Supporting Information

Phosphonate- and Carboxylate-Based Chelators that Solubilize (Hydr)Oxide-Bound Mn\textsuperscript{III}

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Section S1. MnO₂ and MnOOH Characterization by High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM images of the MnO₂ and MnOOH preparations described in the text are presented in Figure S1. MnO₂ exhibited a sheet structure. Many of the sheets are curled, attributable to edge sections thicker than middle sections. MnOOH consists of needle-shaped crystals of uniform size.

Freeze-dried MnO₂ particles weighed 97.10 grams per mole of manganese. Freeze-dried MnOOH particles weighed 91.5 grams per mole of manganese.

Section S2. MnO₂ Dissolution by PP, MDP, and PAA: Additional Time Course Plots

Time course plots for the ligand-assisted dissolution of 200 µM MnO₂ by 5.0, 10.0, 20.0, and 100 mM PP, MDP, and PAA at pH 7.0 are shown in Figure S2. Total dissolved manganese (Mn₉) is consistently equal to total dissolved Mn³⁺ (Mn³⁺(aq), not shown). The three plots to the left illustrate that Mn₉ values approach plateau values after ~ 20 hours of reaction. The three plots to the right highlight the initial fast release of Mn³⁺(aq), and subsequent diminishment in dissolution rate.

Time course plots employing 1.0 mM PP, MDP, and PAA at pH 7.0, shown in Figure S4, are quite distinct from results obtained with higher chelator concentrations. With all three chelators, total dissolved manganese (Mn₉) is consistently equal to total dissolved Mn³⁺ (Mn³⁺(aq), not shown). After nearly twenty hours of reaction, 1.0 mM MDP solubilizes 13 % of TOTMn³⁺, while PP solubilizes 8.3 % of TOTMn³⁺. Solubilization by PAA is negligible (approx. 1 %). With MDP, a fast dissolution stage is followed by a slow dissolution stage, and a plateau value is finally obtained. PP yields an early peak in dissolved manganese that subsequently exhibits a 26 % decline.

MDP is slightly more basic than PP, but otherwise their coordination properties are quite similar. The time course observed with MDP is what would be expected if ligand-assisted dissolution was the only operative process. The decline in dissolved Mn³⁺ observed with 1.0 mM PP suggests that PP breakdown might be significant when the total chelator concentration is low (TOTL is ≤ 1.0 mM). As the concentration of PP is increased, the fraction of PP adsorbed, and hence subject to surface-catalyzed hydrolysis, should decrease substantially. Once the surface is saturated with PP, any additional PP added to the system remains in solution and is protected from surface-catalyzed hydrolysis.

In Figure S5, MnO₂ loadings are increased 2.5-fold from 200 to 500 µM, while keeping the concentration of PP, MDP, and PAA fixed at 5.0 mM (pH 6.0). Higher MnO₂ loadings yield higher initial rates and higher 20-hour plateau values.

Section S3. MnOOH Dissolution by PP, MDP, and PAA: Additional Time Course Plots

Time course plots for the dissolution of 200 µM MnOOH by 5.0 mM PP, MDP, and PAA in the pH range 5-8 are shown in Figure S6. At pH 5.0, Mn³⁺(aq) values are lower than Mn₉ values for all three chelators. As indicated in the pH 5.0 plot, chelator-free MnOOH "blank" suspensions also release Mn₉ over time. At pH 6.0 and at higher pHs (not shown) Mn₉ release in chelator-free MnOOH blank suspensions was not observed.
Section S4. Stoichiometric Considerations

Stoichiometric considerations, i.e., total added chelator (TOTL), total dissolvable metal ion (TOTMn\textsuperscript{III}), total surface sites (ST), and area loading, are important in ligand-assisted dissolution experiments. As noted earlier, the Mn\textsuperscript{III} content of each (hydr)oxide was determined by iodometric titration, enabling us to calculate TOTMn\textsuperscript{III}. Area loading can be calculated from B.E.T. surface area and formula weight. ST can be calculated using an estimated site density of 5 sites/nm\textsuperscript{2}.

\[
\begin{align*}
200 \mu M \text{MnO}_2 \text{ yields:} & \quad 1 \text{ mM TOTL Yields this Stoichiometric Ratio:} \\
44 \mu M \text{ TOTMn} & = 23 \text{ Chelator molecules to one Mn} \text{III} \text{ atom} \\
30 \mu M \text{ ST} & = 33 \text{ Chelator molecules to one surface site} \\
3.4 \text{ m}^2/\text{L Area Loading} & \\
200 \mu M \text{ MnOOH yields:} & \quad 1 \text{ mM TOTL Yields this Stoichiometric Ratio:} \\
200 \mu M \text{ TOTMn} & = 5 \text{ Chelator molecules to one Mn} \text{III} \text{ atom} \\
4 \mu M \text{ ST} & = 250 \text{ Chelator molecules to one surface site} \\
0.5 \text{ m}^2/\text{L Area Loading} & 
\end{align*}
\]

TOTL is therefore in excess of both TOTMn\textsuperscript{III} and ST in most of our experiments.

Section S5. Thermodynamic Considerations

Most experiments with the chelator PAA yielded plateau values for dissolved Mn\textsuperscript{III} that fell short of TOTMn\textsuperscript{III}. Plateau concentrations falling short of TOTMn\textsuperscript{III} were also observed in some experiments with PP and MDP. Here, we investigate the extent to which plateau Mn\textsuperscript{III}(aq) values can be used to gain information about solubility product constants and complex formation constants.

Our previous publication (1) included an estimate for the MnOOH(manganite) solubility product constant (c*K\textsubscript{so}):

\[
\text{Mn} \text{III} \text{OOH(s) + 3H}^+ = \text{Mn}^{3+}(\text{aq}) + 2\text{H}_2\text{O}
\]

\[
c*K_{\text{so}}(\text{manganite}) = \frac{[\text{Mn}^{3+}]}{a_{\text{MnOOH}}[\text{H}^+]^3} = 10^{-1.2} \quad (S1)
\]

\(a_{\text{MnOOH}}\) represents the activity of the MnOOH(s, manganite) solid phase, which according to thermodynamic conventions is set equal to 1.0. It should be noted that a c*K\textsubscript{so} value for Mn\textsuperscript{III} incorporated into MnO\textsubscript{2} is not available. Indeed, the conceptualization of such a quantity is difficult. The activity of the solid phase, \(a_{\text{MnO}_2}\), would likely change as release of Mn\textsuperscript{III} into solution takes place, leaving behind a solid phase enriched in Mn\textsuperscript{IV}. We will return to this issue in Section S6.

Next, consider a generic expression for the formation of Mn\textsuperscript{III}-chelator complexes:

\[
\text{Mn}^{3+}(\text{aq}) + w\text{H}^+ + x\text{L}^{n-} = \text{Mn}^{3+}\text{H}_w\text{L}_x^{(3+w-xn)}
\]
\[ cK = \frac{[\text{Mn}^{III}\text{H}_2\text{L}_x^{(3+w-xn)}]}{[\text{Mn}^{II}(\text{aq})][\text{H}^+]^w[L^{-x}]} \]  \hspace{1cm} (S2)

Summing Eqs. S1 and S2 yields:

\[ \text{Mn}^{III}\text{OOH}(s) + (3+w)\text{H}^+ + x\text{L}^{-x} = \text{Mn}^{III}\text{H}_w\text{L}_x^{(3+w-xn)} + 2\text{H}_2\text{O} \]

\[ c^*K_{\text{so}}cK = \frac{[\text{Mn}^{III}\text{H}_w\text{L}_x^{(3+w-xn)}]}{a_{\text{MnOOH}[\text{H}^+]^{(3+w)}[L^{-x}]}^x} \]  \hspace{1cm} (S3)

\[ [\text{Mn}^{III}\text{H}_w\text{L}_x^{(3+w-xn)}] = c^*K_{\text{so}}cK a_{\text{MnOOH}[\text{H}^+]^{(3+w)}[L^{-x}]}^x \]  \hspace{1cm} (S4)

All experiments performed in this work were conducted at pHs between 5.0 and 8.0. Under these conditions, \( \text{Mn}^{III}(\text{aq}) \) (total dissolved \( \text{Mn}^{III} \)) is solely comprised of \( \text{Mn}^{III} \)-chelator complexes:

\[ \text{Mn}^{III}(\text{aq}) \approx \Sigma [\text{Mn}^{III}\text{H}_w\text{L}_x^{(3+w-xn)}] = (c^*K_{\text{so}}a_{\text{MnOOH}[\text{H}^+]^{3}}) \Sigma (c^*K[\text{H}^+]^{w}[L^{-x}]) \]  \hspace{1cm} (S5)

Equation S5 indicates that solubility determinations (plateau values of \( \text{Mn}^{III}_T \)) can only be converted into equilibrium constants when the stoichiometries and protonation levels of predominant dissolved \( \text{Mn}^{III} \) species have been established. \( c^*K_{\text{so}}a_{\text{MnOOH}[\text{H}^+]^{3}} \) is an expression of how the solid phase controls solubility, while \( \Sigma (c^*K[\text{H}^+]^{w}[L^{-x}]) \) is an expression about how the concentration and identity of chelator control solubility.

What do we know about the stoichiometries and magnitudes of complex formation constants of contributing \( \text{Mn}^{III} \) species? Gordienko et al. (2) examined \( \text{Mn}^{III}-\text{PP} \) speciation below pH 1.8 using acid-base titration. We used their logKs as the basis for equilibrium calculations. Under the conditions employed in our experiments (200 \( \mu \text{M TOTMn}^{III} \), 5 mM < TOTL < 0.1 M, 5.0 < pH < 8.0) calculations based on the Gordienko et al. indicate that \( \text{Mn}^{III} \) should be completely dissolved, and the species \( \text{Mn}^{III}(\text{PP})_2^{5-} \) should be the only significant species. Other species postulated by Gordienko et al., i.e. \( \text{Mn}^{III}(\text{PP})_3^{5-} \), \( \text{Mn}^{III}(\text{H}_2\text{PP})_2^{5-} \), and \( \text{Mn}^{III}(\text{H}_3\text{PP})_3^{5-} \), should be insignificant. Ciavatta and Palombari (3) performed experiments below pH 1.0. Although they were aware of the work by Gordienko et al., their hypothesized species and corresponding logK values were quite different. Using the Ciavatta and Palombari stoichiometries and logK values, our calculations indicate that \( \text{Mn}^{III}(\text{HPP})_6^{9-} \) should be the predominant species, closely followed by \( \text{Mn}^{III}(\text{H}_2\text{PP})_2^{7-} \). Two other species considered by Ciavatta and Palombari, \( \text{Mn}^{III}((\text{H}_2\text{PP})_2^{5-}) \) and \( \text{Mn}^{III}(\text{H}_2\text{PP})(\text{H}_2\text{PP})_2^{3-} \), should be insignificant. Calculations based on Ciavatta and Palombari indicate that the solubility of \( \text{Mn}^{III} \) in the presence of 5 mM to 0.10 M PP should be less than 100 \( \mu \text{M} \) at pHs \( \geq 5.0 \), clearly in discord with our experimental data. Kolthoff and Watters (4) is the only available study that extends across the pH range employed in our experiments. Although they did not report stoichiometries and logK values, they expressed their belief that at pH > 6, only fully deprotonated species should be significant, i.e. \( \text{Mn}^{III}(\text{PP})_2^{5-} \), and possibly \( \text{Mn}^{III}(\text{PP})_3^{9-} \).

We have consulted extensively with Prof. James J. Morgan (California Institute of Technology) and agree with his assessment that the Gordienko et al. and Ciavatta and Palombari findings are inapplicable within the pH range of our experiments. Given the exceptionally high
Lewis Acidity of Mn$^{III}$ (Equation S6) and the known pK$_a$s for pyrophosphoric acid (0.90, 2.28, 6.7, 9.4, (4)), Kolthoff and Watters are likely correct in their assessment that only fully deprotonated Mn$^{III}$-PP species are important.

$$
\text{Mn}^{3+} (\text{aq}) + \text{H}_2\text{O} = \text{Mn}^{3+}\text{OH}^2+ + \text{H}^+
$$

(c)K$_a$ = 10$^{+0.27}$ \quad (25^\circ \text{C}, \ I = 3.0 \ \text{M}, \ (4)) \quad \text{(S6)}

Can any prediction be made regarding the relative significance of the species Mn$^{III}$($\text{PP}$)$^-$, Mn$^{III}$($\text{PP}$)$_2$? Mn$^{III}$ complexes with the bidentate ligand oxalate are the only ones that have been well characterized to date. [Mn$^{III}$($\text{oxalate}$)$_2^-$] exceeds [Mn$^{III}$($\text{oxalate}$)$^+$] when [oxalate$^2-$] is equal to 0.26 mM. [Mn$^{III}$($\text{oxalate}$)$_3^{3+}$] exceeds [Mn$^{III}$($\text{oxalate}$)$_2^-$] when [oxalate$^2-$] exceeds 1.41 mM. Pyrophosphate forms six-membered chelate rings with Mn$^{III}$ while oxalate forms five-membered chelate rings. The higher charge of the fully deprotonated PP$^{4-}$ anion introduces unfavorable electrostatic interactions within the 1:2 and 1:3 complexes.

To summarize, limited information about the protonation level and metal-to-chelator stoichiometries of Mn$^{III}$-PP complexes precludes quantitative estimates of complex formation constants from our data. The pK$_a$s and relevant coordination chemical properties of MDP are quite similar to those of PP, and hence similar precautions apply. The properties of PAA lie somewhere between those of PP and oxalate, and hence would be very suitable for renewed efforts towards determining complex formation constants.

Section S6. Two Models for Addressing (Hydr)Oxide Loading Effects

Experiments in which the MnO$_2$ loading was increased 2.5-fold (Figure S5) provide important clues regarding both the thermodynamics and kinetics of dissolution. In this section, we outline two approaches for interpreting these findings.

The first model employs a conventional solubility equation. Using the approach developed in the preceding section, a new solid phase that contains 22 % Mn$^{III}$ and 78 % Mn$^{IV}$ is first formulated, which matches the MnO$_2$ preparation that we employed. Release of Mn$^{3+} (\text{aq})$ generates a new solid phase enriched in Mn$^{IV}$. For the sake of simplicity, the activities of the two solids are expressed as $a_{\text{Parent}}$ and $a_{\text{Product}}$:

$$
(Mn^{III})_{1.0}(Mn^{IV})_{3.55}(OH)_{1.0}(O)_{8.09}(s) + 3H^+ = Mn^{3+}(aq) + 3.55Mn^{IV}O_2(s) + 2H_2O
$$

$$
e^*K_{so(new)} = \frac{a_{\text{Product}}[Mn^{3+}]}{a_{\text{Parent}}[H^+]^3} \quad \text{(S7)}
$$

An equation analogous to Eq. S5 can then be written:

$$
\text{Mn}^{III}(aq) \approx \left( \frac{e^*K_{so}a_{\text{Parent}}[H^+]^{1.3}}{a_{\text{Product}}} \right) \Sigma \left( c^*K[H^+]^w[L^n]^z \right) \quad \text{(S8)}
$$

$a_{\text{Parent}}$ at the onset of reaction is not affected by raising the (hydr)oxide loading. $a_{\text{Parent}}$ and $a_{\text{Product}}$ may change as the reaction progresses, however. The magnitude of these changes may be
a function of loading, since higher loadings spreads Mn\textsuperscript{III} depletion and Mn\textsuperscript{IV} enrichment across a larger area. Overall, however, changes in $a_{\text{parent}}/a_{\text{product}}$ as reaction takes place should be second-order effects, leading to relatively insignificant changes to plateau values of Mn\textsuperscript{III}(aq).

The second model treats Mn\textsuperscript{III} as a species adsorbed onto MnO\textsubscript{2} particles, fully accessible to chelator molecules in overlying solution:

\begin{equation}
 (>\text{Mn}^{\text{III}}) + \text{wH}^{+} + \text{xL}^{n-} = \text{Mn}^{\text{III}}\text{H}_{\text{wL}_{\text{x}}}^{(3+w-xn)}
\end{equation}

\begin{equation}
 c*K(\text{new}) = \frac{[\text{Mn}^{\text{III}}\text{H}_{\text{wL}_{\text{x}}}^{(3+w-xn)}]}{[>\text{Mn}^{\text{II}}][\text{H}^{+}]^{\text{w}}[\text{L}^{\text{n-}}]^{\text{x}}}
\end{equation}

An equation analogous to Eq. S5 would become:

\begin{equation}
 \text{Mn}^{\text{III}}(\text{aq}) \approx \Sigma (cK[H^{+}]^{w}[L^{n-}]^{x}[>\text{Mn}^{\text{III}}])
\end{equation}

According to this model, any loading increase yields a proportional increase in the plateau value of Mn\textsuperscript{III}(aq). Hence, the second model is more in accord with the results presented in Figure S5.

**Section S7. MnO\textsubscript{2}(Birnessite) Dissolution by PBTC**

PTBC can form one six-membered, PAA-like chelate ring with a central metal ion. (Other, larger chelate rings are also possible.) A time course plot for reaction of 5.0 mM PBTC with 200 \mu M MnO\textsubscript{2} (pH 5.0) is shown in Figure S7. Mn\textsuperscript{III}(aq) nearly matches Mn(aq) during the first 2 hours of reaction. At later times, Mn(aq) increases linearly, but at a lower rate. Mn\textsuperscript{III}(aq), in contrast, reaches a plateau at approx. 10 \mu M. By 20 hours, Mn\textsuperscript{III} makes up less than half of Mn(aq). At 94 hours, Mn(aq) actually exceeds TOTMn\textsuperscript{III} by 10 \mu M, indicating that Mn\textsuperscript{IV} is dissolving as well.

The extent of PBTC adsorption onto MnO\textsubscript{2} should be greater than that of PAA, owing to its two additional carboxylate groups. The greater susceptibility of PBTC towards oxidation may arise from oxidative decarboxylation or oxidative dephosphonation, analogous to the documented oxidation of citrate to ketoglutarate (1).

**References**


Figure S1. Transmission electron micrographs of (a) MnO$_2$(birnessite) and (b) MnOOH(manganite) employed in this study.
Figure S2. Dissolution of 200 µM MnO₂ by 5.0, 10.0, 20.0, and 100.0 mM PP, MDP, and PAA at pH 7.0. (Plots to the right highlight results from the first hour of reaction.)
Figure S3. Dissolution of 200 µM (a) MnO₂ by 5 mM PP, MDP, and PAA at different pH values.
Figure S4. Dissolution of 200 μM MnO₂ by 1.0 mM PP, MDP, and PAA at pH 7.0.
Figure S5. Time course plots for the dissolution of 200 µM MnO₂ (open symbols) and 500 µM MnO₂ (filled symbols) by 5.0 mM PP, MDP, and PAA at pH 6.0. (The two loadings correspond to 44 and 110 µM TOTMn³⁺, which are labeled using two dashed lines.)
Figure S6. Dissolution of 200 µM MnOOH by 5 mM PP, MDP, and PAA at different pH values. The symbol -◊- denotes Mn(aq) released without chelators present.
Figure S7. Dissolution of 200 µM MnO₂ by 5.0 mM PBTC at pH 5.0. The dashed line indicates TOTMn³⁺.