})(VO_4)_2(OH)$: Basso *et al.* 1987], two phases with similar diffraction-patterns, yet different reported atomic arrangements. As analyses of brackebuschite are permissive of either the putative formula or a formula similar to that of gamagarite and arsenbrackebuschite, we have re-examined the atomic arrangement of brackebuschite. The study prompted a compilation of Mn^{3+}-bearing minerals, and provides comments on Mn^{3+} octahedra in minerals.

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EXPERIMENTAL

One reason that brackebuschite has resisted a definitive refinement of its structure is the poor quality of available specimens. In this study, we procured crystals from the original Donaldson & Barnes (1955) study (Harvard Museum, 96255). Results of chemical analyses of the specimen are given by Berry & Graham (1948); a formula calculated from their results, assuming the oxidation states found in the title formula and nine atoms of oxygen, yields $Pb_{1.88}(Mn^{3+}_{0.46}Fe^{3+}_{0.45}Zn_{0.11}Cu_{0.04})_{\Sigma 1.05}(V_{1.92}P_{0.02})O_{7.45}(OH)_{1.55}$ or, ideally, $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$. Thus, the analytical data for the sample are permissive of a formula indicating that brackebuschite is isostructural with gamagarite and arsenbrackebuschite.

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT OF BRACKEBUSCHITE

Dimension	0.08 x 0.08 x 0.04 mm		
Unit cell (space group $P2_1/m$)			
a(Å)	7.650(1)		
b	6.135(1)	β(°)	111.76(1)
c	8.863(1)		
Formula (ideal):	$Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$		
θ limits	0.0 - 30°	Scan type	θ/2θ
Standards:		Scan time(s)	≤120 s
Intensity,	3 per 4 hrs	R_{merge}	0.032
Orientation,	3 per 300 reflections	R	0.056
Data collected	2454 ($\pm h$, $+k$, $\pm l$)	R_w	0.060
Unique data	1236	Goodness-of-fit	1.850
Data > $3\sigma_I$	495	Variables	60

Note: Numbers in parentheses denote 1 esd of last unit cited.

To complement the earlier wet-chemical analyses, an electron- microprobe study of the crystal selected for structure refinement and other crystals from Harvard specimen #96255 was undertaken. The results show that two types of brackebuschite exist, one more Fe-rich, and the other more Mn-rich. An average of 10 analyses of the Fe-rich phase, totaling 99.34 wt.% with H_2O by stoichiometry, yielded $(Pb_{1.96}Sr_{0.01}Ca_{0.01})_{\Sigma 1.98}(Fe_{0.77}Mn_{0.13}Cu_{0.03}Zn_{0.02})_{\Sigma 0.95}(V_{2.04}As_{0.01})_{\Sigma 2.05}O_4(OH)$. An average of 29 analyses of Mn-rich crystals ($total_{mean}$ = 99.56 wt.%) yielded $(Pb_{1.89}Sr_{0.02}Ba_{0.01}Ca_{0.03})_{\Sigma 1.95}(Mn_{0.96}Fe_{0.04}Cu_{0.03}Zn_{0.01})_{\Sigma 1.05}(V_{2.01}As_{0.02})_{\Sigma 2.03}O_4(OH)$, both on the basis of five non-H cations. The crystal has both high-Fe and high-Mn regions. The chemistry of brackebuschite is apparently more complex than revealed by wet-chemical analyses, which showed approximately 1:1 Mn:Fe; that ratio is correct, but is an average of high-Fe and high-Mn regions. In addition, groups of crystals in the high-Mn group can be distinguished on the basis of (Ca + Sr + Ba) content, although the sums of those elements range between 0.01 and 0.10 wt.% only. Thus the microprobe study reveals the chemical complexity of the phase that occurs at a single locality.

TABLE 2. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS FOR ATOMS IN BRACKEBUSCHITE

Atom	x	y	z	B(Å^2)
Pb1	0.3278(3)	–1/4	0.4020(3)	2.01(4)
Pb2	–0.2643(2)	–1/4	0.2514(2)	1.66(3)
Mn	0	0	0	0.7(1)
V1	0.5556(8)	3/4	0.826(1)	1.0(1)
V2	0.958(1)	3/4	0.6615(9)	0.5(1)
O1	0.490(3)	0.978(3)	0.701(2)	1.5(4)*
O2	0.452(4)	3/4	0.955(4)	3.1(8)*
O3	0.798(3)	3/4	0.937(3)	1.0(5)*
O4	0.729(5)	3/4	0.542(5)	3.7(8)*
O5	–0.010(3)	0.009(3)	0.220(2)	1.7(4)*
O6	0.074(4)	3/4	0.536(3)	1.5(5)*
O7 (=OH)	0.175(4)	3/4	0.079(4)	2.2(6)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement-parameter defined as: $(4/3)[a^2{*}\beta_{(1,1)} + b^2{*}\beta_{(2,2)} + c^2{*}\beta_{(3,3)} + ab(\cos\gamma){*}\beta_{(1,2)} + ac(\cos\beta){*}\beta_{(1,3)} + bc(\cos\alpha){*}\beta_{(2,3)}]$.

A single crystal of brackebuschite was selected for X-ray examination. The crystal was oriented on a CAD4 single-crystal diffractometer, and cell parameters were obtained by least-squares refinement of the setting angles of 25 independent diffraction maxima, utilizing graphite-monochromatized Mo*K*α radiation. The cell orientation is not conventional, as $c > a$, but is maintained to be consistent with earlier studies on the phase. Intensity data were collected on the same instrument; absorption effects were corrected by the ψ-scan method ($transmission_{max}$ = 99.72%, $transmission_{min}$ = 46.49%) and, subsequent to structure solution, by the absorption-surface method implemented in program DIFABS (Walker & Stuart 1983). Methods of data collection and the results of the crystal-structure refinement are given in Table 1.

All crystal-structure calculations were undertaken using the Enraf Nonius SDP package of computer programs

TABLE 3. SELECTED BOND-DISTANCES IN BRACKEBUSCHITE

Pb1-	O1 (x2)	2.84(2)	Pb2-	O1 (x2)	2.55(2)
	O1' (x2)	2.55(2)		O2	2.72(3)
	O4	2.85(3)		O3	3.00(3)
	O4' (x2)	3.16(1)		O4	2.59(4)
	O5 (x2)	2.95(2)		O5 (x2)	2.60(2)
	O6	2.63(3)		O6	2.87(2)
	O7 (OH)	2.66(3)	Mean		2.69
Mean		2.83			
V1-	O1 (x2)	1.74(2)	V2-	O4	1.68(3)
	O2	1.61(4)		O5 (x2)	1.77(2)
	O3	1.75(2)		O6	1.66(4)
Mean		1.71	Mean		1.72
Mn-	O3 (x2)	2.10(2)			
	O5 (x2)	1.98(2)			
	O7 (OH)(x2)	1.99(2)			
Mean		2.02			

Note: numbers in parentheses denote 1 esd of last unit cited.

(Frenz 1985). Neutral-atom scattering factors, with corrections for anomalous dispersion, were employed throughout the refinement. The starting parameters were those of gamagarite (Basso *et al.* 1987); the atomic positions and thermal parameters rapidly converged to an atomic arrangement isostructural with that phase.

Anisotropic thermal parameters were applied to all atoms, but several atoms of oxygen refined with non-positive-definite thermal ellipses; thus oxygen atoms were returned to isotropic refinement. Several large, positive-difference peaks (<7 e/Å^3) were noted within 1 Å of each Pb atom; such "ghost" peaks are not uncommon in heavy-atom structures determined on less-than-ideal crystals. It is felt that because of the poor quality of the crystals, the structure refinement is at the limits of its resolution.

Bond-valence sums were calculated for all atoms in brackebuschite, and are in good agreement with the formal valence of the ions suggested in the revised formula. Valence sums for oxygen atoms are between 1.85 and 2.05 *vu* (valence units), and among the cations, the sums for Pb1, Pb2, Mn(Fe), V1, and V2 are 1.82, 1.83, 2.99, 5.20, and 5.05 *vu*, respectively. Bond-valence sums confirm that in brackebuschite, like gamagarite, O7 is the hydroxyl, with a bond-valence sum of 1.32 *vu*.

Table 2 contains positional parameters and equivalent isotropic thermal parameters for atoms in brackebuschite, and Table 3 provides selected interatomic distances. A table of observed and calculated structure-factors has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A OS2.

Discussion of the Atomic Arrangement

The structure refinement described here, undertaken using modern diffractometer methods, refines and corrects the earlier provisional solution undertaken using film methods of structure-factor determination. The refinement confirms that brackebuschite is isostructural with gamagarite (Basso *et al.* 1987), and redefines the formula as $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$.

The atomic arrangement of brackebuschite can be characterized on the basis of decorated chains of (O3–O7) edge-sharing MnO_6 octahedra. Figure 1 depicts the structure, illustrating the chains of octahedra. The chains are decorated with V1 and V2 orthovanadate tetrahedra, and the decorated chains are linked together by Pb1 and Pb2 atoms, which coordinate in irregular polyhedra that link adjacent chains, as $Pb1O_{11}$ and $Pb2O_8$. The $V1O_4$ tetrahedra share an O3 corner with the shared edge of the MnO_6 chain, whereas the $V2O_4$ tetrahedra share two O5 atoms, both O5 atoms being apical atoms of oxygen of adjacent octahedra in the chain.

Although the atomic arrangement of brackebuschite has remained unelucidated for a long time, it became apparent upon solution that the structure is formed of a fundamental building block (FBB) long ago recognized as common in ($M^{3+}O_6$)-bearing minerals. Moore *et al.* (1985) described a $[M^{3+}{}_2\square\phi_2(TO_4)_2]$ sheet, the topology of which is based on a layer of the spinel structure. The sheet is formed of chains of edge-sharing $M^{3+}O_6$ octahedra that are decorated with TO_4 tetrahedra, and the chains are linked laterally by sharing tetrahedra, yielding a 6 × 9 Å sheet that is common to many Mn^{3+}-bearing minerals, as well as phases such as spinel, chloritoid, lawsonite, and pumpellyite. In brackebuschite, the tetrahedra that decorate the chains are not shared with adjacent chains, as each chain that is a component of the sheet described by Moore *et al.* (1985) is now a separate entity. Thus in brackebuschite the chains are not polymerized laterally, yielding an FBB of $[Mn^{3+}{}_2O_2(VO_4)_4]$. The remarkably ubiquitous nature of the FBB described by Moore *et al.* (1985) is thus expanded, although the repeat unit of the FBB is reduced from their sheet of chains to the component chains themselves in brackebuschite; the FBB retains the ~6 Å repeat (*b* in brackebuschite).

As evidenced by the difficult history of the characterization of brackebuschite, determination of the valence state of such elements as Mn must be considered provisional until a definitive crystal-structure determination is obtained. As noted by Peacor (1972), existence of distorted Mn-bearing octahedra "may normally be used as confirmation of the occurrence of manganese in a 3+ oxidation state", and, "where (Mn^{3+}) is not (so coordinated), some doubt may exist as to the accuracy of structure determination or refinement." The 4 + 2 prolate octahedron in brackebuschite is confirmation of the existence of Mn^{3+} in the phase, although the Jahn–Teller distortion is undoubtedly diluted by the significant fraction of Fe^{3+} at the site.

$Mn^{3+}O_6$ Octahedra in Minerals

Manganese is among a small group of elements that occur in three valence states in nature, *e.g.*, Mn^{2+}, Mn^{3+} and Mn^{4+}. The ions each exhibit unique crystal-chemical behavior, and the oxidation state of Mn can be ascertained by the coordination polyhedron defined by the surrounding ligands. Peacor (1972) discussed the crystal chemistry of manganese, and enumerated the coordination polyhedra of Mn^{2+}, Mn^{3+}, and Mn^{4+} in minerals and synthetic compounds. Here we review the coordination of Mn^{3+} by oxygen in minerals and update Peacor's listing of Mn^{3+}-bearing minerals.

Mn^{3+}, with three d^4 valence electrons, can occur with either a high- or low-spin electron configuration, but the high-spin state is almost exclusively found. The high-spin state ($t_{2g}{}^3e_g{}^1$ electron configuration) yields 3/5 Δ_o excess crystal-field stabilization energy in a symmetrical octahedral field. However, the Jahn–Teller theorem dictates that ions with a $t_{2g}{}^3e_g{}^1$ electron configuration must undergo tetragonal distortions in such a crystal field; these lengthen one or two of the three principal axes of the octahedra, to form prolate or oblate octahedra, respectively. This distortion increases the crystal-field stabilization energy

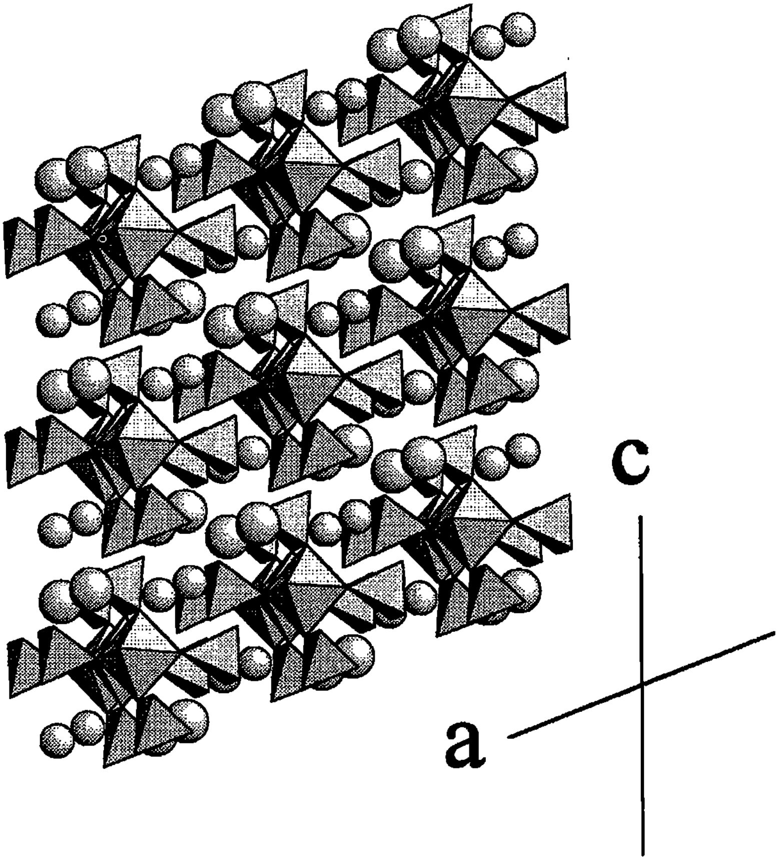

FIG. 1. The atomic arrangement of brackebuschite, illustrating decorated chains of MnO_6 octahedra. To distinguish the Pb atoms, Pb1 atoms are represented by slightly larger spheres.

to $3/5\,\Delta_o + \alpha$, where α is the energy gained from the splitting of the $d_{x^2-y^2}$ and d_{z^2} orbitals (O'Keeffe 1961). Thus, in oxygen-based minerals, a distorted octahedral coordination of Mn^{3+} is essentially the only type observed, save for one $Mn^{3+}O_5$ square-based pyramid in långbanite (Moore *et al.* 1991b). The identity of the e_g orbital that is occupied dictates the nature of the distortion of the octahedron. If the $d_z{}^2$ orbital contains the lone e_g electron, one C_4 axis of the octahedron will lengthen to form a prolate octahedron. Conversely, if the $d_{x^2-y^2}$ orbital contains the single e_g electron, two C_4 axes will lengthen owing to the $d_{x^2-y^2}$ – ligand repulsion, yielding an oblate octahedron. Strens (1965) noted that both types of distortions are known in silicates, although the oblate distortions occur in "more strongly ionic compounds".

Öpik & Pryce (1957) demonstrated that for d^4 ions in an octahedral crystal-field, tetragonal distortions should occur in response to the Jahn–Teller effect, as noted previously. However, they found that in an octahedral crystal-field for a d^4 ion, the lowest energy state most often occurs when the d_{z^2} orbital is occupied, or when a prolate octahedron is formed. We find that, in accord with the study of Öpik & Pryce (1957), Mn^{3+} forms prolate octahedra in virtually all oxygen-based minerals in response to the Jahn–Teller effect; however, in most cases, the distortion yields lower symmetry than tetragonal. Burns *et al.* (1994) have shown an example (fredrikssonite) of how local symmetry can mitigate Jahn–Teller distortion of an octahedron, giving [2 + 2 + 2] "octahedral" coordination. This is true in most Mn^{3+} octahedra (Table 4), but we still apply the term prolate because in virtually all cases, the length of the intermediate bonds is substantially closer to the length of the short bonds than the length of the long bonds, yielding a distorted prolate octahedron.

Table 4 lists all oxygen minerals with essential Mn^{3+} for which the structure is known; all such atoms are coordinated in octahedra except Mn(6) in långbanite (Moore *et al.* 1991b). For each octahedron, the mean bond-length is listed, as well as the standard deviation in bond length and the polyhedral distortion Δ, defined

TABLE 4. DATA CONCERNING Mn^{3+} OCTAHEDRA IN MINERALS*

bermanite, $Mn^{2+}Mn^{3+}_2(PO_4)_2(OH)_2\cdot 4H_2O$	Kampf & Moore (1976)
Mn(1)–O = 1.892, 1.914, 2.200, 2.203; Mn(1)–OH = 1.949, 1.960	<2.020>, 0.143, 0.0042
Mn(2)–O = 1.887, 1.912, 2.211, 2.239; Mn(2)–OH = 1.939, 1.949	<2.023>, 0.158, 0.0051
bixbyite, syn. (orth.), Mn_2O_3	Geller (1971)
Mn(1)–O = 1.963(x2), 1.996(x2), 2.050(x2)	<2.003>, 0.039, 0.0003
Mn(2)–O = 1.960(x2), 1.998(x2), 2.047(x2)	<2.002>, 0.039, 0.0003
Mn(3)–O = 1.889, 1.907, 1.976, 2.001, 2.190, 2.297	<2.043>, 0.164, 0.0054
Mn(4)–O = 1.888, 1.908, 1.981, 1.992, 2.223, 2.268	<2.043>, 0.162, 0.0053
Mn(5)–O = 1.883, 1.911, 1.972, 2.006, 2.215, 2.267	<2.042>, 0.161, 0.0052
bixbyite, (isometric), $(Mn^{3+},Fe^{3+})_2O_3$	Dachs (1956)
(Mn,Fe)(1)–O = 2.01(x6)	<2.01>, 0.00, 0.0
(Mn,Fe)(2)–O = 1.90(x2), 1.92(x2), 2.24(x2)	<2.02>, 0.171, 0.0059
brackebuschite, $Pb_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$	this study
Mn–O = 1.98(x2), 2.10(x2); Mn–OH = 1.99(x2)	<2.02>, 0.06, 0.0007
braunite, $Mn^{2+}Mn^{3+}_6SiO_{12}$	Moore & Araki (1976)
Mn(2)–O = 1.866(x2), 2.028(x2), 2.212(x2)	<2.035>, 0.155, 0.0048
Mn(3)–O = 1.906(x2), 1.971(x2), 2.267(x2)	<2.048>, 0.172, 0.0059
Mn(4)–O = 1.921(x2), 1.946(x2), 2.240(x2)	<2.036>, 0.159, 0.0051
braunite II, Mn_7SiO_{12}	DeVilliers (1980)
Mn(1)–O = 1.883(x2), 1.956(x2), 2.290(x2)	<2.043>, 0.194, 0.0075
Mn(2)–O = 1.993(x2), 1.923(x2), 2.232(x2)	<2.049>, 0.145, 0.0042
Mn(3)–O = 1.918(x2), 1.982(x2), 2.215(x2)	<2.038>, 0.140, 0.0039
Mn(4)–O = 1.896, 1.904, 1.984, 2.001, 2.236, 2.299	<2.053>, 0.172, 0.0059
Mn(5)–O = 1.899, 1.955, 2.006, 2.081, 2.090, 2.093	<2.021>, 0.081, 0.0013
crednerite, $CuMnO_2$	Töpfer *et al.* (1995)
Mn–O = 1.929(x4), 2.226(x2)	<2.039>, 0.171, 0.0059
flinkite, $Mn^{2+}_2Mn^{3+}(AsO_4)(OH)_4$	Moore (1967)
Mn–O = 2.29(x2); Mn–OH = 1.80(x2), 1.91(x2)	<2.000>, 0.230, 0.011
franklinfurnaceite, $Ca_2(Fe^{3+},Al)Mn^{2+}_3Mn^{3+}[Zn_2Si_2O_{10}](OH)_8$	Peacor *et al.* (1988)
Mn–O = 1.879(x2), 2.294(x2); Mn–OH = 1.978(x2)	<2.050>, 0.194, 0.0075
fredrikssonite, $Mg_2Mn^{3+}(BO_3)O_2$	Burns *et al.* (1994)
Mn–O = 1.924(x2), 2.014(x2),2.151, 2.189	<2.036>, 0.112, 0.0025
gamagarite, $Ba_2(Mn^{3+},Fe^{3+})(VO_4)_2(OH)$	Basso *et al.* (1987)
Mn–O = 1.972(x2), 2.079(x2); Mn–OH = 1.990(x2)	<2.014>, 0.051, 0.0005
gaudefroyite, $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)_3$	Yakubovich *et al.* (1975)
Mn–O = 1.86, 1.88, 1.96, 1.99, 2.18, 2.29	<2.03>, 0.172, 0.0060
groutite, MnO(OH)	Dent Glasser & Ingram (1968)
Mn–O = 1.896(x2), 2.178; Mn–OH = 1.968(x2), 2.340	<2.041>,0.179, 0.0064
hausmannite, $Mn^{2+}Mn^{3+}_2O_4$	Jarosch (1987)
Mn–O = 1.930(x4), 2.282(x2)	<2.047>, 0.182, 0.0066
henritermierite, $Ca_3(Mn,Al)_2(SiO_4)_2(OH)_4$	Aubry *et al.* (1969)
Mn–O = 1.901(x2), 1.973(x2), 2.130(x2)	<2.001>, 0.105, 0.0023
kanonaite, $(Mn^{3+},Al)AlSiO_5$	Abs–Wurmbach (1981)
Mn–O = 1.853(x2), 1.918(x2); 2.245(x2)	<2.005>, 0.188, 0.0073
kentrolite, $Pb_2Mn^{3+}_2Si_2O_9$	Moore *et al.* (1991a)
Mn–O = 1.923(x2), 1.977(x2), 2.137(x2)	<2.012>, 0.100, 0.0020
långbanite, $(Mn^{2+},Ca)_4(Mn^{3+},Fe^{3+})_9Sb^{5+}Si_2O_{24}$	Moore *et al.* (1991b)
Mn(3)–O = 1.967, 1.982, 1.994, 2.022, 2.128(x2)	<2.037>, 0.073, 0.0011
Mn(4)–O = 1.910, 1.953, 1.990, 2.008, 2.097, 2.224	<2.030>, 0.114, 0.0026
Mn(6)–O = 1.892(x2), 1.900(x2), 2.311	Square–based pyramid
Mn(7)–O = 1.869, 1.870, 1.904, 1.935, 2.307, 2.371	<2.043>, 0.232, 0.0107
Mn(8)–O = 1.900, 1.936, 1.946, 1.988, 2.211(x2)	<2.032>, 0.141, 0.0040
Mn(9)–O = 1.936, 1.951, 1.997, 2.006, 2.153, 2.390	<2.072>, 0.174, 0.0059
macfallite, $Ca_2Mn^{3+}_3[SiO_4Si_2O_7](OH)_3$	Moore *et al.* (1985)
Mn(1)–O = 1.91(x2), 2.06(x2); Mn(1)–OH = 1.98(x2)	<1.98>, 0.067, 0.0010
Mn(2)–O = 1.91(x2), 2.11(x2), 2.18(x2)	<2.07>, 0.125, 0.0031
Mn(3)–O = 1.94(x2), 2.21(x2); Mn(3)–OH = 1.94(x2)	<2.03>, 0.139, 0.0039
manganite, MnO(OH)	Dachs (1963)
Mn–O = 1.868, 1.878, 2.199; Mn–OH = 1.965, 1.981, 2.333	<2.037>, 0.188, 0.0071
marokite, $CaMn^{3+}_2O_4$	Lepicard & Protas (1966)
Mn–O = 1.90, 1.92, 1.93, 1.96, 2.3, 2.4	<2.07>, 0.221, 0.0095
norrishite, $KLiMn^{3+}_2Si_4O_{12}$	Tyrna & Guggenheim (1991)
Mn(1)–O = 2.092(x4), 2.18(x2)	<2.121>, 0.045, 0.0004
Mn(2)–O = 1.855(x2), 2.023(x2), 2.233(x2)	<2.037>, 0.169, 0.0058
orientite, $Ca_2Mn^{2+}Mn^{3+}_2Si_3O_{10}(OH)_4$	Moore *et al.* (1985)
Mn–O = 1.91(x2), 2.20(x2); Mn–OH = 1.96(x2)	<2.023>, 0.139, 0.0039
orthopinakiolite, $(Mg,Mn^{2+})_2Mn^{3+}(BO_5)$	Takéuchi *et al.* (1978)
Mn(1)–O = 1.983(x4), 2.177(x2)	<2.048>, 0.100, 0.0020
Mn(2)–O = 1.980(x4), 2.180(x2)	<2.047>, 0.103, 0.0021
Mn(3)–O = 1.913(x4), 2.252(x2)	<2.026>, 0.175, 0.0062
Mn(6)–O = 1.908(x2), 1.917(x2), 2.263, 2.330	<2.041>, 0.199, 0.0080
Mn(8)–O = 1.905(x2), 1.963(x2), 2.192, 2.349	<2.046>, 0.183, 0.0066
piemontite, $Ca_2(Al,Mn^{3+},Fe^{3+})_3(SiO_4)_3OH$	Dollase (1969)
Mn–O = 1.861, 1.900, 2.031(x2), 2.274(x2)	<2.062>, 0.178, 0.0062
pinakiolite, $(Mg,Mn^{2+})_2(Mn^{3+},Sb^{3+})BO_5$	Moore & Araki (1974)
Mn(1)–O = 1.916(x4), 2.234(x2)	<2.022>, 0.164, 0.0055
Mn(2)–O = 1.917(x4), 2.261(x2)	<2.032>, 0.178, 0.0064
Mn(3)–O = 1.963(x4), 2.210, 2.227	<2.048>, 0.132, 0.0035
quenselite, $PbMn^{3+}O_2(OH)$	Rouse (1971)
Mn(1)–O = 1.93(x2), 1.98(x2), 2.25(x2)	<2.053>, 0.154, 0.0047
Mn(2)–O = 1.90(x2), 1.95(x2), 2.37(x2)	<2.073>, 0.231, 0.0103
ruizite, $Ca_2Mn^{3+}Si_2O_6(OH)\cdot 2H_2O$	Moore *et al.* (1985)
Mn–O = 1.909(x2), 2.195(x2); Mn–OH = 1.946(x2)	<2.017>, 0.139, 0.0040
taikanite, $BaSr_2Mn^{3+}_2O_2[Si_4O_{12}]$	Yamnova *et al.* (1992)
Mn(1)–O = 1.844(x2), 2.106(x2), 2.176(x2)	<2.042>, 0.157, 0.0049
Mn(2)–O = 1.886(x2), 1.970(x2), 2.293(x2)	<2.050>, 0.192, 0.0073
takéuchiite, $(Mg,Mn^{2+})_2(Mn^{3+},Fe^{3+})BO_5$	Norrestam & Bovin (1987)
Mn(3)–O = 1.906(x4), 2.268(x2),	<2.027>, 0.187, 0.0071
Mn(8)–O = 1.908(x2), 1.904(x2), 2.159,2.261	<2.007>, 0.160, 0.0053
Mn(10)–O = 1.918(x2),1.931(x2), 2.273, 2.169	<2.023>, 0.157, 0.0050
Mn(12)–O = 1.918(x2), 1.979(x2), 2.227, 2.138	<2.027>, 0.127, 0.0033
Mn(14)–O = 1.972(x2), 1.985(x2), 2.175, 2.187	<2.046>, 0.105, 0.0022
Mn(15)–O = 1.963(x2), 1.977(x2), 2.188, 2.174	<2.040>, 0.109, 0.0024

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* After Peacor (1972), updated to 1996. All distances are quoted in Å. For each octahedron, <mean bond-length>, standard deviation of bond lengths, and polyhedron distortion are given. Mineral formulas are taken from Fleischer & Mandarino (1995), although the formulas of some minerals given in the work cited may differ. In addition, the formula for fredrikssonite cited in Fleischer & Mandarino (1995) is incorrect, and corrected here.

as $1/6\ \Sigma[(L_i - \langle L \rangle)/\langle L \rangle]^2$, where L_i is an individual Mn^{3+}–O bond-length, and $\langle L \rangle$ is the average Mn^{3+}–O_6 bond length of that polyhedron. We report the standard deviation in bond lengths for the octahedra because measures of octahedral distortion such as Δ have been shown to be less descriptive of distortion in octahedra that display Jahn–Teller distortion (Robinson *et al.* 1970).

Mean bond-lengths in Mn^{3+}-bearing octahedra vary from 2.00 (flinkite) to 2.12 Å (norrishite), a range of 0.12 Å; much of the deviation from the mean invariably results from the extensive substitution of Fe^{3+} that occurs in Mn^{3+} octahedra. It is also clear that, although Jahn–Teller distortion in Mn^{3+} octahedra can occur by tetragonal distortions that create either prolate or oblate octahedra, one of the C_4 axes almost invariably lengthens to form a prolate octahedron. As noted in Table 4, prolate $Mn^{3+}O_6$ octahedra predominate in oxygen-based minerals, although a few oblate octahedra are noted. The prediction of Öpik & Pryce (1957), that prolate octahedra are a lower-energy response to Jahn–Teller distortion in Mn^{3+}-bearing phases, is thus validated in minerals.

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