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Electron-Transfer Reactions of Manganese(II) and -(III) Polyamino Carboxylate Complexes in Aqueous Media[1]

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The kinetics of electron-transfer reactions involving the manganese(II) and -(III) complexes of ethylenediaminetetraacetate (edta^{4-}) and *trans*-1,2-cyclohexanediaminetetraacetate (cdta^{4-}) have been investigated in aqueous media. The cross-reactants employed in this study are osmium and cobalt tris(polypyridine) complexes, $IrCl_6^{2-}$, and nickel polyaza complexes. The cross-reaction kinetic data have been correlated in terms of the Marcus relationship for outer-sphere electron-transfer reactions, and a self-exchange rate constant of 0.7 ± 0.4 M^{-1} s^{-1} was derived for the Mn(edta)$(OH_2)^{2-/-}$ and Mn(cdta)$(OH_2)^{2-/-}$ couples at 25 °C. Deviations from this correlation were observed for the metal tris(polypyridine) complexes (reduced rate constants attributed to poor orbital overlap and hydrophobic/hydrophilic repulsions) and for a nickel(II) dioxime species, Ni(Hdiox)$^+$ (enhanced reactivity related to a hydrogen-bonded precursor). The self-exchange rate constant is discussed in terms of the inner-sphere reorganization barriers to the exchange of an antibonding dσ^* electron.

Introduction

Electron-exchange reactions of manganese(II/III) couples have received less attention in comparison with other metal(II/III) couples of the first transition row. While the $Mn(H_2O)_6^{3+}$ ion is unstable with respect to disproportionation except in strongly acidic solution, the Mn(III) oxidation state may be stabilized in neutral solutions by chelating ligands, such as Schiff bases and the polyamino carboxylates.[2,3] We have been interested recently in the electron-transfer reactions of octahedral Mn(II/III) complex couples containing oxygen donor ligands and have investigated reactions involving $Mn(H_2O)_6^{2+/3+}$,[4] $Mn(urea)_6^{2+/3+}$,[5a] and Mn-$(bpyO_2)_3^{2+/3+}$ ($bpyO_2$ = 1,1′-dioxo-2,2′-bipyridine).[5b] The cross-reaction kinetic data were analyzed in terms of the Marcus relationship to yield relatively slow rates of electron exchange (10^{-4}–10^{-2} M^{-1} s^{-1}) for the Mn(II)/Mn(III) couples. This observation is consistent with the large barrier originating in the energy required to change the inner-sphere configuration prior to the exchange of an antibonding dσ^* electron. In these high-spin d^5/d^4 complex couples the Mn–O bond distance difference between the Mn(II) and Mn(III) species is 0.18–0.20 Å.[4,5]

In order to extend these investigations to other Mn(II)/Mn(III) complexes, we have studied the electron-transfer reactions of ethylenediaminetetraacetate (edta^{4-}) and *trans*-1,2-cyclohexanediaminetetraacetate (cdta^{4-}) complexes of manganese. The redox reactions of the Mn(edta)$(OH_2)^{2-/-}$ ($E°$ = 0.82 V)[7] and Mn(cdta)$(OH_2)^{2-/-}$ ($E°$ = 0.81 V)[8] couples have previously been studied with a variety of cross-reactants, with the majority of these reactions believed to be proceeding via an inner-sphere mechanism.[6] Relatively few reactions have been identified as outer-sphere processes from which the Mn(II)/Mn(III) self-exchange rate constant may be derived.[9,10] The Mn(cdta)$(OH_2)^-$ ion has also recently been employed in electron-transfer kinetic studies with metalloproteins such as the high-potential iron–sulfur proteins,[11] the blue copper rusticyanin,[12] cytochrome c_{551},[13] and cytochrome oxidase.[13]

In this paper we report the results of kinetic studies of the reactions of the Mn(cdta)$(OH_2)^{2-/-}$ and Mn(edta)$(OH_2)^{2-/-}$ couples with a series of cross-reactants, $IrCl_6^{2-}$, osmium and cobalt tris(polypyridine), and nickel polyaza complexes, in aqueous solution. The kinetic data have been analyzed in terms of the Marcus relations, and self-exchange rate constants have been derived for the two couples. The exchange rate constants are discussed in terms of the structures of the manganese species in solution and the barriers to electron self-exchange. The rate constants for some of the reactions have been studied as a function of pH to determine the relative reactivities of protonated and deprotonated forms of the oxidized (Mn(edta)$(OH_2)^-$ and Mn-(edta)$(OH)^{2-}$) and reducted (Mn(Hedta)$(OH_2)^-$ and Mn-(edta)$(OH_2)^{2-}$) complexes.

Experimental Section

Materials. Manganous perchlorate (Alfa), ethylenediaminetetraacetic acid (BDH), and *trans*-1,2-cyclohexanediaminetetraacetic acid (BDH) were used as received. The manganese(II) complex ions, Mn(edta)-$(OH_2)^{2-}$ and Mn(cdta)$(OH_2)^{2-}$, were generated in solution by the ad-

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Table I. Kinetic and Activation Parameters for the Electron-Transfer Reactions Involving the $Mn(edta)^{2-/-}$ and $Mn(cdta)^{2-/-}$ Couples

reductant	oxidant	$10^{-4}k_{12}$,[a] $M^{-1}\ s^{-1}$	ΔH^*, kcal mol^{-1}	ΔS^*, cal $K^{-1}\ mol^{-1}$
$Mn(edta)^{2-}$	$Os(bpy)_3^{3+}$	1.25 ± 0.05	11.5 ± 0.4	−1 ± 1
$Mn(cydta)^{2-}$	$Os(bpy)_3^{3+}$	2.03 ± 0.12	8.7 ± 0.7	−10 ± 2
$Mn(edta)^{2-}$	$Os(phen)_3^{3+}$	1.44 ± 0.11		
$Mn(cydta)^{2-}$	$Os(phen)_3^{3+}$	4.18 ± 0.10	11.1 ± 0.3	0 ± 1
$Mn(edta)^{2-}$	$Os(5\text{-}Clphen)_3^{3+}$	9.69 ± 0.53	10.0 ± 1.5	−2 ± 4
$Mn(cdta)^{2-}$	$Os(5\text{-}Clphen)_3^{3+}$	13.2 ± 0.9		
$Os(5,6\text{-}Me_2Phen)_3^{2+}$	$Mn(edta)^-$	1.54 ± 0.03		
$Mn(edta)^{2-}$	$IrCl_6^{2-}$	0.296 ± 0.009	8.6 ± 0.5	−14 ± 2
$Mn(cdta)^{2-}$	$IrCl_6^{2-}$	0.0461 ± 0.0031	9.1 ± 0.4	−16 ± 1
$Mn(edta)^{2-}$	$Ni([9]aneN_3)_2^{3+}$	1.34 ± 0.08	13.8 ± 0.8	−7 ± 2
$Mn(cdta)^{2-}$	$Ni([9]aneN_3)_2^{3+}$	2.69 ± 0.06	10.8 ± 1.2	−2 ± 3
$Co(5\text{-}Clphen)_3^{2+}$	$Mn(cdta)^-$	0.148 ± 0.004		

[a] At 25.0 °C and $I = 0.10$ M ($NaClO_4$).

dition of a slight stoichiometric excess of Mn^{2+} to the ligand species.[14] The manganese(III) complexes were prepared by the method of Yoshino et al.[15] or by the electrochemical oxidation of the corresponding Mn(II) species at a platinum electrode. The concentrations of stock solutions were determined spectrophotometrically: for $Mn(edta)(OH_2)^-$, $\epsilon = 467$ $M^{-1}\ cm^{-1}$ at 500 nm, and for $Mn(cdta)(OH_2)^-$, $\epsilon = 345$ $M^{-1}\ cm^{-1}$ at 510 nm.[8,15] The complexes $[Ni(H_2diox)](ClO_4)_2$ (H_2diox = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime)[16] and $[Ni([9]aneN_3)_2](ClO_4)_2$ ($[9]aneN_3$ = 1,4,7-triazacyclononane)[17] were prepared by reported methods. The $[Co(5\text{-}Clphen)_3](ClO_4)_2$ (5-Clphen = 5-chloro-1,10-phenanthroline) complex was prepared by the method of Martin and Waind.[18] The $Co(edta)(OH_2)^{2-}$ ion was prepared by the addition of a 5% excess of the ligand to $Co(ClO_4)_2 \cdot 6H_2O$ in aqueous solution. The tris(polypyridine)osmium(III) ions were prepared by the oxidation of the corresponding osmium(II) complexes[19] using lead(IV) dioxide. The $Ni([9]aneN_3)_2^{3+}$ cation was generated in the same manner.

Kinetic Studies. The kinetic measurements were made by using a TDI Model IIA stopped-flow apparatus (Cantech Scientific) and data acquisition system interfaced to a Zenith ZF-151 microcomputer. Pseudo-first-order conditions of excess manganese(II) or -(III) polyamino carboxylate concentrations were employed, and plots of ln $(A_\infty - A_t)$ or ln $(A_t - A_\infty)$ against time were linear for at least 3 half-lives. The first-order rate constants were determined from the average of four to six replicate experiments. The ionic strength of the reaction medium was generally maintained at 0.10 M by using sodium perchlorate. The pH of the solution was controlled by the use of 0.10 M acetate, 0.025 M phosphate, and 0.025 M borate buffers and measured by using a Fisher Accumet 825 pH meter. Thermostating of the reaction solutions in the range of 5–35 °C was maintained to ±0.1 °C by means of an external water bath.

Results

The kinetics of the electron-transfer cross-reactions of the $Mn(edta)(OH_2)^{2-/-}$ and $Mn(cdta)(OH_2)^{2-/-}$ couples (the coordinated H_2O is omitted in the formulae below, unless required) with a series of well-characterized (known reduction potentials and electron self-exchange rate constants) one-electron redox agents were studied by using stopped-flow methods. The reactions were generally carried out in the pH range 4–6, at an ionic strength of 0.10 M. The redox process was followed by monitoring the first-order changes in the cross-reactant concentrations, under pseudo-first-order conditions of excess Mn(II) or Mn(III) species. A first-order dependence of k_{obs} on the Mn(II) or Mn(III) concentrations was observed for each system, and the values of k_{12} and the corresponding activation parameters are presented in Table I.

The complex couples $Os(bpy)_3^{3+/2+}$ (bpy = 2,2′-bipyridine) and $Os(phen)_3^{3+/2+}$ (phen = 1,10-phenanthroline) are outer-sphere redox reactants whose reduction potentials (0.82 V)[20] are virtually identical with those of the manganese(III) polyamino carboxylate complexes used in this study. By the employment of these osmium complexes and others containing substituted polypyridines, a series of cross-reactions with small but variable thermodynamic driving forces could be studied.

$$Os(bpy)_3^{3+} + Mn(edta)^{2-} \xrightarrow{k_{12}} Os(bpy)_3^{2+} + Mn(edta)^- \quad (1)$$

The reactions were monitored at the λ_{max} of the appropriate OsL_3^{2+} complex (460–480 nm)[19] under conditions of a pseudo-first-order excess of the manganese(II) or -(III) complex ((0.3–11) × 10^{-4} M).

Kinetic studies of the oxidations of $Mn(edta)^{2-}$ and $Mn(cdta)^{2-}$ by $IrCl_6^{2-}$ ($E° = 0.892$ V)[21] were carried out at pH 5.7 (monitored at 480 nm) using a pseudo-first-order excess of the Mn(II) complex ((0.2–2.6) × 10^{-3} M).

$$IrCl_6^{2-} + Mn(edta)^{2-} \xrightarrow{k_{12}} IrCl_6^{3-} + Mn(edta)^- \quad (2)$$

At an ionic strength of 0.10 M the rate constants (25.0 °C) showed a slight dependence on the nature of the electrolyte cation, with k_{12} values of 2.96 × 10^3 and 3.40 × 10^3 $M^{-1}\ s^{-1}$ in $NaClO_4$ and $LiClO_4$ solutions, respectively.

The rate constants for reactions 1 and 2 were also studied over the pH range 2.7–6.5. In both systems the electron-transfer rate constants were independent of pH in the range 4.7–6.5 and decreased below pH 4.7. The decrease in the rate constants with increasing acidity is attributed to a proton equilibrium involving $Mn(edta)^{2-}$, as there is no pK_a associated with either oxidant in this range. A pK_a of 3.1 (20 °C, $I = 0.10$ M) has been reported[22] for the $Mn(Hedta)(OH_2)^-$ ion, and the kinetic data in this study indicate a pK_a value of 3.0 ± 0.3, assuming the protonated species to be unreactive (the protonation of a reductant generally increases $E°$,[24] making it a weaker reductant than the conjugate base).

The Os(II/III) and Ir(III/IV) cross-reaction couples employed above have similar electron self-exchange pathways, involving nonbonding 5dπ orbitals. In order to examine electron-transfer systems in which the cross-reactants' electron-exchange pathways were compatible with the Mn(II/III) couples (involving antibonding 3dσ^* orbitals), Ni(II/III) and Co(II/III) complex couples were employed. The results of kinetic studies using $Ni([9]aneN_3)_2^{3+}$ ($E° = 0.95$ V)[17] as an oxidant ([Mn(II)] = (0.5–2.7) × 10^{-3} M) and $Co(5\text{-}Clphen)_3^{2+}$ ($E° = 0.43$ V)[25] as a reductant ([Mn(III)] = (1.4–9.4) × 10^{-4} M) are presented in Table I. A study of the oxidation of $Co(edta)^{2-}$ ($E° = 0.40$ V)[9] by $Mn(edta)^-$ yielded a rate constant (0.8 ± 0.2 $M^{-1}\ s^{-1}$, pH 3–5) similar to that

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reported by Wilkins and Yelin[9] for the reaction of $Co(edta)^{2-}$ with $Mn(cdta)^-$. Above pH 5 the rate increases as the outer-sphere process is replaced by a postulated hydroxy-bridged inner-sphere pathway[23] ($k \approx 40\ M^{-1}\ s^{-1}$ from this study).

Reduction by Nickel(II) Dioxime. The stoichiometry of the reduction of $Mn(cdta)^-$ by the nickel(II) dioxime complex, determined by spectrophotometric titrations at pH 5, indicated that 2.0 ± 0.1 mol of Mn(III) was consumed for every 1 mol of Ni(II), and the deprotonated Ni(IV) species, $Ni(diox)^{2+}$ ($\lambda_{max} = 500$ nm, $\epsilon = 6300\ M^{-1}\ cm^{-1}$),[16] was identified as the product of the redox process.

$$2Mn(cdta)^- + Ni(H_2diox)^{2+} \rightarrow 2Mn(cdta)^{2-} + Ni(diox)^{2+} + 2H^+ \quad (3)$$

The rate constants for the reduction of $Mn(edta)^-$ and $Mn(cdta)^-$ by $Ni(H_2diox)^{2+}$ were studied at 25.0 °C ($I = 0.10$ M) over the pH ranges 3–7 and 4–9, respectively. Below pH 5 the kinetic traces at 500 nm are monophasic first-order curves. The rate law for the reactions may be expressed as

$$d[Ni(IV)]/dt = k[Mn(III)][Ni(II)] \quad (4)$$

where $k = k_{obs}/[Mn(III)]$ under pseudo-first-order conditions of excess oxidant ($(0.1\text{–}1.0) \times 10^{-3}$ M). Above pH 5 the kinetic traces become biphasic, with a slower second stage well separated from the first. At a wavelength of 500 nm the absorption changes in the two steps are roughly equivalent, suggesting a Ni(III) intermediate (for $Ni(diox)^+$, $\lambda_{max} = 505$, $\epsilon = 2890\ M^{-1}\ cm^{-1}$).[26a] Below pH 5 the oxidation of the nickel(II) complex is expected to be the rate-determining step with a subsequent rapid oxidation of the nickel(III) intermediate to a stable nickel(IV) product. Above pH 5 the reduction potential of the nickel(III/II) couple $Ni(diox)^+/Ni(diox)$ ($E° = 0.42$ V)[27,28] drops below that of the nickel(IV/III) couple, $Ni(diox)^{2+}/Ni(diox)^+$ ($E° = 0.65$ V),[27,28] and the rapid oxidation of the nickel(II) complex is followed by a slower, pH-independent oxidation of $Ni(diox)^+$. For the $Ni(diox)^+/Mn(edta)(H_2O)^-$ cross-reaction, a rate constant of $(7.0 \pm 0.4) \times 10^3\ M^{-1}\ s^{-1}$ was measured.

The pH rate profiles for the oxidation of the Ni(II) species (Figure 1) are bell-shaped curves with peaks in the pH 5–6 region. The nickel(II) complex undergoes two acid dissociation steps involving the deprotonation of the oxime oxygens.

$$Ni(H_2diox)^{2+} \overset{K_1}{\rightleftharpoons} Ni(Hdiox)^+ + H^+ \quad (5)$$

$$Ni(Hdiox)^+ \overset{K_2}{\rightleftharpoons} Ni(diox) + H^+ \quad (6)$$

The acid dissociation constants have been determined from potentiometric titrations,[27] electron-transfer kinetic studies,[28,29] and cyclic voltammetry studies,[26,27] and values of pK_1 and pK_2 have been found in the ranges of 5.9–6.5 and 7.2–8.0, respectively. The electrochemical measurements in 0.10 M $NaNO_3$ yielded values of $pK_1 = 6.47$ and $pK_2 = 7.33$.[26] As the nickel(II) species become deprotonated, the reduction potentials (E_n) of the corresponding $Ni(H_ndiox)^{(n+1)+/n+}$ couple decrease such that $E_2 = 1.07$ V, $E_1 = 0.64$ V and $E_0 = 0.42$ V vs NHE.[28] The reaction between $Mn(edta)^-$ (and $Mn(cdta)^-$) and $Ni(H_2diox)^{2+}$ is therefore thermodynamically unfavorable. On the basis of the reduction potentials the electron-transfer rate constants should increase with pH over the range pH 4–9. The drop in the rate constants at higher pH appears to coincide with the pK associated with the deprotonation of a coordinated water on the Mn(III) species

$$Mn(edta)(OH_2)^- \overset{K_m}{\rightleftharpoons} Mn(edta)(OH)^{2-} + H^+ \quad (7)$$

indicating that the hydroxy species is unreactive as an oxidant (deprotonation of an oxidant results in a decrease in the reduction potential[24]) toward the Ni(II) complexes. A similar reduction in reactivity upon deprotonation of $Mn(cdta)(OH_2)^-$ was observed in its oxidation of a high-potential iron–sulfur protein (HIPIP).[11] From acid–base and spectrophotometric titrations, pK_m values of 5.5 for $Mn(edta)(OH_2)^-$ [15] and 8.1 (7.74 ± 0.08 from the HIPIP/$Mn(cdta)(OH_2)^-$ electron-transfer kinetic study) for $Mn(cdta)(OH_2)^-$ [8] have been determined at 25.0 °C ($I = 0.1$ M).

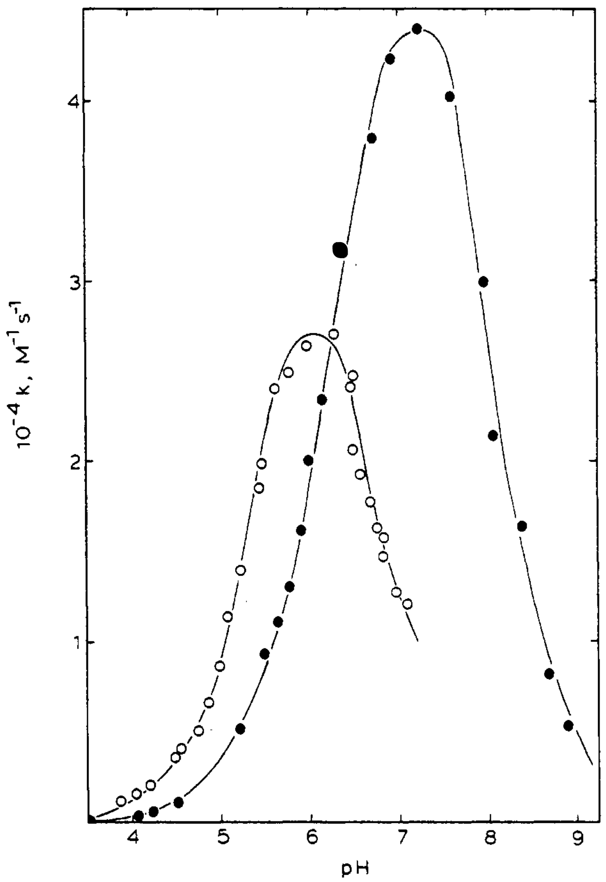

Figure 1. Dependences of the rate constants for the oxidations of $Ni(H_ndiox)^{n+}$ by $Mn(edta)(OH_2)^-$ (○) and $Mn(cdta)(OH_2)^-$ (●) on pH at 25.0 °C and $I = 0.10$ M.

The observed pH dependence, therefore, corresponds to the reaction sequence (H_2O omitted)

$$Ni(Hdiox)^+ + Mn(edta)^- \xrightarrow{k_1} Ni(Hdiox)^{2+} + Mn(edta)^{2-} \quad (8)$$

$$Ni(diox) + Mn(edta)^- \xrightarrow{k_2} Ni(diox)^+ + Mn(edta)^{2-} \quad (9)$$

which leads to the expression in eq 10. The rate and equilibrium

$$k = \frac{k_1K_1/[H^+] + k_2K_1K_2/[H^+]^2}{(1 + K_1/[H^+] + K_1K_2/[H^+]^2)(1 + K_m/[H^+])} \quad (10)$$

constants were calculated from a fit of the experimental data to this expression using a Simplex optimization program. In view of the range of pK_1 and pK_2 reported in the literature, the acid dissociation constants were allowed to vary in the determination. The following rate and equilibrium constants (with estimated errors) were obtained: for $Mn(cdta)(OH_2)^-$, $k_1 = (4.60 \pm 0.15) \times 10^4\ M^{-1}\ s^{-1}$, $k_2 = (1.2 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$, $pK_1 = 6.14 \pm 0.15$, $pK_2 = 7.7 \pm 0.3$, and $pK_m = 7.70 \pm 0.10$; for $Mn(edta)(OH_2)^-$, $k_1 = (1.29 \pm 0.08) \times 10^5\ M^{-1}\ s^{-1}$, $k_2 = (4.3 \pm 0.8) \times 10^5\ M^{-1}\ s^{-1}$, $pK_1 = 6.44 \pm 0.15$, $pK_2 = 7.3 \pm 0.3$, and $pK_m = 5.62 \pm 0.10$. The calculated acid dissociation constants for the nickel(II) and manganese(III) species are in reasonably good agreement with values from previous determinations. While there is considerable uncertainty in the values determined for k_2 and pK_2, much poorer fits were obtained if these terms were not included in the rate expression.

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Table II. Kinetic Parameters for Electron-Transfer Reactions Involving the $Mn(edta)(OH_2)^{2-/-}$ and $Mn(cdta)(OH_2)^{2-/-}$ Couples

reacn no.	reductant	oxidant	$E°$, V	k_{12}, $M^{-1}\ s^{-1}$	k_{11}^{Mn},[a] $M^{-1}\ s^{-1}$
1	$Mn(edta)^{2-}$	$Os(bpy)_3^{3+}$	0.00	1.25×10^4	0.056
2	$Mn(edta)^{2-}$	$Os(phen)_3^{3+}$	0.00	1.44×10^4	0.092
3	$Mn(cdta)^{2-}$	$Os(bpy)_3^{3+}$	0.01	2.03×10^4	0.11
4	$Mn(cdta)^{2-}$	$Os(phen)_3^{3+}$	0.01	4.18×10^4	0.22
5	$Os(5,6\text{-}Me_2phen)_3^{2+}$	$Mn(edta)^-$	0.03	1.54×10^4	0.056
6	$Mn(edta)^{2-}$	$Os(5\text{-}Clphen)_3^{3+}$	0.11	9.69×10^4	0.075
7	$Mn(cdta)^{2-}$	$Os(5\text{-}Clphen)_3^{3+}$	0.12	1.32×10^5	0.085
8	$Mn(edta)^{2-}$	$IrCl_6^{2-}$	0.07	2.96×10^3	0.85
9	$Mn(cdta)^{2-}$	$IrCl_6^{2-}$	0.08	4.61×10^2	0.11
10	$Mn(edta)^{2-}$	$Ni([9]aneN_3)_2^{3+}$	0.13	1.34×10^4	0.54
11	$Mn(cdta)^{2-}$	$Ni([9]aneN_3)_2^{3+}$	0.14	2.69×10^4	0.90
12	$Ni(Hdiox)^{2+}$	$Mn(edta)^-$	0.17	7.0×10^3	0.38
13	$Ni(Hdiox)^+$	$Mn(cdta)^-$	0.17	4.43×10^4	20
14	$Ni(Hdiox)^+$	$Mn(edta)^-$	0.18	1.29×10^5	47
15	Ni(diox)	$Mn(cdta)^-$	0.39	1.2×10^5	1.3
16	Ni(diox)	$Mn(edta)^-$	0.40	4.3×10^5	3.5
17	$Co(5\text{-}Clphen)_3^{2+}$	$Mn(cdta)^-$	0.38	1.48×10^3	0.025
18	$Co(edta)^{2-}$	$Mn(cdta)^-$	0.41	0.9[b]	1.1[c]
19	$Co(edta)^{2-}$	$Mn(edta)^-$	0.42	0.8	0.6[c]
20	$Fe(edta)^{2-}$	$Mn(cdta)^-$	0.69	$\approx 2 \times 10^6$[d]	0.2[e]
21	SO_2^-	$Mn(cdta)^-$	1.07	$\approx 1 \times 10^8$[f]	0.5[g]

[a] Self-exchange rate constant for the $Mn(cdta)^{2-/-}$ or $Mn(edta)^{2-/-}$ couple calculated from the cross-reaction data by using eq 11 (see text). [b] Reference 9. [c] Calculated by using $k_{22} = 2.0 \times 10^{-7}\ M^{-1}\ s^{-1}$ for $Co(edta)^{2-/-}$.[34] [d] Extrapolated from rate and activation parameters in ref 5. [e] Calculated by using $k_{22} = 3.0 \times 10^4\ M^{-1}\ s^{-1}$ for $Fe(edta)^{2-/-}$.[9] [f] Reference 6g. [g] Calculated by using $k_{22} = 3.4 \times 10^2\ M^{-1}\ s^{-1}$ for $SO_2^{-/0}$.[35]

Discussion

In the absence of a direct measurement of the electron-exchange rate constant for a transition-metal-complex couple, estimates may be obtained from semiclassical model calculations or from the application of the Marcus relationship to kinetic data from a series of outer-sphere cross-reactions involving the couple. The cross-reaction kinetic data from this study may be correlated in terms of the Marcus theory equations,[30] which relate the rate constant for a cross-reaction, k_{12}, to the rate constant for the component self-exchange reactions, k_{11} and k_{22}, and the equilibrium constant for the cross reaction, K_{12}, by[31]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (11)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\dfrac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \dfrac{w_{11} + w_{22}}{RT}\right]} \qquad (12)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (13)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{1/2})} \qquad (14)$$

In the above expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of the radii of the ions), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, and $A_{ii} = (4\pi N\sigma^2\nu_n(\delta r)/1000)_{ii}$, where δr is the thickness of the reaction shell (≈0.8 Å).[30] From direct measurements or by the employment of the Marcus relationship to several cross-reactions, the self-exchange rate constants (I = 0.1 M) have been determined for the cross-reactants used in this study [k_{22}, $M^{-1}\ s^{-1}$ (σ_{ii}, Å)]: $Os(bpy)_3^{2+/3+}$ and related couples, 4.2×10^8 (14) (assumed to be the same as the Ru(II)/Ru(III) analogues);[32] $IrCl_6^{3-/2-}$, 2.3×10^5 (6.8);[33] $Ni([9]aneN_3)_2^{2+/3+}$, 6.0×10^3 (I = 1.0 M) (8);[17] $Co(5\text{-}Clphen)_3^{2+/3+}$, 1.0×10^2 (14);[25] $Ni(diox)^{+/2+}$, 4.1×10^4 (10);[27] $Ni(Hdiox)^{+/2+}$, 1.7×10^3;[27] $Ni(diox)^{0/+}$, 4.1×10^2.[27]

The self-exchange rate constants, k_{11}, of the $Mn(edta)(OH_2)^{2-/-}$ and $Mn(cdta)(OH_2)^{2-/-}$ couples calculated from the kinetic data for cross-reactions in this study and from previous reports are presented in Table II. The adherance of the kinetic data to the Marcus relationship is also illustrated in the plot of ln $(k_{12}/k_{22}^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ shown in Figure 2. While the values of k_{11} from a given cross-reaction are generally similar for the two couples, they span several orders of magnitude and show a dependence on the type of cross-reactant employed. In the absence of a direct measurement of k_{11} the best estimate usually is obtained from reactions with complexes of similar size, ligand type, and electron configuration (transfer of an e_g electron). In this respect the reactions with $Ni([9]aneN_3)_2^{3+}$, $Ni(Hdiox)^{2+}$, $Fe(edta)^{2-}$, and $Co(edta)^{2-}$ would appear to be suitable cross-reactants. Considering the data from cross-reactions 8–12, 15,

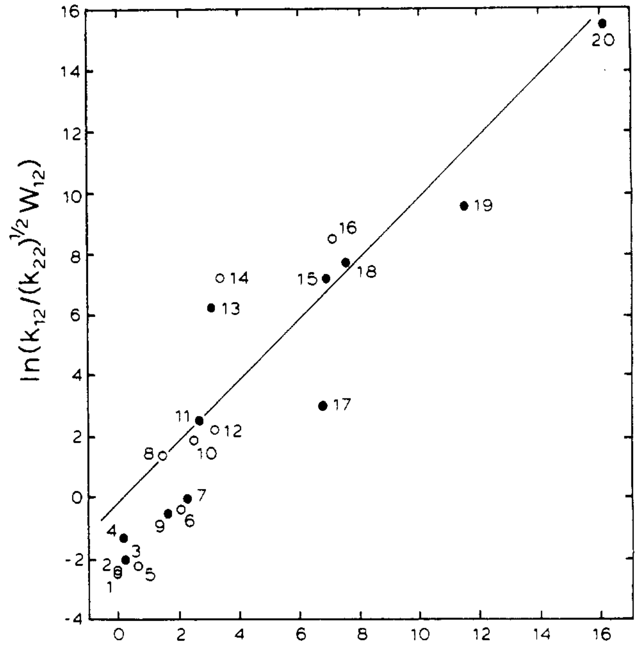

Figure 2. Plot of ln $(k_{12}/k_{22}^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ for electron-transfer cross-reactions involving the $Mn(edta)^{2-/-}$ (○) and $Mn(cdta)^{2-/-}$ (●) couples. The numbering scheme corresponds to the entries in Table II, and the solid line represents the theoretical Marcus curve with k_{11} = 0.7 $M^{-1}\ s^{-1}$.

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16, and 18–21 (Table II), an average value of $k_{11} = 0.7 \pm 0.4$ M^{-1} s^{-1} is calculated. The cross-reactions considered above form a linear correlation in Figure 2 with a slope of 0.97, very close to the theoretical value of unity.[30] If $k_{11} = k_{22} = 0.7$ M^{-1} s^{-1} is used, the cross-reaction rate constant for the oxidation of $Mn(edta)^{2-}$ by $Mn(cdta)^-$ is calculated to be 0.8 M^{-1} s^{-1}, in very good agreement with the reported value of 1.2 M^{-1} s^{-1} at the higher ionic strength of 0.25 M.[9] While the value of k_{11} obtained from the $Mn(cdta)(OH_2)^-$ oxidation of the SO_2^- ion is subject to some uncertainty, it agrees with the average calculated value and (along with the high cross-reaction rate constant) supports an outer-sphere mechanism for this reaction.

The cross-reaction of $IrCl_6^{2-}$ with $Mn(cdta)^{2-}$ yields a k_{11} value that is somewhat smaller than the rate constant from the $Mn(edta)^{2-}$ reaction. It seems likely that this may be a result of the configuration of the respective precursor complexes. The approach of the $IrCl_6^{2-}$ ion to the carboxylate side of the manganese complexes would be electrostatically unfavorable. The presence of the cyclohexane substituent on the diamine side of the $Mn(cdta)^{2-}$ complex would appear to prevent adequate donor-acceptor orbital overlap in this reaction.

The self-exchange rate constants determined from the cross-reactions with the osmium and cobalt tris(polypyridine) complexes are signicantly smaller (average value of 0.09 ± 0.06 M^{-1} s^{-1}) than those derived from the nickel complex reactions. Similar deviations have previously been observed in the cross-reactions of other manganese complexes,[4,5] such as $Mn(H_2O)_6^{3+}$ (as well as other metal aquo ions[36,37]) and $Mn(urea)_6^{3+}$, with metal tris(polypyridine) systems. This behavior has been attributed to several factors, including an incompatibility of the self-exchange pathways ($d\pi$ vs $d\sigma^*$) and hydrophobic/hydrophilic repulsions unfavorable to precursor formations.

The cross-reactions of $Mn(edta)^-$ and $Mn(cdta)^-$ with $Ni(Hdiox)^+$ yield self-exchange rate constants that are significantly larger than the average k_{11} value. A higher than expected rate constant (on the basis of the Marcus relation) has been reported for the reaction between $Ni(Hdiox)^{2+}$ and $Co(edta)^{2-}$ and was rationalized on the basis of a hydrogen-bonded (between the oxime proton and the bound carboxylate on Co) precursor complex.[38] A similar interaction, leading to a strong precursor complex of the type $[Ni(Hdiox)^+, Mn(edta)^-]$, may account for the enhanced rate constant.

In the semiclassical model[31,39] the self-exchange rate constant of a couple, k_{11}, may be expressed as the product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, an electronic factor κ_{el}, a nuclear tunneling factor, and a nuclear factor comprised of the inner-sphere (ΔG_{in}^*) and solvent (ΔG_{out}^*) reorganization energies.

$$k_{11} = K_A \nu_n \kappa_{el} \Gamma_n \exp[-(\Delta G_{in}^* + \Delta G_{out}^*)/RT] \qquad (15)$$

The inner-sphere reorganization energy, required to change the nuclear configurations of the reactants to a common state prior to electron transfer, is a function of the bond length differences (Δd_0) in the two oxidation states and the reduced force constants associated with breathing mode vibrations of the bonds. In comparison with octahedral metal complex couples, to which this model has been applied with success, the $Mn(edta)(OH_2)^{2-/-}$ and $Mn(cdta)(OH_2)^{2-/-}$ couples represent systems requiring much more complicated assessments in terms of their geometry.

The X-ray crystal structure of the $Mn(edta)(OH_2)^{2-}$ ion (in $Mn_3(Hedta)_2 \cdot 10H_2O$)[40] indicates a distorted seven-coordinate geometry about Mn(II), a hexadentate $edta^{4-}$ ligand and a coordinated water molecule. The crystal structures of the $Mn(edta)^-$ (in $K[Mn(edta)] \cdot 2H_2O$)[41] and $Mn(cdta)^-$ (in $K[Mn(cdta)] \cdot H_2O$)[6g] ions reveal distorted octahedral geometries with the closest waters located at distances of 4.08 and 3.6 Å, respectively. There are considerable differences in the Mn–N (0.14–0.17 Å) and Mn–O (0.19–0.37 Å) bond distances between the reduced and oxidized $Mn(edta)^{n-}$ complexes. The large change in the equilibrium bond distances upon oxidation of the Mn(II) species arises from the removal of an electron from an antibonding σ^* orbital of the high-spin d^5 $(d\pi^*)^3(d\sigma^*)^2$ configuration to yield a d^4 species, which is subject to Jahn–Teller distortions. There are also substantial changes in the intramolecular bond angles between the reduced and oxidized species, particularily the O–Mn–O angles between "trans" carboxylate arms.

A definitive prediction of the self-exchange rate constant based on the semiclassical model for this system is unrealistic at present for several reasons. The employment of crystal structural data would require that the species do not change their inner-sphere configurations when in solution. There is considerable evidence for a coordinated water (or hydroxide) on the Mn(III) species in solution, but this is not observed in the solid state. Also, the necessary vibrational frequencies and force constants for the bond stretching and bending motions are not available. A rough semiclassical calculation, made by using vibrational frequencies and force constants estimated from metal aqua and ammine couples[4,39] and ignoring contributions from bond angles changes, places the self-exchange rate constant for the $Mn(edta)(OH_2)^{2-/-}$ couple at $10^{-5\pm2}$ M^{-1} s^{-1}. This value is similar to that measured for the $Co(edta)(OH_2)^{2-/-}$ couple, in which electron exchange also involves an antibonding $d\sigma^*$ orbital.

Recently, a self-exchange rate constant of 17 M^{-1} s^{-1} was reported for the encapsulated $Mn(sar)^{2+}/^{3+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) couple.[42] Crystal structural data indicate a trigonally twisted coordination geometry for the $Mn(sar)^{2+}$ ion, while the $Mn(sar)^{3+}$ ion is in a Jahn–Teller distorted configuration, with substantial changes in the Mn–N distances observed between the two oxidation states.[42] If the ligand configurations of the reduced and oxidized forms are distorted and strained in such a way that they help the system toward the transition state, then a more rapid electron self-exchange may be expected relative to an unstrained system. Calculations of the effect of ligand strain on the reorganization barriers for electron exchange in a similar couple, $Co(sep)^{2+/3+}$ (sep = 1,3,6,8,10,13,16-octaazabicyclo[6.6.6]eicosane) revealed a reduction of 2.5 kcal mol^{-1} in ΔG_{in}^*, when compared with the unstrained $Co(en)_3^{2+/3+}$ (en = ethane-1,2-diamine) couple.[43] The source of the enhanced rate of electron exchange (calculated k_{11}) in the $Mn(edta)(OH_2)^{2-/-}$ and $Mn(cdta)(OH_2)^{2-/-}$ couples, relative to the model calculations, may possibly be associated with ligand strain in these systems. While strain in observed in the glycinate and ethanediamine rings of the $Fe(edta)(OH_2)^-$ and $Fe(cdta)(OH_2)^-$ ions,[44,45] which are free from strain induced by Jahn–Teller distortions, the bond angle and distance distortions are accentuated in the Mn(III) species. An evaluation of the magnitude of this effect, however, would require a knowledge of the structure of the $Mn(edta)(OH_2)^-$ ion in solution.

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Registry No. $Mn(edta)(OH_2)^{2-}$, 96042-39-6; $Mn(edta)(OH_2)^-$, 36444-07-2; $Mn(edta)(OH)^{2-}$, 120410-84-6; $Mn(edta)(OH_2)^-$, 36444-08-3; $Os(5,6\text{-}Me_2phen)_3^{2+}$, 62011-19-2; $Ni(Hdiox)^{2+}$, 83875-36-9; $Ni(Hdiox)^+$, 60306-03-8; Ni(diox), 59980-38-0; $Co(5\text{-}Clphen)_3^{2+}$, 47860-29-7; $Os(bpy)_3^{3+}$, 23648-06-8; $Os(phen)_2^{3+}$, 47837-53-6; $Os(5\text{-}Clphen)_3^{3+}$, 70101-70-1; $IrCl_6^{2-}$, 16918-91-5; $Ni([9]aneN_3)_2^{3+}$, 86709-81-1.

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