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# Electron-Transfer Reactivities of Bis($\mu$-oxo)dimanganese(III,IV) Dimers with $Co(bpy)_3^{2+}$ and Hydroquinone

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## Introduction

Dioxo-bridged, dinuclear manganese complexes are of interest as photosystem II models, as redox catalysts, and as examples of mixed-valence (III,IV) species which may exhibit intervalence electronic transitions.[1-14] Manganese(III,IV) complexes of the type $[N_4MnO_2MnN_4]^{3+}$ ($N_4$ = bispicen (*N,N'*-bis(2-pyridyl)-1,2-ethanediamine),[3,4] tmpa (tris(2-pyridylmethyl)amine),[6,7] $(bpy)_2$, and $(phen)_2$[8-11]) are well-characterized in terms of molecular and electronic structures, but quantitative redox reactivity studies have not been reported. Considering the extraordinary sensitivity of both dimanganese(III,IV/III,III) and dimanganese(IV,IV/III,IV) half-wave reduction potentials to steric factors[1,2] and the substitution of aliphatic by aromatic amine donor ligands,[3] $[N_4MnO_2MnN_4]^{3+}$ dimers offer the opportunity to examine the influence of thermodynamic driving force on reduction rates of Mn(IV) centers within a uniform $N_4O_2$ dinuclear coordination sphere. We report here an exploratory kinetic investigation of $Co(bpy)_3^{2+}$ oxidations by $[Mn_2(bispicen)_2O_2]^{3+}$, $[Mn_2(tmpa)_2O_2]^{3+}$, $[Mn_2(bpy)_4O_2]^{3+}$, and $[Mn_2(phen)_4O_2]^{3+}$, including reactivity comparisons with hydroquinone for the bispicen and tmpa manganese(III,IV) dimers. Our objective is to estimate relative self-exchange electron transfer rate constants ($k_{11}$) defined by reaction 1. It is expected that the intrinsic

$$[N_4Mn^{IV}O_2Mn^{III}N_4]^{3+} + [N_4Mn^{III}O_2Mn^{III}N_4]^{2+} \xrightarrow{k_{11}} [N_4Mn^{III}O_2Mn^{III}N_4]^{2+} + [N_4Mn^{IV}O_2Mn^{III}N_4]^{3+} \quad (1)$$

electron transfer reactivities of $[Mn^{III}O_2Mn^{IV}]^{3+}$ dimers will be particularly sensitive to the extent of Jahn-Teller structural distortion which necessarily accompanies the reduction of a $d^3$ Mn(IV) center to the high-spin $d^4$ Mn(III) state.

## Experimental Section

$[Mn(bispicen)O]_2(ClO_4)_3{\cdot}3H_2O$, $[Mn(tmpa)O]_2(ClO_4)_3{\cdot}H_2O$, $[Mn(bpy)_2O]_2(ClO_4)_3{\cdot}2H_2O$, and $[Mn(phen)_2O]_2(ClO_4)_3$ were prepared and characterized spectroscopically according to literature methods.[4,7,10] Reagent grade chemicals, chromous-scrubbed nitrogen gas, and triply distilled water were used throughout. *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), 2-morpholinoethanesulfonic acid (MES), and [(tris(hydroxymethyl)methyl)amino]propanesulfonic acid (TAPS) buffers were obtained from Sigma. $Co(bpy)_3^{2+}$ solutions were prepared by mixing $Co(NO_3)_2{\cdot}6H_2O$ with a 15% excess of bpy, sufficient to completely transform Co(II) to the tris(2,2'-bipyridine)cobalt(II) complex (log $\beta_3$ = 16.05).[15] The manganese oxidants were dissolved in pure water and mixed with reductant solutions containing sufficient $NaNO_3$ to maintain a constant ionic strength of 0.2 M after 1:1 mixing. Although the $[Mn_2N_8O_2]^{3+}$ oxidants undergo decomposition in aqueous solution, blank determinations showed that decay rates were slow on the time scale required to prepare stock solutions and conduct kinetic measurements. Spectrophotometric observations also showed that the substitution of amine ligands in $[Mn_2N_8O_2]^{3+}$ complexes by excess bpy did not occur during kinetic runs. Solutions were purged with $N_2$ to prevent the aerobic oxidation of $Co(bpy)_3^{2+}$ and hydroquinone ($H_2Q$). Spectrophotometric and pH measurements were made with Shimadzu UV-260 and Brinkmann pH-104 instruments, respectively.

**Table I.** Observed Rate Constants for the Reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ Dimers by $Co(bpy)_3^{2+}$ [a]

| oxidant | $[Co(bpy)_3^{2+}]$, mM | $k_{obsd}$, $s^{-1}$ |
|---|---|---|
| $[Mn_2(tmpa)_2O_2]^{3+}$ | 2.000 | 0.0115 |
| | 4.000 | 0.0203 |
| | 6.000 | 0.0272 |
| | 8.000 | 0.0380 |
| | 12.00 | 0.0546 |
| | 16.00 | 0.0726 |
| | 24.00 | 0.0996 |
| $[Mn_2(bispicen)_2O_2]^{3+}$ | 1.404 | 0.00963 |
| | 3.510 | 0.0231 |
| | 7.020 | 0.0443 |
| | 10.53 | 0.0638 |
| | 14.04 | 0.0801 |
| $[Mn_2(phen)_4O_2]^{3+}$ | 1.404 | 0.136 |
| | 3.510 | 0.260 |
| | 7.020 | 0.375 |
| | 10.53 | 0.479 |
| | 14.04 | 0.620 |
| $[Mn_2(bpy)_4O_2]^{3+}$ | 1.404 | 0.185 |
| | 3.510 | 0.284 |
| | 7.020 | 0.389 |
| | 10.53 | 0.493 |
| | 14.04 | 0.595 |

[a] 25.0 °C, $I$ = 0.2 M ($NaNO_3$), pH 7.5 (0.02 M BES buffer). 15% excess of bpy present to suppress the dissociation of $Co(bpy)_3^{2+}$. Typical uncertainty in $k_{obsd}$ is ±3%.

The kinetics of $[Mn_2N_8O_2]^{3+}$ redox reactions were followed at 432 (bispicen), 443 (tmpa), and 684 or 555 nm (bpy and phen) on a Dionex D-110 stopped-flow apparatus, maintaining pseudo-first-order excesses of $Co(bpy)_3^{2+}$ or $H_2Q$ over the oxidants (0.08 mM). Kinetic measurements, data collection and the analysis of absorbance–time traces followed standard protocols.[16] Reported pseudo-first-order rate constants ($k_{obsd}$) are the mean of at least three determinations. Hydrogen ion concentrations were derived from pH measurements[17] or dilution of a standardized $HNO_3$ stock solution.

Cyclic voltammograms of $[Mn_2N_8O_2]^{3+}$ species in $CH_3CN$ (0.1 M $N(n\text{-}Bu)_4ClO_4$) were acquired at 25.0 °C with a Bioanalytical Systems CV-1B triangular wave generator, displaying output on a Hewlett-Packard Model 7004B recorder. Platinum-button working and Au auxiliary electrodes were utilized in conjunction with an aqueous saturated calomel reference electrode (0.1 M $NaNO_3$). Half-wave potentials were calculated as the average of cathodic and anodic peak potentials, and converted to the NHE scale by using (hydroxyethyl)ferrocene as an internal calibrant.[17]

## Results and Discussion

Aqueous solutions of $[Mn_2(bispicen)_2O_2]^{3+}$, $[Mn_2(tmpa)_2O_2]^{3+}$, $[Mn_2(bpy)_4O_2]^{3+}$, and $[Mn_2(phen)_4O_2]^{3+}$ exhibit first-order decay curves over >90% of the redox reaction when mixed with excess $Co(bpy)_3^{2+}$ at pH 7.5, 25.0 °C, and $I$ = 0.2 M. With $[Co(II)]_{tot}$ = 2.0 mM, observed rate constants for the reduction of $[Mn_2(tmpa)_2O_2]^{3+}$ were found to be independent of [bpy] in the presence of 10–150% excesses of bipyridine. There was no wavelength dependence of the kinetics throughout the visible

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**Table II.** Rate Parameters for the Reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ Dimers by $Co(bpy)_3^{2+}$ [a]

| oxidant | $k_0$, $s^{-1}$ | $k_1$, $M^{-1}\ s^{-1}$ | $E_{1/2}$, V (III,IV/III,III) | $E_{1/2}$, V (IV,IV/III,IV) |
|---|---|---|---|---|
| $[Mn_2(tmpa)_2O_2]^{3+}$ | $(4.3 \pm 1.4) \times 10^{-3}$ | $4.08 \pm 0.11$ | 0.271 | 1.07 |
| $[Mn_2(bispicen)_2O_2]^{3+}$ | $(3.2 \pm 1.6) \times 10^{-3}$ | $5.60 \pm 0.19$ | 0.144 | 0.947 |
| $[Mn_2(phen)_4O_2]^{3+}$ | $(1.1 \pm 0.2) \times 10^{-1}$ | $(3.65 \pm 0.21) \times 10^{1}$ | 0.419 | 1.35 |
| $[Mn_2(bpy)_4O_2]^{3+}$ | $(1.6 \pm 0.1) \times 10^{-1}$ | $(3.16 \pm 0.14) \times 10^{1}$ | 0.384 | 1.30 |

[a] 25.0 °C, $I = 0.2$ M ($NaNO_3$), pH 7.5 (0.02 M BES buffer). 15% excess of bpy present to suppress the dissociation of $Co(bpy)_3^{2+}$. Rate law: $k_{obsd} = k_0 + k_1[Co(bpy)_3^{2+}]$. Half-wave potentials measured at 25.0 °C in acetonitrile (0.1 M $N(n\text{-}Bu)_4ClO_4$), referenced to NHE. Uncertainty in $E_{1/2}$ values estimated at ±5%.

region, and time course spectra showed that complete bleaching of manganese(III,IV) dimer absorbance was achieved at equilibrium. Concentration dependences of $k_{obsd}$ are displayed in Table I. Linear least-squares fits of $k_{obsd}$ vs $[Co(bpy)_3^{2+}]$ profiles yielded a rate law (eq 2) containing both reductant-dependent and in-

$$k_{obsd} = k_0 + k_1[Co(bpy)_3^{2+}] \qquad (2)$$

dependent terms. Half-wave reduction potentials {manganese(III,IV/III,III) and manganese(IV,IV/III,IV)} calculated from cyclic voltammograms of $CH_3CN$ solutions and $k_0$ and $k_1$ parameters are shown in Table II. The possibility that $k_0$ terms correspond to nonredox decay of the oxidants was excluded by blank determinations which showed thermal hydrolysis to be slower by at least an order of magnitude. Rate constants for the phen and bpy complexes are strikingly similar, as are those for the bispicen and tmpa oxidants.

The reactions of all four manganese(III,IV) complexes with hydroquinone were examined at several hydrogen ion concentrations. Nonlinear $k_{obsd}$ vs $[H_2Q]$ correlations pertain for the bpy and phen complexes over the narrow pH range (5–9) for which these oxidants are reasonably stable in aqueous solution. These oxidations are not sufficiently well-understood to be described in detail at this time. In contrast, observed rate constants for hydroquinone reductions of the more robust bispicen– and tmpa–manganese(III,IV) complexes (Table III) follow the rate law of eq 3 over wide acidity ranges at 25.0 °C. Reductant-independent

$$k_{obsd} = (k_2 + k_3/[H^+])[H_2Q] \qquad (3)$$

pathways were not identified in these studies. An exception is the reduction of $[Mn_2(tmpa)_2O_2]^{3+}$ in strongly acidic solution ($[H^+] = 0.100$ M), for which this intercept is $(5.1 \pm 0.2) \times 10^{-3}$ $s^{-1}$.

Rate constants for hydroquinone reductions of $[Mn_2(bispicen)_2O_2]^{3+}$ and $[Mn_2(tmpa)_2O_2]^{3+}$ through the dominant $k_3$ pathway are $(2.29 \pm 0.16) \times 10^{-6}$ and $(1.74 \pm 0.03) \times 10^{-6}$ $s^{-1}$, respectively, at 25.0 °C and $I = 0.2$ M. The rate law of eq 3 is readily attributed to parallel pathways for electron transfer from un-ionized $H_2Q$ (rate constant $k_2$) and its monoanion, $HQ^-$ (rate constant $k(HQ^-) = k_3/K_{a1}(H_2Q)$).[18,19] On this basis ($K_{a1}(H_2Q) = 1.41 \times 10^{-10}$),[20] $k(HQ^-)$ values for $[Mn_2(bispicen)_2O_2]^{3+}$ and $[Mn_2(tmpa)_2O_2]^{3+}$ are $1.62 \times 10^4$ and $1.23 \times 10^4$ $M^{-1}\ s^{-1}$, respectively. Although $k_{obsd}/[H_2Q]$ vs $[H^+]^{-1}$ plots exhibit small positive intercepts, the associated standard deviations place $k_2$ parameters within experimental uncertainty of zero.

**Table III.** Rate Constants for the Reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ Dimers by Hydroquinone[a]

| oxidant | $[H^+]$, M | $[H_2Q]$, mM | $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| $[Mn_2(tmpa)_2O_2]^{3+}$ | $4.58 \times 10^{-8}$ [b] | 50 | 2.13 |
| | | 100 | 4.35 |
| | | 200 | 9.14 |
| | | 300 | 11.5 |
| | $1.66 \times 10^{-6}$ [c] | 0.5 | 0.00577 |
| | | 1.0 | 0.00950 |
| | | 2.5 | 0.0212 |
| | | 5.0 | 0.0336 |
| | | 12.5 | 0.0621 |
| | | 25 | 0.0856 |
| | | 50 | 0.144 |
| | | 100 | 0.0250 |
| | | 200 | 0.484 |
| | | 300 | 0.710 |
| | $1.00 \times 10^{-3}$ | 50 | 0.00578 |
| | | 100 | 0.0107 |
| | | 200 | 0.0221 |
| | | 300 | 0.0405 |
| | $1.00 \times 10^{-2}$ | 50 | 0.00429 |
| | | 100 | 0.00789 |
| | | 200 | 0.0167 |
| | | 300 | 0.0269 |
| | $1.00 \times 10^{-1}$ | 50 | 0.00947 |
| | | 100 | 0.0132 |
| | | 200 | 0.0215 |
| | | 300 | 0.0300 |
| $[Mn_2(bispicen)_2O_2]^{3+}$ | $7.24 \times 10^{-9}$ [d] | 2.0 | 3.03 |
| | | 6.0 | 6.41 |
| | | 14 | 12.3 |
| | | 19 | 16.5 |
| | $3.09 \times 10^{-8}$ [b] | 20 | 5.01 |
| | | 60 | 10.0 |
| | | 140 | 18.6 |
| | | 200 | 17.8 |
| | $2.88 \times 10^{-7}$ [b] | 20 | 0.416 |
| | | 60 | 0.850 |
| | | 140 | 1.75 |
| | | 200 | 2.58 |
| | $9.12 \times 10^{-7}$ [c] | 20 | 0.172 |
| | | 60 | 0.361 |
| | | 140 | 0.691 |
| | | 196 | 0.927 |
| | $4.37 \times 10^{-6}$ [c] | 20 | 0.0476 |
| | | 65.5 | 0.0992 |
| | | 110 | 0.150 |
| | | 155 | 0.209 |
| | | 200 | 0.275 |

[a] 25.0 °C, $I = 0.2$ M ($NaNO_3$). Typical uncertainty in $k_{obsd}$ is ±3%. For $[H^+] \geq 1$ mM, hydrogen ion concentration was adjusted with $HNO_3$. [b] 0.02 M BES buffer. [c] 0.02 M MES buffer. [d] 0.02 M TAPS buffer.

Although the cyclic voltammograms of all four mixed-valence dimers under consideration have been reported previously,[3,4,6-10,21] variations in medium, reference electrode, and *IR* drop make quantitative comparisons difficult from one study to another. For this reason, we have reevaluated manganese(III,IV/III,III) half-wave reduction potentials so that cross reaction rate constants could be used to compare self-exchange rate constants defined by eq 1. Equation 4 states the relative Marcus theory relationship[22]

$$k_{12} = [k_{11}k_{22}\exp(38.94(\Delta E))]^{1/2} \qquad (4)$$

between the rate constant ($k_{12}$) of an outer-sphere redox reaction and cell potential ($\Delta E$, V) for processes with small thermodynamic driving force at 25 °C (electrostatic work and *f* terms omitted); in the present context, $k_{22}$ designates the $Co(bpy)_3^{2+/3+}$ or hydroquinone/semiquinone self-exchange rate constant. The manganese(III,IV/III,III) couples are quasi-reversible, at best, or irreversible in aqueous solution, and shifts in $E_{1/2}$ due to sol-

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**Table IV.** Comparison of Relative Self-Exchange Electron-Transfer Rate Constants and Bond Length Differentials for $[N_4Mn^{III}O_2Mn^{IV}N_4]^{3+}$ Dimers[a]

| redox couple | $R$ | $\Delta$(Mn–O), Å | $\Delta(Mn–N_{ax})$, Å | $\Delta(Mn–N_{eq})$, Å |
|---|---|---|---|---|
| $[Mn_2(tmpa)_2O_2]^{3+/2+}$ | 1.0 | 0.061 | 0.220 | 0.026 |
| $[Mn_2(bispicen)_2O_2]^{3+/2+}$ | $2.6 \times 10^2$ | 0.040 | 0.077 | 0.000 |
| $[Mn_2(bpy)_4O_2]^{3+/2+}$ | $7.4 \times 10^{-1}$ | 0.071 | 0.194 | 0.057 |
| $[Mn_2(phen)_4O_2]^{3+/2+}$ | $2.5 \times 10^{-1}$ | | | |

[a] Relative $[Mn_2N_8O_2]^{3+/2+}$ self-exchange electron-transfer rate constants (eq 1), defined as $R = k_{11}([Mn_2N_8O_2]^{3+/2+})/k_{11}([Mn_2(tmpa)_2O_2]^{3+/2+})$, were calculated from eq 5 as described in the text. $\Delta$(Mn–O), $\Delta(Mn–N_{ax})$, and $\Delta(Mn–N_{eq})$ correspond to the average differences between Mn–O, $Mn–N_{axial}$, and $Mn–N_{equatorial}$ bond lengths on the Mn(III) and Mn(IV) centers of mixed-valence $[Mn_2N_8O_2]^{3+}$ dimers. Bond length data are from refs 4, 6, and 9.

vation are poorly understood for these systems. Consequently, a quantitative extrapolation from $E_{1/2}(CH_3CN)$ to $E_{1/2}(H_2O)$ is not possible, ruling out the calculation of absolute $k_{11}$ values from eq 4. For the purpose of determining *relative* $k_{11}$ values, however, we assume that differentials among $E_{1/2}$(III,IV/III,III) values remain essentially constant from acetonitrile to the aqueous phase. On this basis, $R = k_{11}([Mn_2N_8O_2]^{3+/2+})/k_{11}([Mn_2(tmpa)_2O_2]^{3+/2+})$ is calculated from eq 5, where $\Delta E' = E_{1/2}([Mn_2(tmpa)_2O_2]^{3+/2+}) - E_{1/2}([Mn_2N_8O_2]^{3+/2+})$.

$$R = [k_{12}^2([Mn_2N_8O_2]^{3+/2+})/k_{12}^2([Mn_2(tmpa)_2O_2]^{3+/2+})] \times \exp(38.94(\Delta E')) \quad (5)$$

$R$ ratios based on reductions of manganese(III,IV) dimers by $Co(bpy)_3^{2+}$ are displayed in Table IV with comparisons among $Mn–N_{axial}$, $Mn–N_{equatorial}$, and Mn–O bond lengths for the Mn(III) and Mn(IV) centers.

This approximate Marcus calculation shows the self-exchange electron-transfer rates of the bpy and phen dimers to be slightly smaller than that of $[Mn_2(tmpa)_2O_2]^{3+/2+}$, while the bispicen analogue evidently is more reactive by 2 orders of magnitude. The agreement between $R$ values for the $[Mn_2(bispicen)_2O_2]^{3+/2+}$ couple calculated from cross reactions with $Co(bpy)_3^{2+}$ ($2.6 \times 10^2$) and $HQ^-$ ($2.4 \times 10^2$) reinforces the hypothesis of distinctively high electron-transfer reactivity. From comparisons of both bond lengths and angles, Hodgson and co-workers conclude[3,4,23] that $[Mn_2(tmpa)_2O_2]^{3+}$, $[Mn_2(bpy)_4O_2]^{3+}$, and $[Mn_2(phen)_4O_2]^{3+}$ are fully localized, Robin and Day[24] class I mixed-valence dimers, while $[Mn_2(bispicen)_2O_2]^{3+}$ exhibits partially delocalized, Robin and Day class II bonding characteristics. Thus, the former dimers exhibit large $Mn–N_{axial}$ bond length differences of about 0.2 Å between localized $d^3$ Mn(IV) and Jahn–Teller-distorted $d^4$ Mn(III) centers; smaller, but distinct Mn–O and $Mn–N_{equatorial}$ bond length inequalities also distinguish the Mn(III) and Mn(IV) atoms (Table IV).[4]

Although the Mn atoms of $[Mn_2(bispicen)_2O_2]^{3+}$ are not equivalent, as would be the case in a Robin and Day class III dimer, $\Delta$(Mn–O), $\Delta(Mn–N_{axial})$, and $\Delta(Mn–N_{equatorial})$ values are uniformly smaller than those pertaining to the tmpa, bpy, and phen complexes, signalling electron delocalization between formally Mn(III) and Mn(IV) metal centers.[3,4] Indeed, bond length and angle variations throughout a series of manganese(IV,IV), manganese(III,IV), and manganese(III,III) dimers containing bispicen and its derivatives are remarkably small considering the overall two-electron change and steric crowding which lengthens $Mn–N_{axial}$ bonds in the latter species (bispicen ligand substituted with methyl groups in the 6-pyridyl positions).[2–5] Therefore, crystallographic evidence supports the proposal that $Mn–N_{axial}$ bond lengthening induced by reduction of Mn(IV) to Mn(III) within $[N_4Mn^{III}O_2Mn^{IV}N_4]^{3+}$ should be smallest when $N_4$ = bispicen, specifically promoting $k_{11}$ through a decrease in the inner-sphere rearrangement contribution to the activation free energy. The crystal structure of $[Mn_2(bispicen)_2O_2]^{2+}$ has not been reported, however, so the relative extents to which Mn–O, $Mn–N_{axial}$, and $Mn–N_{equatorial}$ bond length changes govern the self-exchange rate constant of the $[Mn_2(bispicen)_2O_2]^{3+/2+}$ couple cannot be stated with certainty.

Finally, the reductant-independent $k_0$ pathways found in the reactions of $Co(bpy)_3^{2+}$ with all four $[Mn_2N_8O_2]^{3+}$ dimers should be addressed. The oxidants may be ranked according to decreasing $k_1/k_0$ ratio: bispicen ($1.8 \times 10^3$) > tmpa ($9.5 \times 10^2$) > phen ($3.3 \times 10^2$) > bpy ($2.0 \times 10^2$). Thus, the $k_0$ pathways are most important for the bpy and phen complexes, which exhibit the highest susceptibility toward decomposition in aqueous solution.[10] The possibility that the $k_0$ pathways derive from activation by Mn–O bond cleavage is presently under investigation.

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## Synthesis and Characterization of Bis(2,2'-bipyridyl)nitrocarbonylruthenium(II) Hexafluorophosphate

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Reductions of not only carbon dioxide[1] but also nitrite[2] have been of much interest in connection with environmental problems. Carbon dioxide and nitrite ligated on ruthenium(II) complexes

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