Effect of Octahedral Distortion on Mean Mn$^{3+}$--O Distances

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Abstract

Mean octahedral Mn$^{3+}$--O distances, $\bar{R}$, increase with octahedral distortion, $\Delta$, according to the relationship: $\bar{R} = 1.994 + 7.08\Delta$. This dependence of mean distance on distortion is used to help interpret the Mn oxidation state in NaMn$_2$O$_4$ and pinakiolite, Mg$_2$MnBO$_5$.

Analysis of the shape of bond length-bond strength curves shows that mean bond distances in various polyhedra increase with the distortion of the polyhedra (Brown and Shannon, 1973; Hawthorne, 1973; Shannon, 1974). Distances in V$^{5+}$--O, Cu$^{2+}$--O, Mg$^{2+}$--O, Li$^+$--O, Zn$^{2+}$--O and Co$^{2+}$--O octahedra were studied (Brown and Shannon, 1973; Shannon and Calvo, 1973a, 1973b). In this note we show the relationship between mean distance and octahedral distortion in oxides containing the Jahn-Teller ion Mn$^{3+}$.

Because of its 3$d^4$ electronic configuration, Mn$^{3+}$ generally occurs in distorted polyhedra (Dunitz and Orgel, 1960). Although there is relatively little structural data on Mn$^{3+}$ compounds compared to Cu$^{2+}$ or V$^{5+}$ compounds, there is sufficient data to determine the general dependence of mean bond distances on distortion. Table I lists distances in some accurately refined structures containing Mn$^{3+}$ along with mean bond lengths, effective ionic radii, and the octahedral distortion, $\Delta = 1/6 \sum (R_i - \bar{R}/R_i)^2$, where $R_i$ is an individual Mn$^{3+}$--O bond length and $\bar{R}$ is the mean bond length in an individual octahedron.

Figures 1a and 1b show the dependence of mean distance and of effective ionic radius on octahedral distortion. The ionic radius of Mn$^{3+}$ varies between 0.62 and 0.67 depending upon the degree of distortion. The value given by Shannon and Prewitt (1969), 0.64 Å, corresponds to a moderate degree of distortion and thus should not be used in cases where distortion is exceedingly small or large.

The correlation coefficients of 0.82 for $\bar{R}$ vs $\Delta$ and of 0.54 for $\bar{r}$ vs $\Delta$ show that most of the increase in distance is caused by distortion. In contrast to the results for Li$^+$, Mg$^{2+}$, Co$^{2+}$, and Zn$^{2+}$, the correlation coefficient is higher for mean distances uncorrected for oxygen coordination.

It should be noted that 0.007, the maximum distortion ($\Delta$) for Mn$^{3+}$, is approximately 1/8 of that for Cu$^{2+}$, 0.031.

The dependence of mean distance can sometimes be useful in interpreting oxidation states of metal ions in mixed valence compounds. For example, the compound NaMn$_2$O$_4$ (Marezio et al., 1973; Bochu et al., 1974) has a perovskite-like structure with the A sites occupied by Na and 3Mn(1) ions in an ordered manner, and the B site occupied by 4Mn(2) ions with all distances equal to 1.946 Å. The hypothesis that half of the Mn(2) ions were Mn$^{3+}$ HS and half Mn$^{4+}$ led to a large discrepancy between the distance calculated.

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1 Contribution No. 2238.
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Comparison of Mean Octahedral Mn"+—O Distances with Distortion

(Estimated standard errors in parentheses refer to the last digit)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\bar{R}$, Å</th>
<th>$\sigma^{**}$</th>
<th>$\delta^{**}$/6($\bar{R}$—$\bar{R}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(C$_5$H$_7$O$_3$)$_2$</td>
<td>1.981(5)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.002(4)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_4$</td>
<td>2.007(6)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn(C$_5$H$_7$O$_3$)$_2$</td>
<td>1.998(6)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn(C$_5$H$_7$O$_3$)$_2$</td>
<td>2.004(10)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Na$_2$Mn$_2$Ti$_2$O$_7$</td>
<td>2.004(10)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.046(5)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Na$_2$Mn$_2$O$_3$</td>
<td>2.017(5)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.039(6)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.028(5)</td>
<td>0.601</td>
<td>0.0005</td>
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</tr>
<tr>
<td>Mn$_2$O$_3$</td>
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<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.038(20)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.045(6)</td>
<td>0.601</td>
<td>0.0005</td>
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</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.032(5)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.034(3)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>2.037(20)</td>
<td>0.601</td>
<td>0.0005</td>
<td>74 INOCG 13 1864</td>
</tr>
</tbody>
</table>

$\bar{R}$ = mean octahedral Mn"+—O distance with average e.s.d. quoted by authors in parentheses

** $\sigma$ = effective ionic radius of Mn"+

*** Codens for Periodical Titles, Vol. II. ASM Data Series, DS 238, Phila., 1970

Fig. 1a. Mean Mn"+—O distance vs distortion. Vertical bars represent average e.s.d. quoted by authors.

Fig. 1b. Effective ionic radius of Mn"+ HS vs distortion.

from ionic radii, 1.98 Å, and the observed distance, 1.94 Å. When the effect of distortion is taken into account, the predicted distance is 1.994 Å (based on mean $\bar{R}$), or 2.01 Å = 0.62 + 1.39 (based on effective ionic radii) for an undistorted Mn"+—O octahedron, and 1.920 Å for an undistorted Mn"+—O octahedron. This leads to a calculated distance of 1.957 Å (based on $\bar{R}$) or 1.967 Å (based on radii) for the Mn(2) ions and is thus in closer agreement with the hypothesis of $\frac{1}{2}$ Mn"+ and $\frac{1}{2}$ Mn".

A second example is found in the structural analysis of the mineral pinakiolite, Mg$_3$MnBO$_4$. The actual composition found from electron microprobe results is Mg$_{13.90}$Mn$_{2.72}$Al$_{8.00}$Fe$_{0.46}$O$_{40.00}$ and from the structure refinement Mg$_{14.44}$Al$_{8.00}$Mn$_{2.72}$O$_{40.00}$ (Moore and Araki, 1974). In the pinakiolite structure the Mn"+ ions occupy three different crystallographic sites. For refinement purposes the three sites were assumed to be fully occupied by Mn"+. Figure 1 shows that two of these sites are consistent with the distance-distortion relationship but that the third deviates significantly from this plot. This raises the possibility that some Mn(3) may be in the +2 oxidation state. In fact the

In accordance with the structure refinement of CaCu$_2$Mn$_2$O$_4$ (Chenavas, in preparation), of Na$_2$MnNb$_2$O$_6$:50 H$_2$O (Flynn and Stucky, 1969), and with estimated distances in MnO$_2$ (W. H. Baur, personal communication), the effective ionic radius of Mn"+ has been revised to 0.530 Å.
microprobe analysis of pinakiolite showed the presence of some Mn$^{2+}$ which, for lack of a better scheme, was distributed over the Mg$^{2+}$ sites. Based on a mean distance of 2.048 for the Mn(3) site, a mean distance of 2.20 Å for $\text{v}^\text{II} \text{Mn}^{2+} - \text{O}$, and 2.20 Å for a $\text{v}^\text{III} \text{Mn}^{3+} - \text{O}$ site with distortion = 0.0035, we calculate that 0.15 of the Mn(3) site should be occupied by Mn$^{2+}$. This leads to a total Mn$^{3+}$ content of 0.60 and corresponds reasonably well to the Mn$^{3+}$ content from the microprobe analysis of 0.72.

Acknowledgments

We thank Professor P. B. Moore for helpful discussion concerning pinakiolite.

References


Moore, P. B., and T. Araki (1974) Pinakiolite, Mg$_4$Mn$^{3+}$O$_7$ [BO$_4$]; warwickite, Mg(MgTi)O[BO$_4$]; wightmanite, Mg$_2$(O) (OH)$_6$[BO$_4$]·nH$_2$O: Crystal chemistry of complex 3Å wallpaper structures. Am. Mineral. 59, 985–1004.


Manuscript received, February 7, 1975; accepted for publication, March 24, 1975.