Electron Transfer in Mn-Tripod Complexes

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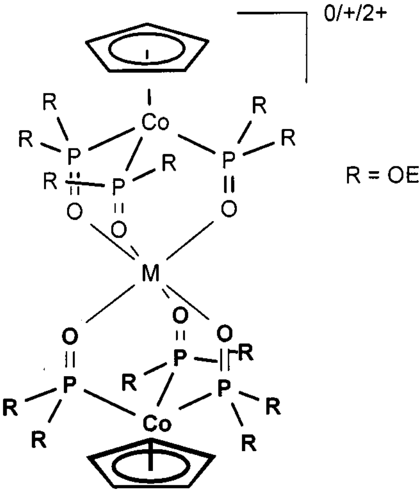
A heterogeneous electron-transfer rate constant $k_0 \approx 7–8 \times 10^{-7}$ cm s^{-1} for the reduction/oxidation of the bis-tripod complex $[CpCo^{III}\{P(OEt)_2O\}_3]_2Mn^{III/II}$ redox couple was measured by cyclic voltammetry. The homogeneous self-exchange rate was calculated as $k_2 = 4.25 \cdot 10^{-3}$ $\text{M}^{-1}\text{s}^{-1}$ from the cross reaction of the Mn^{II} tripod complex with ferrocenium salt. X-ray structure determinations for both complexes showed a near regular octahedral oxygen coordination for the Mn^{II} complex and a sizeable Jahn–Teller distortion for the Mn^{III} complex. Applying current ET theory for the comparison of heterogeneous and homogeneous rates and estimates of reorganization energies leads to the conclusion that the major part of the latter is due to inner reorganization of the Mn tripod.

Introduction

The Kläui Tripod ligand $[CpCo^{III}\{P(OR)_2O\}_3]^-$ (see bold face part in Scheme 1) is unique as a tripodal oxygen ligand as it combines high complex stability constants with a relatively weak ligand field.[1] Thus, nearly all of the main group metals as well as the major part of the d- and f-block elements have been complexed by this ligand in the form of either (Trpd)ML or $(Trpd)_2M$ complexes, where M is fixed in a regular octahedral six oxygen environment. The 3d transition metal complexes are generally high spin with the exception of Co^{III}, which gives rise to a temperature-dependent spin equilibrium,[2−4] which is low spin at low temperatures and partly high spin at higher temperatures.



Scheme 1

These complexes are particularly well suited for redox studies,[5,6] since the ligand $[CpCo^{III}\{P(OR)_2O\}_3]^-$ itself offers a relatively broad potential window where the carrier metal Co^{III} is redox inert. This feature is explored by recording decomposition potentials for $(Trpd)_2M$ complexes featuring a redox-inert central metal. Reduction and oxidation limits depend somewhat on the charge of this central metal and have been determined as −1 and +0.76 V for the reduction and oxidation of the ligand anion $[CpCo\{P(OEt)_2O\}_3]^-$ (as the Na^+ salt), −1 V for $[CpCo\{P(OEt)_2O\}_3]_2Mg$ (reduction only) and −1.75 and +1.75 V for $[(CpCo\{P(OEt)_2O\}_3)_2Al]^+$. Reversible redox transitions for the central metal have been found to occur about 1 V more negative than those of the respective aqua ions $M(H_2O)_6^{3+/2+}$ for a variety of complexes of 3d metals.[5] Since for the latter the $M^{3+/2+}$ potentials become increasingly positive along the d block, tripod complexes allow us to determine redox transitions such as $Mn^{II/III/IV}$ and $Ni^{II/III}$ which are inaccessible for the aqua ions by direct electrochemical measurement. Table 1 lists observed redox transitions in $[CpCo\{P(OEt)_2O\}_3]_2M$ for 3d metals M. As can be clearly seen, a wide potential range is covered

Table 1. Redox transitions in $(Trpd)M^{n+}$ complexes

Electronic configuration	Transition $M^{n+}(L_{OEt})_2/M^{(n\pm1)+}(L_{OEt})_2$	$E_{1/2}$ [a]
d^0/d^1	Ti^{IV}/Ti^{III}	−0.30
d^1/d^2	V^{IV}/V^{III}	0.933
d^2/d^3	V^{III}/V^{II}	−1.54
d^3/d^4	Cr^{III}/Cr^{II}	−1.57
	Mn^{IV}/Mn^{III}	1.53
d^4/d^5	Mn^{III}/Mn^{II}	0.12
d^5/d^6	Fe^{III}/Fe^{II}	−0.72
d^6/d^7	Co^{III}/Co^{II}	0.745
d^7/d^8	Ni^{III}/Ni^{II}	1.255

[a] V vs. SCE in acetonitrile.

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by the accessible redox transitions and each electron configuration change d^{n+1}/d^n from $n = 0$ to 8 is represented by at least one redox pair. A second remarkable feature of the tripod complexes is their ready solubility in relatively nonpolar solvents. Thus neutral $(Trpd)_2M$ complexes (with a central metal M^{II}) are soluble in ether, dichloromethane and slightly soluble even in hydrocarbon solvents. Cationic $[(Trpd)_2M]PF_6$ (with a central metal M^{III}) complexes are readily dissolved in acetonitrile.

Due to the fixed geometry of the ligand sphere and the strictly outer-sphere character of the electron transfer, geometrical factors are identical for each of the above listed redox changes. Moreover, since the molecular dimensions of the complexes [about 27 × 23 Å for $P(OEt)_2$ tripod ligands] are rather large and the periphery of the molecule is strongly hydrophobic, solvation terms in the electron transfer process should play a minor role and are strictly identical in all cases. Therefore the differences in rate constants for transitions between different electron configurations reflect the geometrical change as well as an intrinsic barrier for an electron entering or leaving either a dσ or a dπ orbital, as well as electron repulsion and exchange terms.

The work presented here concentrates on the Mn^{II}/Mn^{III} couple as the most noteworthy and unusual redox couple within the bis tripod series.

Results

Heterogeneous Electron Transfer

Among all the redox couples studied the high spin $Mn^{III/II}$ pair is a highly remarkable case. Figure 1 depicts cyclic voltammograms at different scan rates starting either from the Mn^{II} or the Mn^{III} complex as the species in solution. As can be seen there is an extraordinarily large separation between the anodic and cathodic peak: $\Delta E_p = 1.03$ V at v = 50 mV/s to $\Delta E_p = 1.36$ V at v = 1000 mV/s. The much smaller peak height in the return sweep is not due to a chemical follow up reaction but rather to the diffusional broadening of the concentration gradient at the electrode due to the prolonged time elapsed between the forward and the return sweep. The picture is symmetrical in that Mn^{II} oxidation or Mn^{III} reduction is the higher peak depending on the starting complex. This couple is an extreme case of chemically fully reversible non-Nernstian behavior with a very small heterogeneous electron-transfer constant.

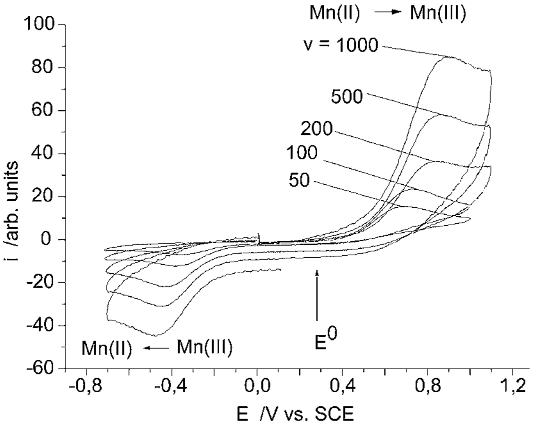

Figure 1. Cyclic voltammogram of $[CpCo\{P(OEt)_2O\}_3]_2Mn^{II}$ in CH_2Cl_2 at different sweep rates, 0.05 to 1.0 V/s

The parameters were evaluated by digital simulation using the Gosser program adapted for Windows.[8] The heterogeneous transfer constant k_0 was adjusted mainly so as to match the experimental peak separation, whereas the transfer coefficient α was adjusted to the ratio of the cathodic to the anodic peak current as well as to the width of the peaks. Diffusion coefficients for the tripod couples had been determined previously as $\approx 3 \cdot 10^{-6}$ cm^2 s^{-1}.[8] The cyclic voltammograms recorded at sweep rates above 0.5 V/s require increasingly smaller k_0 values for simulation. This effect is traced back to the influence of uncompensated solution resistance at higher scan rates. Therefore values at $v = 0.05-0.5$ V s^{-1} giving $k_0 = 7-8 \cdot 10^{-7}$ cm s^{-1} are considered most reliable for this Mn^{II}/Mn^{III} couple.

In such cases the mean of the oxidation and reduction peak of the couple cannot simply be taken as the formal redox potential since this assumption is valid only under Nernstian or near Nernstian behavior. This problem was addressed by scrutinizing the oxidation of Mn^{II} with different ferrocenium salts of known reversible redox potential. Thus Mn^{II} is readily oxidized by the ferrocenium ion ($E_{1/2} = 0.400$ V vs. SCE) but not by the decamethylferrocenium ion ($E_{1/2} = -0.168$ V), whereas Mn^{III} does not oxidize ferrocene but does oxidize decamethylferrocene. The redox potential must thus be located between decamethylferrocene and ferrocene. The value for $E_{1/2}$ determined from simulation of the experimental cyclic voltammogram was 0.280 ± 0.008 V vs. SCE referred to $Fc^{+/0}$ vs. SCE as 0.4000 V.

Homogeneous Cross Reaction with Ferrocenium Ion

Direct determination of the self-exchange rate for the Mn tripod couple was not possible due to the lack of suitable signals in the NMR spectrum. Moreover, it was observed with a variety of other tripod couples that self exchange between tripod complexes is rather slow on the NMR time scale and exchange line broadening is small compared to the paramagnetic linewidth. A cross reaction with a transfer agent of known self-exchange rate was therefore sought in order to arrive at an estimate for the Mn self exchange reaction. The ferrocenium ion was found to be best suited for this purpose since its reversible potential is close to the $(Trpd)_2Mn^{III/II}$ potential. Self-exchange rates for the ferrocene/ferrocenium couple are known in a variety of solvents[9] and have been shown to be not very solvent dependent. Moreover, given the redox potential evaluated above, the driving force of the cross reactions is only about $\Delta E^0 = 0.12$ V. This low driving force places the reaction of Mn^{II}-tripod with the ferrocenium ion in a time domain suitable for stopped flow kinetics despite the rather high self-exchange rate of the latter of $\approx 10^7$ M^{-1} s^{-1}. A dichlorome-

Table 2. Crystal data and structure refinement for $(Trpd)_2Mn^{III}PF_6{\cdot}CH_2Cl_2$ and $(Trpd)_2Mn^{II}$

Empirical formula	$C_{35}H_{72}Cl_2Co_2F_6MnO_{18}P_7$	$C_{34}H_{70}Co_2MnO_{18}P_6$
Molecular weight	1355.47	1125.57
Temperature	258 K	258 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions	a = 21.596(8) Å	a = 12.406(6) Å; α= 92.43(3)°
	b = 12.197(2) Å; β = 107.58(3)°	b = 20.310(8) Å; β = 118.26(5)°
	c = 23.228(4) Å	c = 12.103(6) Å; γ = 75.90(4)°
Volume	5832(3) Å^3	2596(4) Å^3
Z	4	2
Density (calculated)	1.54 Mg/m^3	1.44 Mg/m^3
Absorption coefficient	1.123 mm^{-1}	1.103 mm^{-1}
Crystal size	0.6 × 0.6 × 0.4 mm	0.5 × 0.3 × 0.2 mm
Θ range for data collection	3.1 to 22.0 deg	3.1 to 25.0 deg.
Reflections collected	3676	8094
Independent reflections	3002 [R(int) = 0.039]	5748 [R(int) = 0.040]
Data/restraints/parameters	2479/155/323	3812/6/583
Final R indices	R = 0.103	R = 0.079
[$I > 0.5\sigma(I)$]	R_w = 0.077	R_w = 0.077
Largest diff. peak and hole	1.3931 and 0.8420 e.A^{-3}	0.6799 and −0.4675 e. Å^{-3}

thane solution of $(Trpd)_2Mn^{II}$ ($1.0{\cdot}10^{-2}$ M) and ferrocenium chloride ($1.3{\cdot}10^{-2}$ M) was mixed in a stopped flow cell at ambient temperature (22 °C) and the decay of the ferrocenium absorption [Equation (1)] was followed at 618 nm. Evaluation of the kinetic trace according to 2nd order kinetics gave a rate constant $k_2 = 1400\ s^{-1}\ M^{-1}$.

$$(Trpd)_2Mn^{II} + Fc^+ \rightarrow (Trpd)_2Mn^{III\,+} + Fc \qquad (1)$$

Structural Rearrangement Concomitant with Electron Transfer

A high spin d^4 electronic configuration is usually subject to substantial Jahn−Teller distortion. Since this distortion was originally anticipated as one of the principal factors for the exceptionally slow electron transfer in the $(Trpd)_2Mn$ case a quantization of the effect seemed highly desirable. We have thus undertaken single crystal X-ray structure determinations of both Mn complexes. Though bis-tripod complexes have been prepared throughout the transition series,[1] apart from the structure of a tripod-Na salt,[5] structural details of bis-tripod complexes have not been evaluated. The structures determined in this work are therefore the first X-ray structure determinations on bis-tripod complexes. $[CpCo\{P(OEt)_2O\}_3]_2Mn$ readily crystallizes from ether, whereas $[(CpCo^{III}\{P(OEt)_2O\}_3)_2Mn][PF_6]{\cdot}CH_2Cl_2$ crystallized by diffusion of ether into a dichloromethane solution. The structures were solved by direct methods[10] and refined on F^2.[11] Empirical absorption corrections[12] were applied to both data sets. Parameters for the structure determinations of the Mn^{II} and the Mn^{III} complex are given in Table 2.

$(Trpd)_2Mn^{II}$ crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. Since the most relevant structural features are expected to occur in the Mn−O bond lengths and angles we concentrate on these. Mn−O bond lengths in the two independent molecules are (three unrelated by symmetry in each molecule) 2.137(7), 2.146(7), 2.160(6) and 2.160(6), 2.155(7), 2.161(7) Å for Mn^{II}. They are nearly equal within the limits of error. The coordination environment of the Mn^{II} ion is a slightly distorted octahedron, with bond angles of 87.6(3) and 92.4(3)°.

The Mn^{III} complex crystallizes in the monoclinic space group $C2/c$ with the complex molecule on a crystallographic inversion center. As far as Mn−O bond lengths are concerned, three distinctly different distances [1.981(5),

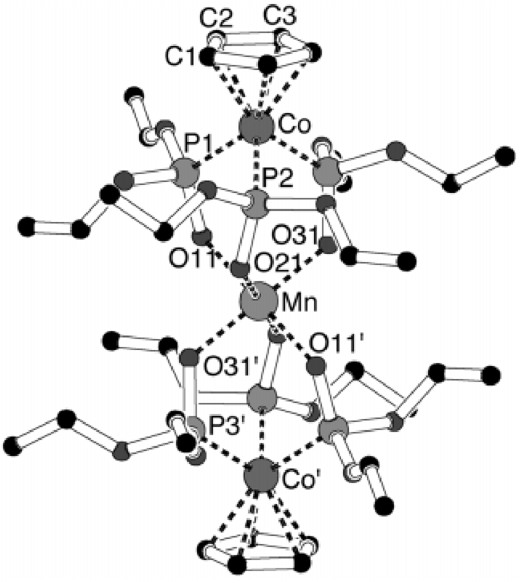

Figure 2. Perspective view of the $[(CpCo\{P(OEt)_2O\}_3)_2Mn]^+$ cation; see text for bond lengths and angles

2.053(4) and 1.923(4) Å] are found. The O−Mn−O bond angles differ only by about 2 °, ranging from 89 to 91°. There is thus a distinct deviation from the octahedral geometry, with each ligand giving rise to three different O−Mn bond lengths. The molecular symmetry of the MO_6 core in $[(Trpd)_2Mn^{III}]^+$ is thus C_i. Figure 2 shows a view of the molecule showing the overall atom connectivity.

Discussion

Comparison of Heterogeneous and Homogeneous Rate Constants

In view of the similarity of homogeneous electron transfer with electron transfer through an interface the rate constants k_{ex} and k_0 for either process of a given redox couple are related, as shown in Equation (2):

$$\frac{k_0}{A_{electrode}} = \left(\frac{k_{ex}}{A_{solution}}\right)^{1/2} \tag{2}$$

The applicability of Equation (2) to practical cases is, however, hampered by the inaccessibility of the frequency factors A.

Weaver[13] has suggested an expression [Equation (3)] that allows a direct comparison of the heterogeneous transfer rate of a redox couple with the rate of a cross reaction between this couple and a second oxidant/reductant:
$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$
where in our case index 1 refers to the Mn tripod and index 2 to ferrocene. The basic idea is to convert the heterogeneous constant to a pseudo-homogeneous one by treating the electrode as a surface with the dimensions of the coreactant in the bimolecular reaction [first term of the l.h.s. of Equation (3)].

$$\log\left(4\pi N_A r_h{}^2 k_{0.cor}\right) - \log(k_{ex}) = \log\left(\frac{\kappa_e \delta r_e}{\kappa_h \delta r_h}\right) + \ldots$$
$$\ldots \left[\Delta G^{\#}{}_{i,2} + \frac{N_A e^2}{4\pi\varepsilon_0}\left(\frac{1}{2r_2} - \frac{1}{(r_1 + r_2)} + \frac{1}{4r_{1-e}}\right)\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_s}\right)\right] / 2RT \tag{3}$$

In this equation $k_{0,cor}$ is the heterogeneous rate constant corrected for the driving force in the homogeneous reaction (0.12 V), κ a transmission coefficient, δr a reaction zone thickness and r_1, r_2, r_{1-e} are reactant radii and reactant electrode distances, respectively. The second term of the r.h.s. is the inner-shell reorganization of the coreactant (ferrocene) and the difference in outer-shell reorganization of self exchange and cross reaction. In general, κ and δr will be similar for both reactions, and for a fast reacting coreactant $\Delta G^{\#}_{i,2}$ will be small as well as $\Delta G^{\#}_{out}$ ($2r_2 \approx r_1 + r_2 < 4r_{1-e}$), which means that the first term of the r.h.s. vanishes and also that the bracketed term will be small, leading to Equation (4):

$$4\pi N_A r_h{}^2 k_{0,cor} = k_{ex} \tag{4}$$

Correcting k_0 for the driving force (0.12 V) gives $k_{0,cor} = 7.5 \cdot 10^{-6}$ cm s^{-1} and taking r_h as 27 Å, the radius of the tripod ligand, gives a value of $4.5 \cdot 10^3$ M^{-1} s^{-1} for the r.h.s. of Equation (4) compared to $1.4 \cdot 10^3$ M^{-1} s^{-1} for the measured rate of the cross reaction. Application of Equation (3) gives 3.5 for the r.h.s. as compared to 2.2 for the l.h.s., i.e. one order of magnitude difference. In view of the inherent assumptions, the similarity of the two values demonstrates that the same physical factors are responsible for homogeneous and heterogeneous electron transfer. Thus the very slow heterogeneous rate for the Mn couple is not an "electrochemical" effect

Estimate of the Self-Exchange Rate for the $(Trpd)_2Mn^{+/0}$ Couple

Self-exchange rates from cross reactions can be obtained using Marcus' cross relation [Equation (5)]:[14]

$$k_{12} = (\sqrt{k_{11} k_{22} K_{12} f_{12}}) W_{12} \tag{5}$$

which in the case of a small driving force and largely canceling work terms w_{ij} simplifies to Equation (6):

$$k_{12} \cong (\sqrt{k_{11} k_{22} K_{12}}) \tag{6}$$

Inserting the stopped flow determined value of k_{12} (1400 s^{-1} M^{-1} see above), the value 4.3 10^6 M^{-1}s^{-1} as given for k_{ii}(ferrocene) in dichloromethane,[15] and the driving force of 0.12 V into Equation (6) gives a self exchange rate of $4.25 \cdot 10^{-3}$ M^{-1}s^{-1} for the $(Trpd)_2Mn^{+/0}$ couple. This value signifies a rather slow exchange, surpassed among simple transition metal complexes only by a number of $Co^{II/III}$ couples with amine and pyridine ligands.[16]

Activation and Reorganization Energies

Using transition state theory[17] we may calculate activation and reorganization energies from Equation (7):

$$\frac{k_{obs}}{K_{os}} = k_{ex} = \nu_n \kappa \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \tag{7}$$

Equation (7) is appropriate for homogeneous self exchange where k_{obs} in the domain far from the diffusion limit is directly related to k_{ex} only through the outer sphere complex formation constant K_{os}. In the case of one neutral reactant there will be no coulombic barrier to outer sphere complex formation, so K_{os} reduces to Equation (8):

$$K_{os} = \frac{4\pi N_A r^2 \delta r}{1000} \tag{8}$$

For the Mn tripod couple we set $\kappa = 1$ (adiabatic limit) and the frequency factor $\nu_n = 17.4 \cdot 10^{12}\ \mathrm{s}^{-1}$ from a tentative assignment of a band at 580 cm^{-1} in the IR spectrum of M(tripod)$_2$ complexes to the M−O stretching vibration (a deviation from this value will have little influence on the final result).[18] Taking r = 27 Å and δr = 0.6 Å[19] gives K_{os} = 3.2 M^{-1} and, from Equation (7), $\Delta G^{\#}_{\mathrm{MnMn}}$ = 92 kJ/mol.

Alternatively we may set $r^2 = r_{\mathrm{Fc}} \cdot r_{\mathrm{Mn}} = 3.8 \cdot 27$ Å^2 in Equation (8) for the cross reaction Equation (1) and 0.6 Å for δr, giving K_{os} = 0.46 M^{-1}. Similarly, the introduction of a frequency factor of $10^{13}\ \mathrm{s}^{-1}$, as a mean of the values derived for the Mn tripod and ferrocene,[9] and $k_{\mathrm{obs}} = 1.4 \cdot 10^{3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in Equation (7) leads to $\Delta G^{\#}_{\mathrm{FcMn}}$ = 54 kJ/mol.

For the cross reaction $\Delta G^{\#}$ can be divided into the driving force and reorganization free energy λ according to Equation (9):

$$\Delta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0}}{\lambda}\right)^{2} \tag{9}$$

leading to λ = 238 kJ/mol. (for $\Delta G^{\circ} < \Delta G^{\#}$ and $\lambda \approx \Delta G^{\#}$) which must be compared to the value of approx. 370 kJ/mol for the self exchange reaction. To obtain the inner reorganization energy for the cross reaction from Equation (10):

$$\lambda = \lambda_{in} + \lambda_{out} \tag{10}$$

we estimate the outer (solvent) reorganization part through the familiar expression of Equation (11):

$$\lambda_{out} = \frac{e^2 N_A}{4\pi\varepsilon_0}\left(\frac{1}{2r_{Fc}} + \frac{1}{2r_{Mn}} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_s}\right) \tag{11}$$

where r_{Fe}, r_{Mn} and R are the radii of ferrocene, Mn tripod and intercomplex distance in the transition state, and $\varepsilon_{\mathrm{opt}}$ and ε_{s} are the optical (n^2) and static dielectric constants of the solvent (dichloromethane). Inserting the radii as above and taking R as the sum of the reactant radii one obtains λ_{out} = 62.4 kJ/mol (i.e. $\Delta G^{\#}_{\mathrm{out}}$ = 15.6 kJ/mol) which is about one quarter of the total reorganization energy of the cross reaction. Since the inner reorganization energy for ferrocene as extracted from ferrocene/ferrocenium self exchange is small ($\Delta G^{\#}_{\mathrm{in}} \cdot$= 3.8 kJ/mol[20]) the major part, i.e. about 40 kJ/mol is left as the internal reorganization for the Mn part in the cross reaction. Doubling this value and adding the solvent reorganization energy evaluated through the appropriate version of Equation (11), ($\Delta G^{\#}_{\mathrm{out}}$ = 6.4 kJ/mol) one arrives at 86.5 kJ/mol for the self exchange, in fair agreement with the value obtained from the rate calculated for Mn self exchange (92 kJ/mol, see above).

The most relevant species to compare with the tripod complexes are the aqua ions $\mathrm{M(H_2O)_6}^{n+}$. In the case of the $\mathrm{Mn(H_2O)_6}^{3+/2+}$ couple no direct measurement of the self-exchange rate constant exists. Whereas Diebler and Sutin[21] in earlier work proposed $k_{11} \approx 10^{-4}\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ from cross reactions in different acid media, Macartney and Sutin in later work[22] extracted a range of self-exchange constants ranging from 10^{-9} to about $10^{-3}\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ dependent on the partner in the cross reaction. These electron transfer reactions involving the strongly acidic $\mathrm{Mn(H_2O)_6}^{3+}$ ion show branched kinetics in the rate law comprising acid dependent and acid independent paths. The nature of the actual transition state therefore cannot be deduced with certainty from the experiments, and neither is the outer sphere character of the redox transitions granted in each case. In spite of these uncertainties $\mathrm{Mn(H_2O)_6}^{\mathrm{III/II}}$ electron transfer appears to be among the slowest observed for first row transition metal aqua ions.

In view of a value of k_{ex} of $4 \cdot 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ found for the outer sphere tripod-Mn$^{\mathrm{III/II}}$ self-exchange rate constant, the greater value of Macartney and Sutin appears as the more probable one since an outer-sphere reaction of the aqua ions should not be slower than that of the much larger tripod complexes.

It may be tempting to trace the rather slow Mn$^{\mathrm{III/II}}$ self exchange back to the Jahn−Teller distortion of Mn$^{\mathrm{III}}$ and the mean value (0.167 Å) geometric rearrangement accompanying the redox change. However, the X-ray structure determination of a Mn$^{\mathrm{III}}$ alum did not reveal such an effect, not even an indication for a dynamic Jahn−Teller distortion.[23] Thus, Mn$^{\mathrm{III/II}}$ electron exchange seems to be slow with and without Jahn−Teller distortion. Moreover, ET in other M$^{\mathrm{II}}$/M$^{\mathrm{III}}$ tripod couples which can be expected to show similar differences in M−O distances in the two oxidation states is found to be orders of magnitude faster [$\log(k_{\mathrm{het}}) \approx 10^{-2}$ cm s^{-1}]. There appears thus to be no simple relationship between the geometry difference of the two oxidation states and the electron transfer rate.

The particular kinetic inertness of the Mn$^{\mathrm{III/II}}$ couple in electron transfer is obviously related to the high thermodynamic stability of the Mn$^{\mathrm{II}}$ state towards oxidation as well as reduction. This feature dominates the coordination chemistry of Mn$^{\mathrm{II}}$ and is even evident in organometallic complexes such as high spin manganocenes.[24] The origin of slow electron transfer kinetics is thus traced back to the destruction of the half-filled d shell, i.e. the loss of exchange energy, when going from Mn$^{\mathrm{II}}$ to Mn$^{\mathrm{III}}$, a fact that hitherto has not been considered as a parameter in electron transfer theory.

Experimental Section

Tripod complexes were prepared from $[\mathrm{CpCo\{P(OEt)_2O\}_3}]\mathrm{Na}$ and the respective metal salt in water or dichloromethane according to ref.[5] Samples of neutral tripod complexes were recrystallized from toluene or diethyl ether and for cationic complexes from dichloromethane/ether. Crystals of $[(\mathrm{CpCo\{P(OEt)_2O\}_3})_2\mathrm{Mn}][\mathrm{PF_6}]\cdot\mathrm{CH_2Cl_2}$ were grown by diffusion of ether into a dichloromethane solution.

Electrochemical measurements were performed using EG&G equipment as previously described.[7] The kinetics of the homogeneous cross reaction was performed with a home-made stopped flow apparatus built around a High-Tech Scientific optical mixing cell and recorded with a J&M Tidas Diode array spectrophotometer taking spectra at 12 ms intervals. At 22 °C a 10^{-2} M solution of $[CpCo\{P(OEt)_2O\}_3]_2Mn$ in CH_2Cl_2 was mixed with an equal volume of a 1.3 10^{-2} M solution of ferrocenium chloride in CH_2Cl_2 giving a final concentration of $5 \cdot 10^{-3}$ and $6.5 \cdot 10^{-3}$ M, respectively. The decay of the ferrocenium absorption at 618 nm was monitored. Under these conditions the reaction had a half-life of 0.84 s. The absorption decay was fitted to second order kinetics leaving k and the initial absorption as adjustable parameters.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-162976 for $[CpCo^{III}\{P(OEt)_2O\}_3]_2Mn$ and -162977 for $[(CpCo^{III}\{P(OEt)_2O\}_3)_2Mn][PF_6] \cdot CH_2Cl_2$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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