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# Kinetics of the Oxidation of Metal Complexes by Manganese(III) Aquo Ions in Acidic Perchlorate Media: The $Mn(H_2O)_6{}^{2+}$–$Mn(H_2O)_6{}^{3+}$ Electron-Exchange Rate Constant

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The kinetics of the reduction of manganese(III) aquo ions by a series of $ML_3{}^{2+}$ complexes (M = Os, Fe, Ru and L is 2,2′-bipyridine and 1,10-phenanthroline or a substituted derivative), by $Fe(H_2O)_6{}^{2+}$ ions, and by $Ni(H_2oxime)^{2+}$, $Ni([14]aneN_4)^{2+}$, and $Ni(Me_6[14]4,11\text{-}dieneN_4)^{2+}$ were investigated in acidic perchlorate media at 25.0 °C. The second-order rate constants are given by $\{(k_1 + k_2K_{1h}/[H^+]\}/(1 + K_{1h}/[H^+])$, where $k_1$ and $k_2$ are rate constants for the $Mn^{3+}$ and $MnOH^{2+}$ pathways and $K_{1h}$ is the hydrolysis constant of $Mn(H_2O)_6{}^{3+}$ ($K_{1h} = 1.02 \pm 0.14$ M, $\mu = 2.0$ M). The presence of a significant $MnOH^{2+}$ pathway for the Ni(II) complexes and for $Fe(H_2O)_6{}^{2+}$ is interpreted in terms of an inner-sphere mechanism. An electron-exchange rate constant of $1 \times 10^{-9}$ $M^{-1}$ $s^{-1}$ for the $Mn(H_2O)_6{}^{2+/3+}$ couple was estimated from the $ML_3{}^{2+}/Mn^{3+}$ cross-reaction data by using a modified Marcus relationship. This value is lower than the exchange rate constant of $10^{-4\pm1}$ $M^{-1}$ $s^{-1}$ calculated by using a semiclassical outer-sphere model and is also lower than the value of $4 \times 10^{-3}$ $M^{-1}$ $s^{-1}$ calculated from the oxidation of $Fe(H_2O)_6{}^{2+}$ by $Mn(H_2O)_6{}^{3+}$. The kinetics of the oxidation of $Mn(H_2O)_6{}^{2+}$ by $Co(H_2O)_6{}^{3+}$ were also studied, and the redox reactions of $Mn(H_2O)_6{}^{3+}$ and $Co(H_2O)_6{}^{3+}$ are compared. Various mechanisms for the reactions of these strong oxidants are considered.

## Introduction

The experimental[1-5] and theoretical[6-8] aspects of electron-exchange reactions of metal aquo ions have been investigated for over three decades. Recently, structural studies[9-11] have been used in conjunction with kinetic measurements to probe the role of inner-sphere configuration changes in determining electron-exchange rates. These studies have demonstrated the relationship between the nature of the donor–acceptor orbital ($d\pi$ vs. $d\sigma^*$) and the magnitude of the exchange rate constant. For $M(H_2O)_6{}^{2+/3+}$ couples such as $Cr(H_2O)_6{}^{2+/3+}$, in which the transferring electron resides in an antibonding $d\sigma^*$ orbital, a large difference ($\Delta d^0 \approx 0.20$ Å)[9] in the M–O bond distances between the oxidized and reduced forms is accompanied by a very slow electron-exchange rate ($k_{11} \leq 2 \times 10^{-5}$ $M^{-1}$ $s^{-1}$).[2]

The $Mn(H_2O)_6{}^{2+/3+}$ exchange, which also involves the transfer of a $d\sigma^*$ electron, has received comparatively little attention, perhaps due to the experimental difficulties encountered with the $Mn(H_2O)_6{}^{3+}$ ion. It is a strong oxidant, is partially hydrolyzed even in very acidic media, and is unstable with respect to disproportionation to $Mn^{2+}$ and $MnO_2$.[12] However, if prepared in strongly acidic solution in the presence of excess $Mn^{2+}$, the $Mn^{3+}$ ion is stable even in noncomplexing perchlorate media. There have been a number of kinetic studies on the reaction of $Mn^{3+}$ with a variety of organic[13-19] and inorganic reductants,[20,21] but relatively few for which an outer-sphere mechanism has been assigned.

In the present paper, we report the results of a kinetic investigation of the reduction of $Mn(H_2O)_6{}^{3+}$ by tris(polypyridine) complexes of osmium(II), iron(II), and ruthenium(II), by $Fe(H_2O)_6{}^{2+}$, and by several nickel(II) chelate complexes. The oxidation of $Mn(H_2O)_6{}^{2+}$ by $Co(H_2O)_6{}^{3+}$ was also studied. The $Mn(H_2O)_6{}^{2+/3+}$ exchange rate constant is estimated from the cross-reaction data and is also calculated by using a semiclassical model.[22] The electron-exchange behavior of the $Mn(H_2O)_6{}^{2+/3+}$ couple is compared with that of other transition-metal aquo ions.

## Experimental Section

**Materials.** Solutions containing manganese(III) and cobalt(III) perchlorate were prepared by the electrochemical oxidation of 0.10 M solutions of $Mn(ClO_4)_2{\cdot}6H_2O$ (G. F. Smith) and $Co(ClO_4)_2{\cdot}6H_2O$ (Alfa), respectively, in 3.0 M $HClO_4$ at a platinum-mesh electrode. The electrolyses were performed at 0 °C, and the resulting solutions were filtered and stored at 0 °C until use. Fresh Mn(III) solutions ($(2-5) \times 10^{-3}$ M) were prepared daily and analyzed spectrophotometrically at 470 nm; $\epsilon = 80$ $M^{-1}$ $cm^{-1}$ in 3.0 M $HClO_4$. Iron(II) perchlorate was prepared by the electrochemical reduction of a 0.10 M solution of the iron(III) salt in 2.0 M $HClO_4$ at a platinum electrode and analyzed as $Fe(phen)_3{}^{2+}$ at 510 nm ($\epsilon = 11\,100$ $M^{-1}$ $cm^{-1}$). Lithium perchlorate was prepared by the neutralization of $HClO_4$ with $Li_2CO_3$ followed by several recrystallizations from distilled water. Stock solutions were analyzed by the titration with sodium hydroxide of an aliquot that had been passed through a Dowex 50W-X8 (50–100 mesh) ion-exchange column in the $H^+$ form.

The tris(polypyridine) complexes $ML_3{}^{2+}$, where L is 2,2′-bipyridine and 1,10-phenanthroline or a substituted derivative of bpy or phen and M is osmium,[23] iron,[24] and ruthenium,[24] were prepared as chloride or perchlorate salts as described previously. Published procedures were used to synthesize[25] the nickel(II) complexes $[Ni([14]aneN_4)](ClO_4)_2$,[26] $[Ni(Me_6[14]4,11\text{-}dieneN_4)](ClO_4)_2$,[27] and $[Ni(H_2oxime)](ClO_4)_2$.[28]

**Kinetic Measurements.** Kinetic studies were performed on a Durrum D-110 stopped-flow apparatus or a Cary 210 spectrophotometer. With the exception of the reduction by $Fe(H_2O)_6{}^{2+}$, where $[Fe^{2+}] \geq 10[Mn^{3+}]$, and the oxidation by $Co(H_2O)_6{}^{3+}$, where $[Mn^{2+}] \geq 10^2[Co(III)]$, all experiments were performed under pseudo-first-order conditions with

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Mn(III) in excess. In order to suppress the disproportionation of Mn(III) to $Mn^{2+}$ and $MnO_2$, $Mn^{2+}$ was present in at least a 100-fold excess. Acid concentrations were varied from 0.50 to 1.95 M with the ionic strength maintained at 2.0 M with added $LiClO_4$. The temperature was maintained at 25.0 ± 0.1 °C by means of an external water bath. Plots of ln $(A_\infty - A_t)$ or ln $(A_t - A_\infty)$ against time were linear for at least 3 half-lives, yielding pseudo-first-order rate constants that were reproducible to within 5%.

## Results

The rate of reduction of Mn(III) by $OsL_3^{2+}$, $FeL_3^{2+}$, and $RuL_3^{2+}$ (L is 2,2′-bipyridine and 1,10-phenanthroline or a substituted derivative of bpy or phen) was first order in $[ML_3^{2+}]$ and [Mn(III)]

$$-\frac{d[ML_3^{2+}]}{dt} = k_0[ML_3^{2+}][Mn(III)] \quad (1)$$

and increased with increasing acid concentration over the range $[H^+] = 0.50–1.95$ M ($\mu = 2.0$ M, 25 °C). The measured $k_0$ values are presented in supplementary Table I. The acid dependence of the rate constants is attributed to the hydrolysis of $Mn(H_2O)_6^{3+}$:

$$Mn(H_2O)_6^{3+} \overset{K_{1h}}{\rightleftharpoons} Mn(H_2O)_5OH^{2+} + H^+ \quad (2)$$

$$Mn^{3+} + ML_3^{2+} \xrightarrow{k_1} Mn^{2+} + ML_3^{3+} \quad (3)$$

$$MnOH^{2+} + ML_3^{2+} \xrightarrow{k_2} MnOH^+ + ML_3^{3+} \quad (4)$$

The above reactions suggest a rate law of the form shown in eq 5, which may be rearranged to give eq 6. In order to fit the kinetic

$$k_0 = \frac{k_1 + k_2K_{1h}/[H^+]}{1 + K_{1h}/[H^+]} \quad (5)$$

$$k_0(K_{1h} + [H^+]) = k_1[H^+] + k_2K_{1h} \quad (6)$$

data to eq 6, a value of $K_{1h}$ is needed. This was obtained from spectrophotometric measurements. The molar absorptivity $\epsilon$ of a Mn(III) solution at a given $[H^+]$ can be expressed in terms of the molar absorptivities $\epsilon_1$ and $\epsilon_2$ of the $Mn(H_2O)_6^{3+}$ and $Mn(H_2O)_5OH^{2+}$ ions, respectively, by means of eq 7, which can be rearranged to eq 8. The visible spectrum of $Mn^{3+}$ is insensitive

$$\epsilon([H^+] + K_{1h}) = \epsilon_1[H^+] + \epsilon_2K_{1h} \quad (7)$$

$$\left(1 - \frac{\epsilon_1}{\epsilon}\right)[H^+] = \frac{K_{1h}\epsilon_2}{\epsilon} - K_{1h} \quad (8)$$

to ionic strength ($\mu = 1–6$ M) in perchlorate media,[12,29] and at 470 nm, a $\lambda_{max}$ for both $Mn^{3+}$ and $MnOH^{2+}$, $\epsilon_1 = 58$ $M^{-1}$ $cm^{-1}$ and $\epsilon_2 = 165$ $M^{-1}$ $cm^{-1}$. The $Mn^{2+}$ ion, even when present in large excess, does not interfere with the absorbance measurements ($\epsilon \simeq 0.004$ $M^{-1}$ $cm^{-1}$).[30] The absorbance at 470 nm was measured for $6.0 \times 10^{-4}$ M Mn(III) solution at acidities from 0.4 to 1.8 M $HClO_4$ ($\mu = 2.0$ M with $LiClO_4$), and $(1 - \epsilon_1/\epsilon)[H^+]$ was plotted against $\epsilon_2/\epsilon$. A $K_{1h}$ value of 1.02 ± 0.14 M was derived from this plot.[31] With use of this value, plots of $k_0(K_{1h} + [H^+])$ against $[H^+]$ (eq 6) were constructed (supplementary Figure 1). The data for the $ML_3^{2+}$ complexes displayed linear $[H^+]$ dependences with negligible intercepts ($k_2 = 0$). The values of $k_1$ at 25.0 °C determined from the slopes of these plots are summarized in Table I.

**Table I.** Acid-Independent Rate Constants for the Reaction of $ML_3^{2+}$ Complexes with $Mn(H_2O)_6^{3+}$

| reductant | $E°$, V[a] | $k_{12}$, $M^{-1}$ $s^{-1}$ [b] |
|---|---|---|
| $Os(4,4'-(CH_3)_2-bpy)_3^{2+}$ | 0.66 | $2.5 \times 10^6$ (2.0) |
| $Os(phen)_3^{2+}$ | 0.78 | $7.0 \times 10^5$ (2.0) |
| $Os(bpy)_3^{2+}$ | 0.78 | $5.2 \times 10^5$ (2.0) |
| $Os(5-Cl-phen)_3^{2+}$ | 0.89 | $1.2 \times 10^5$ (2.0) |
| $Fe(5-CH_3-phen)_3^{2+}$ | 0.96 | $3.3 \times 10^4$ (3.0)[c] |
| $Fe(bpy)_3^{2+}$ | 1.02 | $9.1 \times 10^3$ (2.0) |
| $Fe(phen)_3^{2+}$ | 1.00 | $2.0 \times 10^4$ (3.0)[c] |
| $Fe(5-Cl-phen)_3^{2+}$ | 1.08 | $3.8 \times 10^3$ (3.0)[c] |
| $Fe(5-NO_2-phen)_3^{2+}$ | 1.20 | $5.5 \times 10^2$ (3.0)[c] |
| $Ru(4,4'-(CH_3)_2-bpy)_3^{2+}$ | 1.09 | $6.1 \times 10^3$ (2.0) |
| $Ru(bpy)_3^{2+}$ | 1.22 | $7.2 \times 10^2$ (2.0) |
| $Ru(5-NO_2-phen)_3^{2+}$ | 1.42 | $2.2 \times 10$ (2.0) |

[a] Reduction potentials of $ML_3^{3+}$ extrapolated from values in ref 45 and 46. [b] Cross-reaction rate constants at 25 °C; ionic strengths in parentheses. [c] Reference 20.

The rate constants for the oxidations of $Ni([14]aneN_4)^{2+}$ and $Ni(Me_6[14]4,11\text{-}dieneN_4)^{2+}$ to the corresponding nickel(III) species by Mn(III) decrease with increasing $[H^+]$ (Table I). For $Ni([14]aneN_4)^{2+}$ the values of $k_1$ and $k_2$ determined from a plot of $k_0(K_{1h} + [H^+])$ against $[H^+]$ (supplementary Figure 2) are $8.2 \times 10^3$ and $1.8 \times 10^4$ $M^{-1}$ $s^{-1}$, respectively, while for $Ni(Me_6[14]4,11\text{-}dieneN_4)^{2+}$, $k_1 = 28$ $M^{-1}$ $s^{-1}$ and $k_2 = 48$ $M^{-1}$ $s^{-1}$. A similar acid dependence, with $k_1 = 5.2 \times 10^3$ $M^{-1}$ $s^{-1}$ and $k_2 = 2.0 \times 10^4$ $M^{-1}$ $s^{-1}$, was observed for the reduction of Mn(III) by $Fe(H_2O)_6^{2+}$ (supplementary Table II).

The oxidation of $Ni(H_2oxime)^{2+}$ by Mn(III) yields a nickel(IV) species, $Ni(oxime)^{2+}$, in two one-electron steps with the rate-determining step being the oxidation of $Ni(H_2oxime)^{2+}$ to a nickel(III) intermediate,[33,34] followed by a rapid oxidation to $Ni(oxime)^{2+}$:

$$Mn^{3+} + Ni(H_2oxime)^{2+} \xrightarrow{k_1} Mn^{2+} + Ni(Hoxime)^{2+} + H^+ \quad (9)$$

$$MnOH^{2+} + Ni(H_2oxime)^{2+} \xrightarrow{k_2} MnOH^+ + Ni(Hoxime)^{2+} + H^+ \quad (10)$$

$$Mn^{3+} + Ni(Hoxime)^+ \xrightarrow{k_3} Mn^{2+} + Ni(Hoxime)^{2+} \quad (11)$$

$$Mn(III) + Ni(Hoxime)^{2+} \xrightarrow{fast} Mn^{2+} + Ni(oxime)^{2+} + H^+ \quad (12)$$

The rate law for this reaction may be expressed in the form

$$k_0(K_{1h} + [H^+]) = k_1[H^+] + (k_2K_{1h} + k_3K_a)$$

where $K_a$ is the acid dissociation for $Ni(H_2oxime)^{2+}$ ($pK_a = 5.90$).[35a] It is not possible to distinguish between eq 10 and eq 11 from the rate law and the limited range of $[H^+]$ over which $k_0$ was measured (Figure 2). The observed rate constants (Table I) increase with $[H^+]$, and the values of $k_1$ and $(k_2K_{1h} + k_3K_a)$ determined from a plot of $k_0(K_{1h} + [H^+])$ against $[H^+]$ are 780 $M^{-1}$ $s^{-1}$ and 86 $s^{-1}$, respectively.

The kinetics of the oxidation of $Mn(H_2O)_6^{2+}$ by cobalt(III) aquo ions were studied over an acid concentration range of 0.25–1.75 M at an ionic strength of 2.0 M ($H^+/LiClO_4$). The observed rate constants (supplementary Table III) increased with a decrease in $[H^+]$, consistent with a rate law of the form in eq 5 and suggestive of analogous $Co(H_2O)_6^{3+}$ ($k_1$) and $Co(H_2O)_5OH^{2+}$ ($k_2$) pathways. With $K_h << [H^+]$ for Co(III) aquo ions, a plot of $k_0$ against $1/[H^+]$ yielded $k_1 = 48$ $M^{-1}$ $s^{-1}$ and $k_2 = 4.8 \times 10^4$ $M^{-1}$ $s^{-1}$ ($K_h = 2 \times 10^{-3}$ M).

In order to compare the relative reactivities of $Mn(H_2O)_6^{3+}$ and $Co(H_2O)_6^{3+}$ toward a series of outer-sphere reductants, the

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(31) The $K_{1h}$ value determined in this work may be compared with 0.93 ± 0.06 M at $\mu = 4.0$ M[29] and 1.05 ± 0.26 M at $\mu = 5.6$ M[32a] determined in other spectrophotometric studies. On the other hand, Biederman and Palombari[32b] have reported $K_{1h} = 2.5 \pm 0.6$ M for $Mn(H_2O)_6^{3+}$ and $K_{2h} = 0.5 \pm 0.3$ M for $Mn(H_2O)_5OH^{2+}$ using electrochemical measurements at $\mu = 3.0$ M. The $K_{1h}/K_{2h}$ ratio determined in the electrochemical work seems unreasonably low for a +3 aquo ion, and we shall assume that $K_{2h}/[H^+] << 1$ under the conditions used in the present study.

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kinetics of the reduction of cobalt(III) aquo ions by several tris(polypyridine) complexes were studied. At 25.0 °C in 2.0 M $HClO_4$ ($k_{12}$ was independent of [$H^+$] over the range 0.50–2.0 M) the following rate constants ($M^{-1}\ s^{-1}$) were measured: $Os(bpy)_3^{2+}$, $6.9 \times 10^4$; $Os(5\text{-}Cl\text{-}phen)_3^{2+}$, $5.5 \times 10^4$; $Fe(5\text{-}NO_2\text{-}phen)_3^{2+}$, $9.8 \times 10^2$; $Ru(bpy)_3^{2+}$, $3.3 \times 10^3$; $Ru(5\text{-}NO_2\text{-}phen)_3^{2+}$, $2.3 \times 10^2$. The rate constants for the oxidation of $Fe(H_2O)_6^{2+}$ were also measured: the values of $k_1$ and $k_2$ for oxidation by $Co(H_2O)_6^{3+}$ and $Co(H_2O)_5OH^{2+}$ were 48 and $2.1 \times 10^5\ M^{-1}\ s^{-1}$ (based on $K_h = 2 \times 10^{-3}$ M), respectively, at 25.0 °C and 2.0 M ionic strength ($H^+/LiClO_4$), in good agreement with earlier values.[35b]

## Discussion

Several of the systems studied feature both acid-independent and inverse-acid ($MnOH^{2+}$) pathways. For an outer-sphere process the $MnOH^{2+}$ rate constant would be expected to be very much smaller than the corresponding rate constant for $Mn^{3+}$. The reduction potential of the $MnOH^{2+}/MnOH^+$ couple is ~0.95 V ($pK_h(Mn^{2+}) = 10.5$)[36a] compared with 1.56 V for $Mn^{3+}/Mn^{2+}$, and if the self-exchange rate constants of the $Mn^{2+/3+}$ and $MnOH^{+/2+}$ couples are assumed to be comparable, $k_1$ should be much greater than $k_2$ for a given outer-sphere reductant. The kinetics of the reduction of Mn(III) by tris(polypyridine) complexes of osmium(II), iron(II), and ruthenium(II) follow a rate law in which the $Mn^{3+}$ ion is the main oxidizing species with the absence of a significant inverse-acid pathway. The inverse-acid pathway is also absent in the reactions of Mn(III) with a series of *N*-alkylphenothiazines.[19] These reactions very probably proceed by an outer-sphere mechanism.

The $Mn(H_2O)_6^{3+}$ pathway predominates in the reaction of Mn(III) with $Ni(H_2oxime)^{2+}$. The intercept in Figure 2 may be attributed to either $Mn^{3+}/Ni(Hoxime)^+$ or $MnOH^{2+}/Ni(H_2oxime)^{2+}$ pathways; both are consistent with the rate law. If only the former process were occurring, then a second-order rate constant of $\sim 7 \times 10^7\ M^{-1}\ s^{-1}$ is implicated by the intercept ($K_a = 1.3 \times 10^{-6}\ M^{-1}$).[35a] This value is larger than the rate constant for the $Mn^{3+}/Ni(H_2oxime)^{2+}$ reaction, consistent with the relative thermodynamic driving forces for the oxidation of $Ni(H_2oxime)^{2+}$ ($E° = 1.23$ V)[33] and $Ni(Hoxime)^+$ ($E° = 0.64$ V)[34] by $Mn^{3+}$.

A $MnOH^{2+}$ pathway with $k_2 > k_1$ is observed in the reaction of the two nickel(II) macrocycle complexes. Since these complexes are not significantly hydrolyzed below pH 12,[36b] the $k_2$ pathway cannot readily be ascribed to the reaction of $Mn^{3+}$ with a deprotonated Ni(II) species. The square-planar nickel(II) macrocycles have axial positions which are accessible to the $MnOH^{2+}$ ion for possible inner-sphere bridging; such a bridged complex would promote overlap of the $\sigma^*$d nickel(II) and manganese(III) orbitals. The oxidations of nickel(II)[37] and cobalt(II)[38] macrocyclic complexes by aquo Co(III) ions also proceed predominantly by a $CoOH^{2+}$ pathway. An outer-sphere hydroxide-mediated pathway has been proposed for the reaction of $CoOH^{2+}$ with the square-planar nickel(II) macrocycle.[37] A similar pathway could also operate in the $MnOH^{2+}$ reaction, but there is very little evidence at this time to support such an interpretation.

**The $Mn(H_2O)_6^{2+/3+}$ Exchange Rate Constant.** Direct measurements of the $Mn(H_2O)_6^{2+/3+}$ self-exchange rate constant have been attempted by Adamson[39] and by Diebler and Sutin[20] using $Mn^{54}$ labeling. A rapid exchange was observed in both studies, but this was attributed to induction by the separation procedure used. In the absence of a direct measurement the exchange rate constant may be estimated from the cross-reaction data or calculated from the semiclassical model.[9,22] In order to provide a point of reference for the cross-reaction results, we first estimate the exchange rate theoretically.

In terms of the semiclassical model the exchange rate constant is the product of a preequilibrium constant $K_A$, an effective nuclear vibration frequency $\nu_n$, an electronic factor $\kappa_{el}$, and a nuclear factor $\kappa_n$ (eq 13). For the $Mn(H_2O)_6^{2+/3+}$ couple, the preequilibrium

$$k = K_A \nu_n \kappa_{el} \kappa_n \qquad (13)$$

constant is calculated[9,22] to be 0.050 $M^{-1}$ at $\mu = 2.0$ M based on a Mn–Mn separation of 6.5 Å. For an exchange reaction the nuclear factor is given by eq 14, where $\Gamma_\lambda$ is a nuclear tunneling

$$\kappa_n = \Gamma_\lambda \exp[-(\lambda_{out} + \lambda_{in})/4RT] \qquad (14)$$

factor and $\lambda_{out}$ and $\lambda_{in}$ are the solvent and inner-shell reorganization energies, respectively. The value of $\lambda_{out}$ depends only upon the sizes of the complexes, their separation, and the properties of the solvent while $\lambda_{in}$ depends upon the inner-shell nuclear configuration change accompanying the electron transfer and is given by

$$\lambda_{in} = \tfrac{1}{2}\textstyle\sum f_i(\Delta d_0)_i^2 \qquad (15)$$

where $f_i$ is the reduced force constant for the $i$th inner-shell vibration and $(\Delta d_0)_i$ is the bond length difference for bond $i$ in the two oxidation states.

The $Mn(H_2O)_6^{2+/3+}$ exchange reaction involves the transfer of an electron from a high-spin $d^5$ [$(\pi d)^3(\sigma^* d)^2$] $Mn^{2+}$ ion to a high-spin $d^4$ [$(\pi d)^3(\sigma^* d)^1$] $Mn^{3+}$ ion. The electron exchange involves a ligand-directed metal orbital of antibonding character and should, therefore, be accompanied by a substantial change in the Mn–O bond distances. The Mn–O distance in $Mn(H_2O)_6^{2+}$ has been reported as 2.181 Å in $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 2.177 Å in solution, determined with use of X-ray diffraction[40] and EXAFS[41] techniques, respectively. The Mn–O distance in $Mn(H_2O)_6^{3+}$ in a cesium alum, determined by X-ray diffraction methods, is 1.991 Å;[42] consequently $\Delta d_0$, the difference in the manganese–oxygen bond lengths in the two oxidation states, is 0.19 ± 0.01 Å. The reduced force constant for the Mn–O bonds in the $Mn(H_2O)_6^{2+/3+}$ couple is calculated to be $2.0 \times 10^5$ dyn $cm^{-1}$ by using stretching frequencies of 395 $cm^{-1}$ for $Mn(H_2O)_6^{2+}$[43a] and 490 $cm^{-1}$ for $Mn(H_2O)_6^{3+}$.[43b] From these parameters the inner-shell reorganization energy is calculated to be 15.5 kcal $mol^{-1}$ while the solvent reorganization energy calculated from the dielectric continuum expression[6] is 6.9 kcal $mol^{-1}$. With the nuclear tunneling correction,[22] the nuclear factor $\kappa_n$ is calculated to be $2 \times 10^{-16}$. The nuclear frequency $\nu_n$ is related to the solvent and inner-sphere reorganization terms;[22] for $Mn(H_2O)_6^{2+/3+}$ $\nu_n = 1.1 \times 10^{13}\ s^{-1}$. With use of the above parameters, $k_{11}/(\kappa_{el})_{11}$ for the $Mn(H_2O)_6^{2+/3+}$ exchange is calculated to be $10^{-4\pm1}\ M^{-1}\ s^{-1}$.

Next we consider the cross-reaction data in terms of a recent modification[22] of the Marcus relationship, which relates 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

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (16)$$

where

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

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

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

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(36) (a) Smith, R. M.; Martell, A. E. "Critical Stability Constants": (a) Plenum Press: New York, 1976; Vol. 4, p 5. (b) Plenum Press: New York, 1982; Vol. 5, p 185.

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(40) Montgomery, M.; Chastain, R. V.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 731.

(41) Sham, T. K.; Hastings, J. B.; Perlman, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5904.

(42) Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 2105. The structure of the $Mn(H_2O)_6^{3+}$ does not reveal appreciable Jahn–Teller distortion; the manganese–oxygen bond lengths are similar, and there is no evidence for exceptionally large thermal parameters.

(43) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 228. (b) The Mn–O stretching frequency in $Mn(H_2O)_6^{3+}$ has not been determined but is assumed to be the same as for $Cr(H_2O)_6^{3+}$.

**Table II.** Calculated Self-Exchange Rate Constants $k_{11}$ for $Mn(H_2O)_6^{2+/3+}$ from Cross-Reaction Rate Constants at 25 °C and 2.0 M Ionic Strength

| reactant | $E°$, V[a] | $k_{12}$, $M^{-1}$ $s^{-1}$ [b] | $k_{11}$, $M^{-1}$ $s^{-1}$ [c] |
|---|---|---|---|
| $ML_3^{3+}$ | 1.4–0.6 | $10–10^6$ | $1 \times 10^{-9}$ |
| $Fe(H_2O)_6^{2+}$ | 0.74 | $5.2 \times 10^3$ | $3 \times 10^{-6}$ |
| $Ni([14]aneN_4)^{2+}$ | 0.96 | $8.2 \times 10^3$ | $1 \times 10^{-5}$ |
| $Ni(H_2oxime)^{2+}$ | 1.23 | $7.8 \times 10^2$ | $6 \times 10^{-4}$ |
| $Co(H_2O)_6^{3+}$ | 1.86 | 48 | $4 \times 10^{-3}$ |

[a] Reduction potentials from ref 49 and 50 and from: Warnquist, B. *Inorg. Chem.* **1970**, *9*, 682. [b] Cross-reaction rate constants at 25 °C; ionic strengths in parentheses. [c] Calculated self-exchange rate constant for $Mn(H_2O)_6^{2+/3+}$ using eq 16: $k_{22} = 4.2$ $M^{-1}$ $s^{-1}$ ($\mu = 0.55$ M) for $Fe(H_2O)_6^{2+/3+}$;[1] $k_{22} = 3 \times 10^3$ $M^{-1}$ $s^{-1}$ ($\mu = 1.0$ M) for $Ni(H_2oxime)^{2+/3+}$;[33] $k_{22} = 2 \times 10^3$ $M^{-1}$ $s^{-1}$ ($\mu = 1.0$ M) for $Ni([14]aneN_4)^{2+/3+}$ (McAuley, A.; Macartney, D. H.; Oswald, T. *J. Chem. Soc., Chem. Commun.* **1982**, 274); $k_{22} = 13.5$ $M^{-1}$ $s^{-1}$ ($\mu = 3.0$ M) for $Co(H_2O)_6^{2+/3+}$.[4] These rate constants were used in Figure 3 together with the following values: $k_{22} = 4 \times 10^8$ $M^{-1}$ $s^{-1}$ ($\mu = 0.10$ M) for $OsL_3^{2+/3+}$ and $RuL_3^{2+/3+}$ (Young, R. C.; Keene, F. R.; Meyer, t. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468); $k_{22} = 3 \times 10^8$ $M^{-1}$ $s^{-1}$ ($\mu = 5.5$ M) for $FeL_3^{2+/3+}$ (Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18*, 515).

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 $\sigma_{ij}$ (taken equal to the sum of the radii of the ions), $D_s$ is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, $A_{ii} = (4\pi N\sigma^2\nu_n(\delta r)/1000)_{ii}$, and $\delta r$ is the thickness of the reaction shell. The values of $\sigma_{ij}$ used in these calculations are 13.6 Å for $ML_3^{2+/3+}$ and 6.5 Å for $Mn^{2+/3+}$, and $A_{ii}A_{jj}$ was taken equal to $10^{25}$ $M^{-2}$ $s^{-2}$.

The application of eq 16 to the cross-reaction rate constants for the $Mn^{3+}/ML_3^{2+}$ reactions (Table II) yields values for the $Mn(H_2O)_6^{2+/3+}$ self-exchange rate constant in the range of $(0.5–1.6) \times 10^{-9}$ $M^{-1}$ $s^{-1}$.[44-46] A plot of ln $[k_{12}/((k_{11}k_{22})^{1/2}W_{12})]$ against ln $(K_{12}f_{12})^{1/2}$ with $k_{11} = 1 \times 10^{-9}$ $M^{-1}$ $s^{-1}$ is presented in Figure 1. An even lower $Mn(H_2O)_6^{2+/3+}$ exchange rate constant ($1 \times 10^{-10}$ $M^{-1}$ $s^{-1}$) is implicated in the reduction of $Mn(H_2O)_6^{3+}$ by a series of *N*-alkylphenothiazines.[19] On the other hand, a $Mn(H_2O)_6^{2+/3+}$ exchange rate of $3 \times 10^{-6}$ $M^{-1}$ $s^{-1}$ is required to fit the rate constant for the $Mn(H_2O)_6^{3+}–Fe(H_2O)_6^{2+}$ reaction[20] and a somewhat higher exchange rate is required for the reactions of $Mn(H_2O)_6^{3+}$ with $Ni([14]aneN_4)^{2+}$, $Ni(H_2oxime)^{2+}$, and $Co(H_2O)_6^{3+}$ (Table II). Thus the $Mn(H_2O)_6^{2+/3+}$ exchange rate constants calculated from eq 16 span a range of 5 orders of magnitude depending on the system considered.

If it is assumed that the $Mn(H_2O)_6^{2+/3+}$ exchange is adiabatic[47] (i.e., that $\kappa_{el} = 1$ for this exchange), then the $Mn(H_2O)_6^{2+/3+}$ exchange rate constant estimated from the $ML_3^{2+}$ cross-reaction data (using eq 16) is a factor $10^5$ smaller than the value $10^{-4\pm1}$ calculated from the semiclassical expression. Similar behavior is also observed in the reactions of the $ML_3^{3+}$ (M = Os,[48,49] Fe,[49] Ru,[49] and Ni[50]) complexes with $Fe(H_2O)_6^{2+}$ and is not uncommon for reactions involving metal aquo ions.[49,50] It has also been reported that reactions of the *N*-alkylphenothiazines with $Fe(H_2O)_6^{3+}$ are 300–500 times slower than predicted,[51] similar to the discrepancy observed in their reactions with $Mn(H_2O)_6^{3+}$. Among the various explanations put forward to account for the breakdown of eq 16 in certain systems are nonadiabaticity of the cross reactions, the interpenetration of ligands, differences in the solvation of hydrophobic/hydrophilic reactants, anharmonicity, and a change in mechanism.[24,49,50,52-55] It is likely that the first of these factors is primarily responsible for the relatively slow rates of the $Mn^{3+}/ML_3^{2+}$ reactions:[50] thus when the exchange reactions are adiabatic (or only marginally nonadiabatic), a cross reaction with $\kappa_{el} \approx 10^{-2}$ will yield an apparent self-exchange rate constant that is a factor $10^4$ smaller than the real (outer-sphere) value. Differences in the solvation of the reactants could also be important in the $Mn^{3+}/ML_3^{2+}$ systems. In contrast to the $ML_3^{2+}$ reactions, the $Mn(H_2O)_6^{2+/3+}$ exchange rate calculated from the other reactions in Table II are in better agreement with the exchange rate calculated from the semiclassical model. There is, however, a tendency for the exchange rates calculated from eq 16 to decrease with increasing driving force, a trend that has previously been remarked upon.[49,56,57]

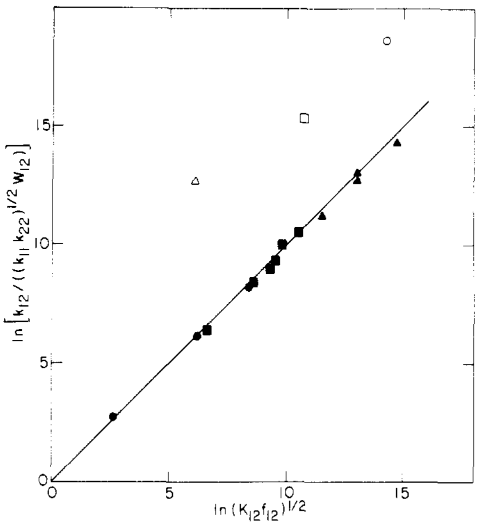

**Figure 1.** Plot of ln $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ for the reduction of $Mn(H_2O)_6^{3+}$ by (▲) $OsL_3^{2+}$, (■) $FeL_3^{2+}$, (●) $RuL_3^{2+}$, (○) $Fe(H_2O)_6^{2+}$, (△) $Ni(H_2oxime)^{2+}$, and (□) $Ni([14]aneN_4)^{2+}$. The solid line was calculated with a $Mn(H_2O)_6^{2+/3+}$ exchange rate constant of $1 \times 10^{-9}$ $M^{-1}$ $s^{-1}$.

Although generally consistent with the free-energy trends noted above, the reaction of $Mn(H_2O)_6^{2+}$ with $Co(H_2O)_6^{3+}$ requires further comment. The experimental $Co(H_2O)_6^{2+/3+}$ exchange rate was used in the cross relation, yet in an extensive series of cross reactions[38] the effective $Co(H_2O)_6^{2+/3+}$ exchange rate is $10^{-12\pm2}$, some 12 orders of magnitude smaller than the experimental value. In view of its implications for the mechanism of the $Mn(H_2O)_6^{2+/3+}$ exchange, we discuss the $Co(H_2O)_6^{2+/3+}$ system further.

**Comparisons of $Mn(H_2O)_6^{3+}$ and $Co(H_2O)_6^{3+}$ Reactions.** In many respects the redox properties of the $Mn(H_2O)_6^{2+/3+}$ and $Co(H_2O)_6^{2+/3+}$ couples are similar. $Mn(H_2O)_6^{3+}$ and $Co(H_2O)_6^{3+}$ are both very strong oxidants, and the two couples possess similar inner-shell and outer-shell reorganization barriers: the rate constants for the $Mn(H_2O)_6^{2+/3+}$ and $Co(H_2O)_6^{2+/3+}$ exchange calculated from the structural parameters (with $\kappa_{el} = 1$) are $10^{-4\pm1}$ and $10^{-5\pm1}$ $M^{-1}$ $s^{-1}$, respectively. In each case lower exchange rates are implied by certain cross-reaction studies. For $Mn(H_2O)_6^{3+}$, reactions with tris(polypyridine)metal complexes and *N*-alkyl-

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(44) (a) In these calculations a value of 1.56 V was used for the reduction potential of the unhydrolyzed $Mn(H_2O)_6^{3+}$ ion.[29,31,44b] For the reduction potentials of the $ML_3^{3+}$ complexes, the values measured in 2.0 M $H_2SO_4$[45] or extrapolated to 2.0 M $H_2SO_4$ from 0.5 M $H_2SO_4$[46] were employed. (b) Ciavatta, L.; Grimaldi, M. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3071.

(45) Schilt, A. A. "Analytical Applications of 1,10-Phenanthroline and Related Compounds"; Pergamon Press: New York, 1969; pp 113–122.

(46) Creutz, C.; Sutin, N. *Adv. Chem. Ser.* **1978**, *No. 168*, 1.

(47) This assumption seems reasonable since the electronic coupling in aquo or ammine systems in which a σ*d electron is transferred is, in general, enhanced relative to πd systems by mediation via the ligands.[22] See also: Logan, J.; Newton, M. D.; Noell, J. O. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1984**, *18*, 213.

(48) Macartney, D. H., unpublished observations.

(49) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(50) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

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(52) Weaver, M. J.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1936.

(53) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

(54) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557.

(55) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(56) Böttcher, W.; Brown, G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447.

(57) Mok, C.-Y.; Zanella, A. W.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1984**, *23*, 289.

phenothiazines are consistent with an effective $Mn(H_2O)_6^{2+/3+}$ exchange rate of $\sim 1 \times 10^{-9}$ $M^{-1}$ $s^{-1}$: for $Co(H_2O)_6^{3+}$, reactions with these and other[38] reductants yield an effective $Co(H_2O)_6^{2+/3+}$ exchange rate of $1 \times 10^{-12}$ $M^{-1}$ $s^{-1}$. The directly measured $Co(H_2O)_6^{2+/3+}$ exchange rate constant is 5 $M^{-1}$ $s^{-1}$, considerably higher than the calculated and cross-reaction values. In order to account for this difference, it has been proposed that the $Co(H_2O)_6^{2+/3+}$ exchange proceeds by a more complex mechanism, specifically a spin preequilibrium[58] or a water-bridged[38] pathway. Indeed a multiplicity of mechanisms for $Co(H_2O)_6^{3+}$ and $Mn(H_2O)_6^{3+}$ reactions with substitution-labile reductants need to be considered: the reactions can be outer sphere or inner sphere, and ligand-to-metal charge-transfer and/or ligand-field excited states may be involved; these excited states may lie above, close to, or below the transition state for the reaction of the ground-state configurations, and acid-dependent as well as acid-independent reaction channels for the formation and decomposition of the transition states and/or the chemical intermediates may obtain.

We first consider the assumptions in the outer-sphere model used. In order to account for the $Co(H_2O)_6^{2+/3+}$ exchange rate within an outer-sphere model, the calculated[22] zero-interaction barrier needs to be reduced by 6–8 kcal $mol^{-1}$. Reactions such as the $Co(H_2O)_6^{2+/3+}$ exchange involve very large inner-shell reorganization, and errors in $\Delta d_0$ can yield barriers that are significantly in error. Thus for the $Co(H_2O)_6^{2+/3+}$ exchange an error of 0.02 Å in $\Delta d_0$ results in an overestimation (or underestimation) of the inner-shell barrier by as much as 3 kcal $mol^{-1}$. Another assumption concerns $\kappa_{el}$: although the value of $\kappa_{el}$ is uncertain, the exchange reactions have been assumed to be adiabatic so that $\kappa_{el}$ has already been assigned its maximum value of unity. However, the possibility that the electronic coupling of the reactants is strong enough to significantly lower the barrier from its zero-interaction value needs also to be considered. Such a strong interaction could arise from the involvement of low-lying electronically excited states of the reactants, and we consider this possibility next.

We denote the vertical energy difference between the excited state and the transition state at the nuclear configuration of the transition state by $\Delta E^*$, and we distinguish three cases depending on the magnitude of $\Delta E^*$. (a) If $\Delta E^* >> 0$, then the interaction of the excited state with the reorganized ground states will not significantly lower the height of the barrier from its zero-interaction value ($(\lambda_{out} + \lambda_{in})/4$) but could increase the value of $\kappa_{el}$ for the reaction (if $\kappa_{el}$ had been <1).[59a] (b) If $\Delta E^* \approx 0$, then the reactant, product, and excited states will be nearly degenerate and their interaction will be quite strong (provided that it is symmetry allowed) and appreciable barrier lowering will result.[59b] (c) If $\Delta E^* << 0$, that is, if the *intersection* of the surface for the excited state with the reactant surface occurs below the intersection of the reactant and product surfaces, then the excited state will be formed as an intermediate and the barrier for the reaction will be considerably reduced (chemical mechanism). Mechanisms b and particularly c could account for the observed exchange results if suitably located electronically excited states are present. Note also that since the rates of the pathways in the chemical mechanism are limited by the rate of formation of the intermediates or by their equilibrium concentrations; such pathways will contribute less to reactions with large driving forces. The chemical mechanism thus will be competitive when the "normal" pathway is slow because of an unfavorable electronic factor, λ parameter, or driving force and therefore can, in principle, account for the smaller effective $Co(H_2O)_6^{2+/3+}$ (and $Mn(H_2O)_6^{2+/3+}$) exchange rates in highly exergonic reactions (subject to the usual constraints on the application of the cross relation to reactions with high driving forces[49]).

Two types of electronically excited states need to be considered: these are the ligand-to-metal charge-transfer (LMCT) and ligand-field (LF) excited states. We first consider the LMCT states. The redox potential of the $H_2O^+/H_2O$ couple is $\geq 3.9$ V[60] so that $\Delta G°$ for reaction 17 is $\geq +2.0$ eV. Since $K_{19} = K_{17}K_{18}$, the value

$$Co(H_2O)_6^{3+} + H_2O = Co(H_2O)_6^{2+} + H_2O^+ \qquad (17)$$

$$Co(H_2O)_6^{2+} + H_2O^+ = (H_2O)_5Co^{2+}(H_2O^+) + H_2O \qquad (18)$$

$$Co(H_2O)_6^{3+} = (H_2O)_5Co^{2+}(H_2O^+) \qquad (19)$$

of $K_{19}$ can be calculated if $K_{18}$ is known. Unfortunately the value of $K_{18}$ is not known independently, but it is very probably <<1 so that $\Delta G°$ for reaction 19 is unlikely to be less than 2 eV. The value of $\Delta G°$ for reaction 19 can also be estimated from spectroscopic considerations. On the basis of the position of the LMCT band in $Co(H_2O)_6^{3+}$ ($E_{op} \approx 5.9$ eV[61a]) and the λ value of the excited state we estimate[61b] $\Delta G°$ [$E_{op} = \lambda + \Delta G° + E^*(Co(II))$] for reaction 19 to be $2.4 \pm 0.5$ eV so that $\Delta E^* > 0$ for the LMCT state of $Co(H_2O)_6^{3+}$. Consequently an outer-sphere chemical mechanism involving the thermal population of LMCT states[62] can be ruled out and significant barrier reduction from the mixing of the LMCT with the ground states (in an outer-sphere transition state) seems unlikely.

We next consider the LF states of $Co(H_2O)_6^{3+}$ and $Co(H_2O)_6^{2+}$ (the ligand-field states of $Mn(H_2O)_6^{3+}$ are of higher energy).[63a] As discussed for the LMCT states, the LF states could mix with the ground states in a superexchange mechanism (provided that they are of suitable symmetry) or they could be formed as chemical intermediates. Since the $Co(H_2O)_6^{2+/3+}$ exchange is formally spin forbidden, some (superexchange) mixing with the ligand field states of $Co(H_2O)_6^{3+}$ (or $Co(H_2O)_6^{2+}$) has, in fact, been presumed in order to obtain $\kappa_{el} \approx 1$ but, because of the small value of the spin–orbit interaction responsible for this mixing, significant barrier lowering does not result.[22] There remains the question of whether a high-spin state of $Co(H_2O)_6^{3+}$ or a low-spin state of $Co(H_2O)_6^{2+}$ could be formed as an intermediate. If thermal population of a LF state is sufficiently rapid,[64a] then this interpretation is identical with the spin preequilibrium mechanism previously proposed[58] for the $Co(H_2O)_6^{2+/3+}$ exchange. The zero–zero energy difference

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(58) Creutz, C.; Sutin, N. In "Inorganic Reactions and Methods"; Zuckerman, J. J., Ed.; Verlag Chemie: Weinheim/Bergstr., West Germany, in press.

(59) (a) In a superexchange treatment of the three-site system abc the electronic coupling of the end sites a and c by b is equal to $H_{ab}H_{bc}/\Delta E^*$ provided that $\Delta E^* >> H_{ab}$ and $H_{bc}$ ($\Delta E^* = (E_c - E_a) = (E_c - E_b)$ at the intersection of the surfaces for a and c), i.e., the extent of mixing of an excited state configuration with the ground-state configurations is inversely proportional to the vertical energy separation. See, for example: Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1966**, *29*, 32. Kuznetsov, A. M.; Ulstrup, J. *J. Chem. Phys.* **1981**, *75*, 2047. (b) Although a superexchange framework is being used, this is equivalent to the three-center bonding description used earlier[38] and the same criteria that were considered necessary for a strong three-center interaction are also relevant here.

(60) (a) Based on the $E°$ of 1.89 V for the $\cdot OH/OH^-$ couple[60b] and a $pK_a$ of $\leqslant -20$ for $H_2O^+$.[60c] (b) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1984**, *88*, 3643. (c) Schwarz, H. A., personal communication.

(61) (a) Winkler, J., unpublished observations. (b) Note that the LMCT transition in $Co(H_2O)_6^{3+}$ produces a low-spin Co(II) and it is necessary to correct for the energy difference, $E^*(Co(II))$, between the vibrationally relaxed low-spin state and the ground state of Co(II) in order to obtain the $\Delta G°$ for reaction 19. The estimate of $\Delta G°$ is very approximate largely because of the uncertainty in the λ value for $H_2O^+/H_2O$. An assumption underlying this approach is that the transition in the far-UV spectrum of $Co(H_2O)_6^{3+}$ solutions is ligand to metal rather than solvent to metal in character.

(62) The chemical mechanism would contribute most to the observed rate for the $Co(H_2O)_6^{2+/3+}$ exchange, be less favorable for $Mn(H_2O)_6^{2+/3+}$, and be much less favorable for $Fe(H_2O)_6^{2+/3+}$ (paralleling the $E°$'s for the $M(H_2O)_6^{3+/2+}$ couples, Table II).

(63) (a) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33. (b) Winkler, J. R.; Rice, S. F.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 47. (c) Navon, G. *J. Phys. Chem.* **1981**, *85*, 3547.

(64) (a) Under normal circumstances the spin conversion is likely to be sufficiently rapid for the preequilibrium to be maintained. See, for example: Dose, E. V.; Hoselton, M. A.; Sutin, N.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1141. (b) The diffusion-controlled and the maximum activation-controlled rate constants for the preequilibrium spin-change mechanism are $K_AK_S\kappa_{el}\nu_n$ and $K_Sk_{diff}$ ($M^{-1}$ $s^{-1}$), respectively, where $K_S$ is the spin conversion equilibrium constant. In this model, reactions with faster rate constants involve direct reaction with the ground state in an "ordinary" (but superexchange-enhanced) outer-sphere mechanism.

between the low-spin $(\pi d)^6$ $^1A_{1g}$ ground state of $Co(H_2O)_6^{3+}$ and the high-spin $(\pi d)^4(\sigma^*d)^2$ $^5T_{2g}$ excited state has been estimated to be 4.2 ± 4.6 kcal mol$^{-1}$ from optical spectroscopy[63b] and >5.4 kcal mol$^{-1}$ by NMR methods.[63c] The thermally equilibrated $(\pi d)^5(\sigma^*d)^1$ $^3T_{1g}$ excited state is of higher energy. The $\lambda_{in}/4$ values will be smaller for outer-sphere $Co(H_2O)_6^{2+}$ exchange with either of the high-spin $Co(H_2O)_6^{3+}$ excited states than with the low-spin ground state: exchange with the $^5T_{2g}$ excited state will involve $\pi$d transfer for which $\lambda_{in}/4$ is likely to be smaller than for the $^3T_{1g}$ excited state; however, since exchange with the $^3T_{1g}$ state can be effected by $\sigma^*$d transfer, the electronic coupling should be larger for this excited state.[22] To the extent that these effects are favorable, they offset the unfavorable preequilibrium constant for the formation of the excited state (this constant will, of course, be larger for the formation of the $^5T_{2g}$ state) and the spin preequilibrium mechanism could account for the relatively rapid $Co(H_2O)_6^{2+/3+}$ exchange. Similar considerations also apply to the $(\pi d)^6(\sigma^*d)^1$ $^2E_g$ excited state of $Co(H_2O)_6^{2+}$: this state is relatively low lying,[63a] and its electronic coupling to the $Co(H_2O)_6^{3+}$ ground state should be large. Such spin-change mechanisms could be important for the $Co(H_2O)_6^{2+/3+}$ exchange and for $Co(H_2O)_6^{3+}$ reactions with low to moderate driving forces[64b] but do not afford any obvious advantage for $Mn(H_2O)_6^{3+}$ reactions.

Although the above discussion has focused upon the outer-sphere mechanism, the results can also be rationalized in terms of an inner-sphere, water-bridged mechanism.[38] On the basis of the earlier discussion, the energy of the water-bridged transition state for the $Co(H_2O)_6^{2+/3+}$ exchange needs to be 6–8 kcal mol$^{-1}$ lower than that of the (zero-interaction) outer-sphere transition state considered earlier, both measured relative to the energy of the separated reactants. The precursor complex formed in the outer-sphere reaction will be considerably more stable than the bridged precursor complex (i.e. $K_A(OS) >> K_A(IS)$)[65,66] because the metal–metal repulsions will be larger in the latter complex (since the separation of the charges is smaller) and the bonding interactions will be very weak (because a coordinated oxygen in $Co(H_2O)_6^{3+/2+}$ is an extremely poor base (ligand)).[67] On the other hand, the inner-shell reorganization energy for the water-bridged pathway could be about 1 kcal mol$^{-1}$ lower than for the outer-sphere pathway[68] while the solvent reorganization energy (based on two-sphere and ellipsoidal models for the outer- and inner-sphere transition states, respectively) will be ~2 kcal mol$^{-1}$ lower for the water-bridged pathway. On the basis of the above considerations, the barrier lowering due to the electronic coupling of the two metal centers needs to be at least $3 + RT \ln (K_A(OS)/K_A(IS))$ for the inner-sphere mechanism to be viable. If $K_A(OS)/K_A(IS) \leq 10^3$, this would correspond to a barrier lowering of about 7 kcal mol$^{-1}$, which is very similar to the barrier lowering required to rationalize the $Co(H_2O)_6^{2+/3+}$ exchange rate in terms of the outer-sphere mechanism (but arrived at in a different manner).

Larger electronic couplings are possible in a water-bridged[38] than in an outer-sphere transition state. In addition, the same mechanisms that were considered for enhancing the coupling and lowering the barrier in the outer-sphere model are, of course, also relevant to the inner-sphere case. These will not be discussed in detail here. However, one aspect of the chemical mechanism merits further comment. In the inner-sphere chemical mechanism the activation process primarily involves oxidation of the bridging water molecule and stretching of an O–H$^+$ bond. Since the bridging group is bonded to two positively charged metal centers and the p$K_a$ of $H_2O^+$ is ≤–20,[60c] the oxidized bridging group will be a very strong acid and could rapidly dissociate a proton (eq 21). Interestingly, the rate constant for the above scheme is equal

$$Co^{3+}(H_2O) + (H_2O)Co^{2+} \rightleftharpoons Co^{3+}(H_2O)Co^{2+} + H_2O \qquad (20)$$

$$Co^{3+}(H_2O)Co^{2+} \rightleftharpoons Co^{2+}(\cdot OH)Co^{2+} + H^+ \qquad (21)$$

$$Co^{2+}(\cdot OH)Co^{2+} \rightarrow Co^{2+}(OH^-)Co^{3+} \qquad (22)$$

to $K_{20}k_{21}/2$ and is acid independent regardless of the relative magnitudes of $k_{22}$ and $k_{-21}[H^+]$.[69] A hydroxyl-bridged transition state could thus provide a viable mechanism for the $Co(H_2O)_6^{2+/3+}$ exchange.

## Concluding Remarks

The $Mn(H_2O)_6^{2+/3+}$ exchange rate constant calculated from a semiclassical model is $10^{-4\pm1}$ M$^{-1}$ s$^{-1}$. The effective manganese exchange rate constant ranges from $4 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ for reaction with $Co(H_2O)_6^{3+}$ (using the experimental $Co(H_2O)_6^{2+/3+}$ exchange rate constant) to $10^{-9}$ M$^{-1}$ s$^{-1}$ for reaction with $ML_3^{2+}$ complexes. A similar (but more pronounced) trend of decreasing effective exchange rate with increasing driving force is also noted for $Co(H_2O)_6^{3+}$ reactions. While it is very difficult to draw any definite conclusions regarding the detailed mechanisms of the

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(65) The water-bridged mechanism as formulated by Endicott et al.[38] involves a consideration of the relative energies of the following states: (i) A precursor complex consisting of noninteracting $(H_2O)_5Co(OH_2)^{3+}$ and $Co(H_2O)_5^{2+}$ (i.e. a $Co(H_2O)_6^{2+}$ that has lost a coordinated water molecule). This definition of the precursor complex for an inner-sphere reaction differs from the usual definition[66] in that the bridging group is not bonded to both metal centers. (ii) An unbound state consisting of noninteracting $Co(H_2O)_5^{2+}$, $H_2O^+$, and $Co(H_2O)_5^{2+}$. The difference between the energy of this unbound state and that of the precursor complex defined above is the $Co^{III}$–$OH_2$ (homolytic) bond dissociation energy. (iii) The transition state formed by reorganization of the nonbridging water ligands and the surrounding solvent and stretching of the bridging $Co^{III}$–$OH_2$ bond along the homolytic bond dissociation coordinate. In the zero-interaction inner-sphere precursor complex considered in ref 38, the bond formation to the reducing center is included along with the donor–acceptor interaction in calculating the energy of the transition state. Here we use the conventional inner-sphere model,[66] namely one in which the bridging group is directly bonded to both metal centers in the precursor complex. These are alternative computation procedures: the important quantity in each case is, of course, the difference between the energy of the *transition state* and that of the *separated reactants*.

(66) See, for example: Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225. Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273.

(67) (a) No structures in which a water molecule is the sole bridging group have been reported. However, double-bridged structures, in which one bridging group is a water molecule and the other a fairly basic oxygen, have been described. The two iron(II) centers in $Fe_3(PO_4)_2 \cdot 4H_2O$ (Ludlamite) are bridged by a water molecule and a phosphate oxygen (iron–iron distance 3.27 Å): Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1966**, *44*, 2223. See also: Abrahams, S. C. *J. Chem. Phys.* **1966**, *44*, 2230. Evidence has recently been presented for the presence of a double $\mu$-aquo, $\mu$-oxo bridge in a binuclear copper(II) system (copper–copper distance 3.03 Å): Chadhuri, P.; Ventur, D.; Wieghardt, K.; Peters, E.-M.; Peters, K.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 57. (b) The rate constant for protonation of a coordinated water molecule in $Cr(H_2O)_6^{3+}$ has been estimated to be $5.0 \times 10^4$ M$^{-1}$ s$^{-1}$, $\Delta H^* = 0.5 \pm 0.5$ kcal mol$^{-1}$, and $\Delta S^* = -36 \pm 2$ cal deg$^{-1}$ mol$^{-1}$: Swift, T. J.; Stephenson, T. A. *Inorg. Chem.* **1966**, *5*, 1100. (c) Theoretical calculations show that the formation of a hydrogen bond to the oxygen in $H_3O^+$ is endergonic: Newton, M. D. *J. Chem. Phys.* **1977**, *67*, 5535.

(68) (a) The reorganization of the inner-coordination shells, even for relatively large displacements as in the $Co(H_2O)_6^{2+/3+}$ exchange, is adequately calculated by harmonic oscillator expressions (with nuclear tunneling corrections as appropriate). For the $Co(H_2O)_6^{2+/3+}$ exchange, the difference between the inner-shell reorganization energy for the outer-sphere mechanism calculated with harmonic and Morse potential functions for the M–$OH_2$ bonds is less than 0.3 kcal mol$^{-1}$ (with the Morse potential giving the *larger* reorganization energy).[68b] Interestingly, despite the similarity in the reorganization energies, the nuclear configuration of the outer-sphere transition state is quite different in the harmonic and Morse calculations. The calculation of the inner-shell reorganization energy is somewhat more complicated for the bridged mechanism. The reorganization energy for the ten nonbridging water molecules is presumably similar to the value for the outer-sphere mechanism, while the reorganization energy for the bridging water molecule is quite sensitive to the assumptions made about the cobalt–cobalt separation and the cobalt–oxygen distances in the precursor and transition states. However, calculations[68b] using reasonable values for these parameters and Morse functions show that the inner-shell reorganization energy in the water-bridged mechanism is unlikely to be more than 1 kcal mol$^{-1}$ lower than the value for the outer-sphere mechanism. (b) Brunschwig, B. S., unpublished calculations.

(69) The same hydroxyl-bridged intermediate could, of course, also be formed in the reaction of $CoOH^{2+}$ with $Co^{2+}$ and can be accommodated in the above scheme by introducing the reverse rate constant in eq 22. Note that the equilibrium constant for the reaction

$$Co(H_2O)_6^{3+} + OH^- = Co(H_2O)_6^{2+} + \cdot OH$$

is approximately equal to unity.

$Co(H_2O)_6^{3+}$ and $Mn(H_2O)_6^{3+}$ reactions, it is likely that pathways involving electronically excited states of the reactants need to be invoked, at least in the case of the $Co(H_2O)_6^{3+}$ reactions. Analogous considerations may also be relevant to the $Mn(H_2O)_6^{2+/3+}$ exchange, but in the absence of a direct measurement of the $Mn(H_2O)_6^{2+/3+}$ exchange constant, we have focused our attention on the $Co(H_2O)_6^{2+/3+}$ system.

In order to rationalize the $Co(H_2O)_6^{3+}$ results in terms of an outer-sphere mechanism, it is necessary that the thermal population of ligand-field excited states (of $Co(H_2O)_6^{3+}$ or $Co(H_2O)_6^{2+}$) provide a viable reaction pathway. For an inner-sphere water-bridged mechanism,[38] viable pathways are obtained through superexchange coupling of LMCT states or, perhaps, through actual oxidation of the bridging water molecule to form a hydroxyl-bridged transition state. A more complete characterization of these systems must await the results of spectroscopic and structural studies currently in progress.

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**Registry No.** $Mn(H_2O)_6^{3+}$, 18976-26-6; $Os(4,4'\text{-}(CH_3)_2bpy)_3^{2+}$, 33247-24-4; $Os(phen)_3^{2+}$, 31067-98-8; $Os(bpy)_3^{2+}$, 23648-06-8; $Os(5\text{-}Cl\text{-}phen)_3^{2+}$, 71692-76-7; $Fe(bpy)_3^{2+}$, 15025-74-8; $Ru(4,4'\text{-}(CH_3)_2\text{-}bpy)_3^{2+}$, 32881-03-1; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(5\text{-}NO_2phen)_3^{2+}$, 54360-17-7; $Mn(H_2O)_6^{2+}$, 15365-82-9; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Ni(H_2oxime)^{2+}$, 55188-31-3; $Ni([14]aneN_4)^{2+}$, 68344-00-3; $Ni(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$, 18444-42-3.

**Supplementary Material Available:** Plots of $k_0(K_{1h} + [H^+])$ vs. $[H^+]$ for the reduction of Mn(III) by $OsL_3^{2+}$ complexes (supplementary Figure 1) and by Ni(II) macrocycles (supplementary Figure 2) and kinetic data for the oxidation of $ML_3^{2+}$ complexes (Table SI) and $Fe^{2+}$ (Table SII) by Mn(III) and for the reduction of Co(III) by $Mn^{2+}$ (Table SIII) (5 pages). Ordering information is given on any current masthead page.

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# Ligand Substitution Kinetics and Equilibria in the Systems Formed by Tetrabromoaurate(III) Anion and Heterocyclic Nitrogen Donors

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The kinetics of the forward and reverse reactions $[AuBr_4]^- + am = [AuBr_3(am)] + Br^-$ has been studied in 95/5 vol % methanol/water mixtures at 25.0 °C for am = pyridine and a variety of substituted pyridines. When there is methyl substitution on both the 2- and 6-positions, the low stability of the amine complexes precludes a study of the kinetics of their formation. However, they can be prepared and the kinetics of their decomposition are reported. The second-order rate constants for the forward and reverse reactions depend upon the amine basicity and take the form $\log k^f_2 = a(pK_a) + b$ and $\log k^r_2 = -a'(pK_a) + b'$, where $a$ and $a'$ are independent of the extent of ortho substitution in the ligand. In contrast to the case for the chloro analogues, the reactions in both directions are retarded by 2(6)-methyl substituents in the pyridine ring, manifested by a change in $b$ and $b'$.

## Introduction

During the past 20 years, ligand substitution processes at planar tetracoordinate $d^8$ gold(III) complexes have been studied, frequently with chloride as either leaving group or entering nucleophile, both in simple systems involving complexes of monodentate ligands and in those involving bi- or polydentate chelating molecules.[3] Apart from some cases where bromide ion has been used as nucleophile[4] and the solvolysis of $[AuBr_4]^-$ anion in water,[5] a relatively small amount of data is available for gold(III) systems involving bromide as ligand(s) or nucleophile.

When, many years ago, we studied[6,7] the kinetics of the processes of the type

$$[AuCl_4]^- + am \rightarrow [Au(am)Cl_3] + Cl^-$$

(where am is an heterocyclic nitrogen donor of the group of pyridine) the corresponding study of the $[AuBr_4]^-$ system seemed to be a trivial extension of the work and was not pursued. However, in the course of a routine examination of this system we found that the change in behavior, on changing from the chloro to the bromo system, was much more significant than we had anticipated and so the kinetics of the forward and reverse reactions, for the process

$$[AuBr_4]^- + am \rightleftarrows [Au(am)Br_3] + Br^-$$

in 95/5 vol % methanol/water at 25 °C, are reported in this paper.

## Experimental Section

**Materials.** The various pyridines are all reagent grade products (Aldrich), which were distilled, when necessary, over KOH pellets. $HAuCl_4 \cdot 3H_2O$, HBr, LiBr, and methanol were all reagent grade products (Engelhard and Hoechst).

**$HAuBr_4 \cdot 5H_2O$, Hydrogen Tetrabromoaurate(III) Pentahydrate.** The compound was prepared by treating $HAuCl_4 \cdot 3H_2O$ (3 g) dissolved in water (10 cm$^3$) with a large excess of HBr. After the color had changed from yellow to dark red, the solution was allowed to evaporate completely in the dark in a desiccator over NaOH. The dark red, very hygroscopic, crystalline product was obtained in virtually 100% yield; mp 80 °C dec.

**$[AuBr_3(C_5H_5N)]$, Tribromo(pyridine)gold(III).** In a typical preparation $HAuBr_4 \cdot 5H_2O$ (0.2 g, 0.35 mmol) dissolved in water (10 cm$^3$) was first neutralized with the stoichiometric amount of $NaHCO_3$ and then treated with a slight excess of pyridine (0.03 g, 0.38 mmol) dissolved in methanol (5 cm$^3$), with stirring. After a few minutes, the red precipitate that formed was filtered off, washed with methanol and diethyl ether, and dried under a vacuum; yield 80%. The product can be crystallized from hot methanol.

The other complexes of the type $[AuBr_3(am)]$ were synthesized in the same way. The analytical data are summarized in Table I.

**Kinetics.** The kinetics were followed by measuring the absorbance changes of the reaction mixture with time by using a Varian-Cary 219

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