

A consistent diminution of signal intensity of a given sample was observed as the temperature was raised from 8 to 100 K. The loss of signal intensity was not due to decomposition of the sample since return to lower temperature gave all of the original absorption. One possible explanation for the disappearance of signal with increasing temperature is an increasing rate of relaxation, which leads to broadening of the signal. However, our observations of the nonlinear Curie-Weiss behavior of the solid and changes in magnetic moment with temperature support an interpretation of an oxidation-state change at temperatures above 100 K. The electronic spectrum, solid-state magnetic moment, and absence of an EPR signal for **1** all support its characterization as a Mn(III) π cation radical at temperatures above 100 K, while at temperatures between 8 and 50 K the solid-state magnetic moment and EPR spectrum indicate a Mn^{IV}TPP species. Thus **1** mimics the behavior of nickel tetraphenylporphyrin, where the room-temperature species is Ni^{II}TPP⁺ while at 77 K it is characterized as [Ni^{III}TPP]⁺.¹¹ The ground state of MnTPP(CF₃SO₃)₂ appears to be a Mn(IV) oxidation level. However, there must be a very closely related structural configuration that favors an oxidation-state change to a Mn(III) π -cation-radical state since this isomerization occurs in the solid state.

Summary

A survey of recent papers on oxidized Mn tetraphenylporphyrins demonstrates the importance of the axial ligands on the Mn in determining the electronic properties of the compound. Species with one coordinating anion such as Cl⁻ and a poorly coordinating anion such as ClO₄⁻ or SbCl₆⁻ are characterized as Mn(III) π cation radicals over all temperature ranges, but they can be converted to Mn(IV) porphyrins by addition of such ligands as CH₃O⁻ or N₃⁻. The present paper describes MnTPP(CF₃SO₃)₂, a species with two poorly coordinating anions, which has a Mn(IV) ground state and a low-lying Mn(III) π -cation-radical configuration. There is another report of a MnTPP(Cl)₂ compound that also exhibits a temperature-dependent oxidation-state change.¹² However, in this compound with two coordinating anions the ground state appears to be a Mn(III) π cation radical and the predominant species at room temperature is a Mn^{IV}TPP species.

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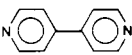
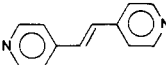
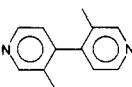
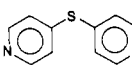
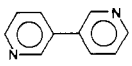
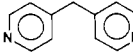
Correlation between Electron-Transfer Rate Constants and Intervalence-Transfer Energies

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Long-range intramolecular electron-transfer reactions, especially those involving proteins, have become a topic of great excitement and intense research. Recent work has included the study of metal-to-metal electron transfer through covalently modified proteins such as cytochrome *c*,¹⁻⁶ azurin^{7,8} and myoglobin,⁹ protein

Table I. Literature Data for Electron Transfer in Complexes of the Form [(NH₃)₄(H₂O)Ru^{II}-L-Co^{III}(NH₃)₅]⁵⁺ ^a

L	10 ³ k ₂₉₈ , s ⁻¹	ΔH*, kJ/mol	ΔS*, J/(mol K)	ΔG* ₂₉₈ , kJ/mol
	44 ^b	84.1 ± 1.3	10.9	80.9
	18.7 ^b	84.6 ± 1.3	5.0	83.1
	5.5 ^b	84.6 ± 1.3	-4.6	86.0
	4.9 ^b	83.7 ± 1.3	-8.0	86.1
	4.2 ^c	<i>d</i>	<i>d</i>	86.5
	2.1 ^c	77.0 ± 2	-37 ± 7	88.0

^aIn 0.4 M CF₃COOH. ^bReference 25. ^cReference 26. ^dNot reported.

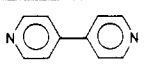
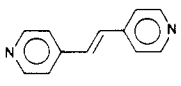
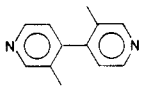
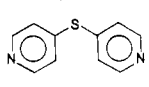
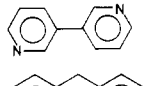
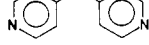
dimers and tetramers,¹⁰⁻¹⁵ and several oligopeptide systems,¹⁶⁻¹⁸ over distances of as much as 25 Å. Several reviews of the topic have also appeared.¹⁹⁻²¹ These studies not only hold the promise of revealing how such all-important biological redox processes as photosynthesis, respiration, and nitrogen fixation occur but may also hold the answers to some of the most fundamental questions about electron transfer.

Perhaps one of the most interesting questions addressed by these studies is, what is the effect of the donor-acceptor (reductant-oxidant) separation distance on the rate constant of electron transfer? Empirically, a fairly clear picture is emerging. The general trend, which is seen plainly in studies with oligopeptides as bridging ligands and is also apparent in the protein work, is that the first-order rate constant decreases with increasing separation. However, the fundamental question remains, what is the

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Table II. Literature Data on Intervalence-Transfer Absorptions for $[(\text{NH}_3)_5\text{Ru}^{\text{II}}-\text{L}-\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ Complexes^a

L	M-M dist, Å	E_{IT} , cm^{-1}	ϵ , $\text{M}^{-1} \text{cm}^{-1}$
	11.5	9520; ^b 9710 ^c	400; ^{b,e} 920 ^c
	13.5	10 400 ^{b,c}	400; ^{b,e} 760 ^c
	11.5	11 600; ^b 11 200 ^c	90; ^{b,e} 165 ^c
	10.0	11 700 ^b	70 ^{b,e}
	7.9–10.0	12 050 ^d	60 ^{d,e}
	11.0	12 200; ^d 12 300 ^c	5; ^{d,e} 30 ^c

^aIn D_2O . ^bReference 25. ^cReference 28. ^dReference 26. ^eUncorrected for disproportionation.

origin of the activation barrier imposed by increasing the distance? The answer to such questions is usually sought by using the Marcus theory of electron transfer.^{22,23} This theory, as applied to bimolecular electron-transfer processes, breaks the activation barrier down into contributions from driving force, work, inner-sphere (ligand) reorganization, outer-sphere (solvent) reorganization, and electronic terms. In the intramolecular systems of interest here, the driving force and inner-sphere reorganizational energy are generally held constant across a series of compounds, and the work term is zero for an intramolecular reaction. Thus the source of the distance effect on the activation barrier is restricted to the solvent reorganizational energy and the electronic terms.

Both of these terms are expected to act to decrease the rate constant of reaction with increasing donor-acceptor distance. The solvent reorganizational energy term inherently becomes larger as the charge displacement of the electron transfer increases. The transmission coefficient is also expected to decrease from unity (for an adiabatic reaction) to less than unity (nonadiabatic) as the orbital overlap between the metals decreases with increasing separation. The problem, then, is to separate these two terms to see if just one or both are contributing to the observed effect.

An Interesting Correlation

The purpose of this note is to show that existing data may be used to examine the source of the effect of donor-acceptor distance on the rate constant. This insight may be obtained by reexamining the elegant studies of Taube and co-workers^{24–27} that formed the basis for the current protein and peptide work. Taube's seminal studies involved measuring the rate constants for intramolecular electron-transfer reactions in several systems. Those of interest here involve complexes of the form $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Ru}^{\text{II}}-\text{L}-\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$, where L is a bridging ligand related to 4,4'-bipyridyl. The Ru(II)-Co(III) electron-transfer rate constant was determined for a number of bridging ligands, and the reported results are summarized in Table I. For these complexes with inter-metal distances ranging from 7.9 to 13.5 Å, the rate constants vary over a range of about a factor of 20, with the rate constant apparently not simply a function of inter-metal distance.

The key to understanding the origin of the changing activation barrier is found when these electron-transfer results are correlated with the intervalence-transfer absorption band energies of the

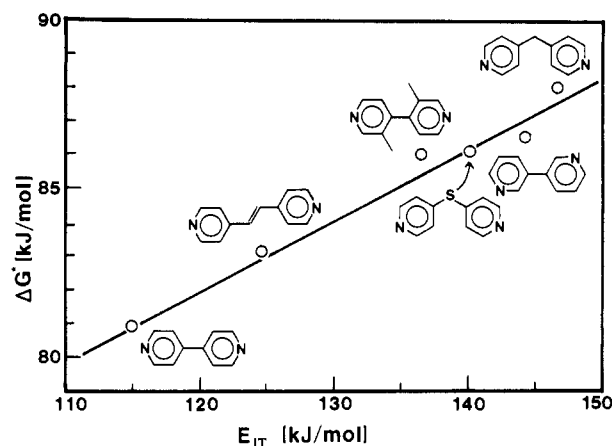


Figure 1. Plot of activation free energy for electron transfer in $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Ru}^{\text{II}}-\text{L}-\text{Co}(\text{NH}_3)_5]^{5+}$ vs intervalence-transfer band energy in $[(\text{NH}_3)_5\text{Ru}^{\text{II}}-\text{L}-\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ for six bridging ligands.

corresponding Ru(II)-Ru(III) complexes. These have been measured for a variety of bridging ligands, and the IT energies with the bridging ligands of Table I are presented in Table II. The energies of these absorption bands range from 9500 to 12 300 cm^{-1} , and the extinction coefficients vary from about 30 to 920 $\text{M}^{-1} \text{cm}^{-1}$.

A plot of ΔG^\ddagger for the Ru(II)-Co(III) reaction vs E_{IT} for the corresponding Ru(II)-Ru(III) complexes is given in Figure 1. The points lie near a straight line (least-squares slope 0.21 ± 0.02 ; intercept = 56.8 ± 2.9 kJ/mol, 95% *t*-test confidence). This correlation was first noted by Tom²⁹ and has been discussed.³⁰ It is this correlation which strongly suggests that it is the outer-sphere reorganizational energy, not the electronic term, which is responsible for the difference in electron-transfer rate constants across the series.

To explain this correlation, several points should be noted. For the Ru-Ru intervalence-transfer absorption, because the complex is symmetrical, the energy of the IT band is the sum of the inner-sphere and outer-sphere reorganizational energies

$$E_{\text{IT}} = \lambda_o + \lambda_i \quad (1)$$

The λ_i term is small for ruthenium complexes, about 1100 cm^{-1} in this case,³¹ and should certainly be essentially constant throughout the series. Thus the variation in E_{IT} reflects a variation in λ_o for these complexes.

The free energy of activation of the thermal Ru(II)-Co(III) electron-transfer reaction has contributions from the outer-sphere and inner-sphere reorganizational energies and the standard free energy change for the reaction. The general expression is

$$\Delta G^\ddagger = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{4\lambda} \quad (2)$$

where $\lambda = \lambda_o + \lambda_i$ and ΔG° is the standard free energy change for the electron-transfer reaction.²² Note that λ_i has contributions from the ruthenium and cobalt centers.

If we assume that for a given bridging ligand λ_o has the same value for the Ru-Ru and Ru-Co electron transfers, then the value of λ in (2) may be expressed as

$$\lambda = E_{\text{IT}} + \lambda_{\text{diff}} \quad (3)$$

where λ_{diff} represents the difference in the λ_i term between a cobalt and a ruthenium center. Now (2) can be rewritten as

$$\Delta G^\ddagger_{\text{Ru-Co}} = \frac{E_{\text{IT}} + \lambda_{\text{diff}}}{4} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{4(E_{\text{IT}} + \lambda_{\text{diff}})} \quad (4)$$

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It is easiest to consider the relationship of E_{IT} and ΔG^* if ΔG° is constant, as is true for the series of interest. The value of ΔG° may be estimated based on the electrode potentials of the corresponding Ru(III/II) and Co(III/II) couples. For the bis(ruthenium) complexes, the average electrode potentials for the (III,III)/(III,II) and (III,II)/(II,II) couples have been reported for all but the 3,3'-bipyridyl complex.^{25,28} The values are all 0.355 ± 0.015 V. The cobalt complexes' potentials may be estimated as approximately 0.10 V, based on values^{32,33} of $E^\circ = 0.06$ V for $[\text{Co}(\text{NH}_3)_6]^{3+/2+}$ and $E^\circ = 0.34$ V for $[\text{Co}(\text{bpy})_3]^{3+/2+}$, and are presumably quite insensitive to differences in the bridging ligand. The value of ΔG° for the reaction may be safely estimated as +25 kJ/mol, with the variation between the different ligands small enough to ignore. For ΔG° and λ_{diff} constant, differentiating (4) yields

$$\frac{d(\Delta G^*)}{dE_{IT}} = \frac{1}{4} - \frac{(\Delta G^\circ)^2}{4(E_{IT} + \lambda_{\text{diff}})^2} \quad (5)$$

λ_{diff} may be estimated by using calculated λ_i values for the $[\text{Co}(\text{NH}_3)_6]^{3+/2+}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ couples^{30,31} to be approximately 140 kJ/mol. Thus the expected slope of the $\Delta G^*_{\text{Ru-Co}}$ vs E_{IT} plot is about 0.25. The y intercept corresponds to the value of ΔG^* when $E_{IT} = 0$ and is calculated to be approximately 48 kJ/mol.

The observed slope of 0.21 is in good agreement with the calculated value of 0.25. The calculated intercept of 48 kJ/mol is somewhat below the observed value of 57 kJ/mol, but several approximations went into its calculation. The main conclusion to be drawn here is that the difference in rate constants across the series of complexes is essentially entirely due to variation in the outer-sphere reorganizational energy. This would imply that the transmission coefficient is constant across the series, despite the considerable difference in the bridging ligands and inter-metal separation. The simplest conclusion is that the value of κ is unity in each case. It appears that Ru-Co intramolecular electron transfer across as much as 14 Å is adiabatic.

Two interesting related bridging ligands have not been included in this series: pyrazine and imidazolate. The bridged Ru-Ru and Ru-Co complexes of these ligands have been studied.³⁹⁻⁴¹ Pyrazine is a particularly interesting case due to the attention given the Taube-Creutz ion, $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$. These ligands have been omitted from consideration here because of their large effect on the potentials of the Ru(III/II) couples, making estimation of the driving force in the Ru(II)-Co(III) reactions difficult.

Implications

The evidence that each of the electron-transfer reactions in the Ru-Co series is probably adiabatic is consistent with the conclusions of Szczy and Haim.^{42,43} They found a distance dependence of the rate constants in a series of Fe(II)-Co(III) electron-transfer reactions through bipyridyl bridging ligands that they attributed to the changing outer-sphere reorganizational energy, and they inferred that these reactions were adiabatic. These cases point to the necessity of accounting for outer-sphere reorganizational energy when examining other systems for the

effect of distance on electron-transfer rate.

Theoretical estimation of the value of the λ_0 term is usually done by using the Hush equation^{22,23}

$$\lambda_0 = e^2 \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \left(\frac{1}{2a_1} - \frac{1}{2a_2} - \frac{1}{r} \right) \quad (6)$$

where D_{op} and D_s are the optical and static dielectric constants of the solvent, a_1 and a_2 are the radii of the two separated metal complexes, and r is the separation distance. For example, λ_0 for the bridged bis(ruthenium) complexes may be calculated by assuming $a_1 = a_2 = 4.0$ Å and using values³⁴ of $D_{\text{op}} = 1.777$ (at 589 nm) and $D_s = 78.5$. For $r = 8.0$ – 13.5 Å, it is calculated that $\lambda_0 = 8000$ – 11200 cm⁻¹. Since λ_i for these complexes is about 1100 cm⁻¹,³¹ it is obvious that for the data in Table II the Hush equation gives an approximate value for λ_0 . However, the values of outer-sphere reorganizational energy in this series do not consistently correlate with the metal-metal distance. For example, the dipyriddyethylene complex, with the longest inter-metal distance of the six complexes, has E_{IT} smaller than that for most of the other complexes. Other models for the outer-sphere reorganizational energy have been proposed,³⁵ but it is not clear that any of these is capable of rationalizing these structural effects. The solvent reorganization is obviously a subtle factor, but a substantial one that must be reckoned with. The possibility that even the long-range (up to 25 Å) electron-transfer reactions that have been reported are adiabatic cannot be ruled out until the solvent reorganizational energy is carefully accounted for.

Knowing that the rate decrease in these systems is due to the solvent reorganizational energy also sheds more light on how the solvent reorganizational energy is manifested. As seen in Table I, most of the change in ΔG^*_{298} is found in the ΔS^* term (although the dipyriddyethylene complex may be an exception). This is similar to what would be expected if the rate decrease were due to a decreasing transmission coefficient: a fairly constant enthalpy and a decreasing entropy of activation. Thus the activation parameters alone for a reaction cannot be used to distinguish a nonadiabatic reaction from one with a large solvent reorganizational term.

The demonstration that the Ru-Co electron-transfer reactions are adiabatic bears on the general question of the magnitude of the electronic coupling matrix element for electron transfer. It is generally believed that this matrix element decreases with increasing donor-acceptor separation according to

$$H_{AB} = H_{AB}^\circ \exp[-\beta'(r - \sigma)] \quad (7)$$

where H_{AB} is the matrix element, r is the inter-metal distance, H_{AB}° is the value of H_{AB} when $r = \sigma$, and β' is a factor estimated to have a value between 1.0 and 2.5 Å⁻¹.²³ This is based on both theory and studies of long-range electron transfer in glasses.³⁶ The effect of the matrix element is usually calculated by using the Landau-Zener equation, leading to the general conclusion that for H_{AB} sufficiently large, the transmission coefficient, κ , is unity; for H_{AB} small, κ is proportional to H_{AB}^2 .²³ Thus, within some critical donor-acceptor separation radius, the transmission coefficient is expected to be unity; at greater separation, the coefficient should fall off sharply with distance, by a factor of between 7 and 150 Å⁻¹ based on the above values for β' . The analysis presented here strongly indicates that the Ru^{II}-L-Co^{III} system is in the adiabatic regime at least up to 14 Å. There is considerable discussion as to whether typical bimolecular electron-transfer reactions, in which metal complexes can approach to closer than 10 Å, are adiabatic.^{23,37,38} This analysis would suggest that they are. At what distance the nonadiabatic regime begins remains one of the most intriguing questions. Continued study of the long-distance intramolecular electron-transfer reaction, with careful consideration of outer-sphere reorganizational energy, promises to answer that question.

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