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INTRAMOLECULAR ELECTRON TRANSFER

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Abstract - Measurements of rate constants for intramolecular electron transfer in binuclear complexes $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ where L is a bridging nitrogen heterocylic ligand are reviewed. Mechanisms of communication between the metal centers are discussed, and it is suggested that, depending on detailed structural features of the bridging ligands, either through the ligand or ligand bypass mechanisms are operative. For the systems which feature through the ligand electron transfer, the free energy of activation depends inversely upon the distance between the metal centers. The trend is rationalized on the basis of increasing solvent reorganization with increasing distance, the inner shell reorganization and the thermodynamic factors remaining constant along the series of related ligands. The question of adiabaticity is discussed, and it is suggested that the limiting adiabatic regime has been reached.

INTRODUCTION

Since the discovery of the bridged activated complex nearly 30 years ago (Ref.1), a very large number of inner sphere electron transfer reactions has been examined kinetically and mechanistically (Ref.2). The great majority of the reactions that have been studied obey mixed second order kinetics, first order with respect to the oxidant and first order with respect to the reductant. The classic (Ref.3) three-step mechanism

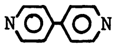
$$M^{III}L_5X^{2+} + N^{II}L'_6{}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_5M^{III}XN^{II}L'_5{}^{4+} + L \qquad (1)$$

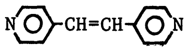
$$L_5M^{III}XN^{II}L'_5{}^{4+} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} L_5M^{II}XN^{III}L'_5 \qquad (2)$$

$$L_5M^{II}XN^{III}L'_5{}^{4+} + S \xrightarrow{k_3} M^{II}L_5S^{2+} + N^{III}L'_5X^{2+} \qquad (3)$$

consisting of formation of the precursor complex (eq.1), intramolecular electron transfer (eq.2), and dissociation of the successor complex (eq.3), is, under most circumstances, compatible with the observed second order kinetics. In eq. 1-3, $M^{III}L_5X^{2+}$ and $N^{II}L_6^{2+}$ represent the oxidant (inert) and the reductant (labile), respectively, and the dissociation of the successor complex is assumed to result in transfer of the ligand X^- from oxidant to reductant. Assuming that the dissociation of the successor complex is rapid compared to the preceding steps, depending on whether eq. 1 or eq. 2 is rate-determining, we are dealing with a substitution-controlled or a redox-controlled reaction, respectively (Ref.4). In the former case, the observed second-order rate constant has the significance of k_1, and under such circumstances not much is learned about electron transfer. This is the situation prevailing, for instance, in many reductions by $V(OH_2)_6^{2+}$. If eq. 1 is a rapid, unfavorable equilibrium ($k_1/k_{-1} = Q_p$, the equilibrium constant for the formation of the precursor complex), then the observed second order rate constant has the significance of Q_pk_{et}, and again not much is learned about the act of electron transfer itself. Reactivity patterns may be associated with changes in Q_p and/or k_{et}. The great majority of redox-controlled reactions belong to this category and a great deal of interest has existed for a long time in dissecting the measured rate constants into their elementary components Q_p and k_{et}, and in particular in obtaining rates of electron transfer uncomplicated by the need of assembling the reactants. However, it was not until 1973 (Ref.5) that an indirect (and extremely ingenious) method for synthesizing high concentrations of precursor complexes (and thus of measuring k_{et}) was devised, and it was not until 1974 (Ref.6) that a system was found where the stability of the precursor complex was sufficiently high so that both Q_p and k_{et} could be measured in the same system. Even at the time of the present writing, there are, as far as I am aware, only three types of systems, (all involving nitrogen heterocycles as bridging ligands and $Co(NH_3)_5^{3+}$ as the electron acceptor), where there exists unequivocal evidence (and values of k_{et}) for thermally induced intramolecular electron transfer within binuclear complexes: Ru(II)ammine-Co(III)ammine (Ref.5,7-9), Fe(II)cyanide-Co(III)ammine (Ref.6,10-12), and Ru(II)EDTA-Co(III)ammine (Ref.13,14).

In the present paper, I discuss the mechanisms of intramolecular electron transfer in binuclear complexes containing $Fe(CN)_5^{3-}$ and $Co(NH_3)_5^{3+}$ moieties bridged by 4,4 -bipyridine, BP, and related nitrogen heterocycles, BPEy, BPEa, BPP, BPM, BPA, BPB, PYZ, IM, and DMPB.


BP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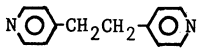
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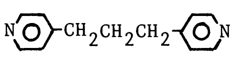

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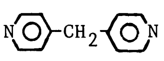

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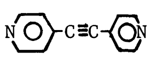
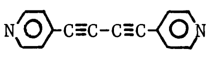
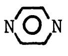


BPA

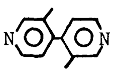


BPB



PYZ

IM



DMBP

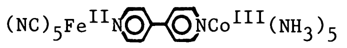
In particular, I inquire about channels of communication between ligand-bridged metal centers, and address the question of adiabaticity in intramolecular electron transfer.

THE PROTOTYPE SYSTEM: $(NC)_5Fe^{II}BPCo^{III}(NH_3)_5$

There are many difficulties associated with the finding of appropriate pairs of metal centers coordinated to auxiliary and potentially bridging ligands that lead to the desired properties with regard to oxidation states, redox potentials, substitution properties, and self exchange rate constants. These difficulties can be traced to a variety of factors, notably little affinity of the reactant mononuclear complexes for each other. However, even when there is an anticipated high precursor complex formation constant, intramolecular electron transfer studies may be thwarted by competitive outer sphere pathways. For example, the $Ru(NH_3)_5OH_2^{2+}$ - $Co(NH_3)_5BP^{3+}$ system appeared (Ref.15) to be ideal for a study of intramolecular electron transfer. The coordinated water in $Ru(NH_3)_5OH_2^{2+}$ (Ref. 16) is rather labile and the affinity of the $Ru(NH_3)_5^{2+}$ moiety for nitrogen heterocycles is extemely high (Ref.16). However, upon mixing $Ru(NH_3)_5OH_2^{2+}$ and $Co(NH_3)_5BP^{3+}$ solutions all that can be detected (Ref.15) is the outer sphere pathway, and if the formation of the plausible precursor complex $(NH_3)_5Ru^{II}BP$-$Co^{III}(NH_3)_5$ is competitive with the outer sphere pathway, the yield is too small to be of any use.

Having failed in the attempts to obtain intramolecular electron transfer rate constants in the $Ru(NH_3)_5OH_2^{2+}$ - $Co(NH_3)_5BP^{3+}$, system attention was shifted to the analogous $Fe(CN)_5OH_2^{3-}$ - $Co(NH_3)_5BP^{3+}$ system (Ref.6). Again, one of the rationales in choosing this system relates to the high affinity of the $Fe(CN)_5^{3-}$ moiety for nitrogen heterocycles (Ref.17), undoubtedly the result of efficient back bonding (filled t_{2g} iron orbitals overlapping with empty π^* ligand orbitals). An additional advantage of $Fe(CN)_5OH_2^{3-}$ over $Ru(NH_3)_5OH_2^{2+}$ relates to the faster water substitution rate in Fe(II) as compared to Ru(II) (a factor of more than 10^3) (Ref.18), a circumstance that favors inner sphere complex formation over outer sphere electron transfer. In fact, by simply mixing millimolar solutions of $Co(NH_3)_5BP^{3+}$ with $\simeq$ 10^{-5} M solutions of

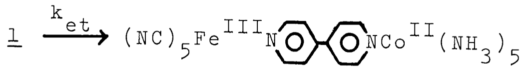
$Fe(CN)_5OH_2^{3-}$, essentially quantitative yields of the transient binuclear complex 1 are produced.



1

The formulation of 1 as a Fe(II)-Co(III) complex, e.g., a precursor complex (rather than a Fe(III)-Co(II) successor complex) is based on kinetic and spectroscopic studies. Rates of formation of complexes $Fe(CN)_5L^{n-}$ have been studied extensively (Ref.18,19), and, except for charge effects, have been found to be independent of the nature of the incoming ligand L. Thus, rate constants (at 25°C and ionic strength 0.10M) for reactions between $Fe(CN)_5OH_2^{3-}$ and uncharged pyridines fall in the narrow range (3-4) x 10^2 M^{-1} s^{-1}. For instance, the rate constant for the reaction between $Fe(CN)_5OH_2^{3-}$ and BP is 4.0 x 10^2 M^{-1} s^{-1}. For the substitution (non-redox) reaction between $Fe(CN)_5OH_2^{3-}$ and $Ru(NH_3)_5BP^{2+}$ the rate constant is 1.7 x 10^2 M^{-1} s^{-1}, typical of other reactions of dipositively charged pyridines (Ref.10). Finally, the higher value 5.5 x 10^3 M^{-1} s^{-1} for the reaction of $Co(NH_3)_5BP^{3+}$ is characteristic (Ref.11,20) of tripositively charged incoming ligands. The visible spectrum of the transient exhibits a maximum at ca. 505 nm with a molar absorbance of 6 x 10^3 M^{-1} cm^{-1}. This is the characteristic metal to ligand charge transfer band of $Fe(CN)_5^{3-}$ coordinated to a pyridine. For comparison, the MLCT band of $Fe(CN)_5BP^{3-}$ occurs at 432 nm with molar absorbance 5 x 10^3 M^{-1} cm^{-1}. The longer wavelength for 1 as compared to $Fe(CN)_5BP^{3-}$ is consistent with the strong electron withdrawing effect of the $Co(NH_3)_5^{3+}$ moiety coordinated to the remote N of $Fe(CN)_5BP^{3-}$. Similar shifts are observed when other electron withdrawing substituents are bound to the remote N of $Fe(CN)_5BP^{3-}$: for H^+, λ and ε are 510 nm and $\simeq$ 4 x 10^3 M^{-1} cm^{-1}, respectively; for CH_3^+, the values are 515 nm and 5 x 10^3 M^{-1} cm^{-1}. Therefore, it is seen that the transient species formed when $Fe(CN)_5OH_2^{3-}$ and $Co(NH_3)_5BP^{3+}$ are mixed is produced at rates characteristic of the substitution reactions of $Fe(CN)_5OH_2^{3-}$, and exhibits a MLCT band characteristic of complexes of $Fe(CN)_5^{3-}$ with pyridines, and therefore the formulation of the transient as the precursor complex 1 appears to be on firm grounds.

The transient disappears by a first-order process with k_{et} = 2.6 x 10^{-3} s^{-1} (25°C, 0.10 M ionic strength) and yields Co(II) and $Fe(CN)_5BP^{2-}$. The rate determining step for the disappearance of 1 is assigned to the electron transfer event given by eq. 4



(4)

and the formation of $Fe(CN)_5BP^{2-}$ proves that ligand transfer obtains in the overall reaction.

REACTIVITY PATTERNS FOR INTRAMOLECULAR ELECTRON TRANSFER IN $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ - THROUGH LIGAND AND LIGAND BYPASS MECHANISMS

The rate constants (25°C, ionic strength 0.10M) for intramolecular electron transfer in a series of binuclear $Fe(CN)_5^{3-}$ - $Co(NH_3)_5^{3+}$ complexes bridged by various bidentate N-heterocycles are listed in Table 1. Included in the table are the wavelengths for the MLCT bands of the corresponding mononuclear $Fe(CN)_5L^{3-}$ and binuclear $(NC)_5FeLCo(NH_3)_5$ complexes. From a comparison between rate constants for electron transfer and the shift in the MLCT band of the $Fe(CN)_5L^{3-}$ complex upon coordination of the $Co(NH_3)_5^{3+}$ moiety to the remote nitrogen of L, two mechanisms of electron transfer were proposed (Ref.11): through the ligand, e.g., resonance mechanism with the bridging ligand serving the role of coupling the two metal centers, and bypassing the bridging ligand, e.g., the bridging ligand serves to bring the metal centers near each other and "outer sphere" electron transfer through the auxiliary ligands obtains.

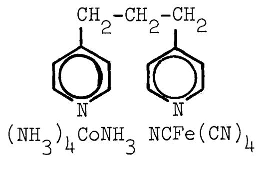
TABLE 1. Rate constants (25°C, ionic strength 0.10M) for electron transfer and wavelengths for MLCT bands of $(NC)_5FeLCo(NH_3)_5$ complexes

L	k_{et}, s^{-1}	λ, nm[a]	λ, nm[b]
IM[c]	0.17	-	-
PYZ[d]	$5.5x10^{-2}$	452	630
BP[e]	$2.6x10^{-3}$	432	505
BPEy[e]	$1.4x10^{-3}$	460	500
BPA[f]	$1.7x10^{-3}$	460	495
BPB	$6.9x10^{-4}$	483	498
DMBP[f]	$2.3x10^{-3}$	383	405
BPM[e]	$6x10^{-4}$	370	370
BPEa[e]	$2.1x10^{-3}$	365	365
BPP[e]	$4.8x10^{-3}$	360	360

[a] For $Fe(CN)_5L^{3-}$. [b] For $(NC)_5LCo(NH_3)_5$ [c] Ref.12 [d] Ref.21 [e] Ref.11 [f] Ref.14.

It was suggested that the extent and nature of the communication between the two metal centers

(Ref.10,11) can be assessed by two criteria: the rate constant for electron transfer from one metal ion to the other, and the shift in the energy of MLCT band of $Fe(CN)_5L^{3-}$ upon coordination of $Co(NH_3)_5{}^{3+}$ to the remote N atom of L. It has been shown (Ref.17) that the energies of the MLCT bands of $Fe(CN)_5L^{3-}$ complexes where L is a pyridine derivative, are very sensitive to substituent effects in the pyridine ring. Electron withdrawing substitutents produce a bathochromic shift whereas electron releasing substituents give a hypsochromic shift, the effects being considerably more important in the 2 or 4 positions than in the 3 position. Bipyridines where the conjugation between the two pyridine rings is interrupted (BPM, BPEa, BPP) yield $Fe(CN)_5L^{3-}$ complexes that exhibit their MLCT band very near that(362 nm) of the pyridinepentacyanoferrate(II) complex. $Fe(CN)_5L^{3-}$ complexes which feature conjugation between the two pyridine rings (L = BP, BPEy, BPA, BPB, DMBP) exhibit their MLCT bands at longer wavelengths than the pyridine complex. Moreover, addition of the $Co(NH_3)_5{}^{3+}$ moiety to the remote pyridine N of $Fe(CN)_5L^{3-}$ results in a bathochromic shift when the two pyridine ligands in L are conjugated, but has no effect on the energy of the MLCT band when the two pyridine rings are separated by insulating groups. On the basis of the spectroscopic considerations, the ligands can be classified into two groups: those that transmit electron withdrawing effects and those that do not. Both classes of ligands, with the exception of BPM, lead to measurable electron transfer rates. Therefore, at first glance, it would appear that the requirements for net electron transfer and for transmission of electron withdrawing effects from one metal to the other are not the same, e.g., uninterrupted conjugation between the two pyridine rings may be necessary for transmission of electron withdrawing effects but not for net electron transfer. However, on closer examination it becomes apparent that the ligands that feature interrupted conjugation <u>and</u> measurable electron transfer rates are those that have a saturated hydrocarbon chain between the two rings such that through appropriate rotation around the C-C single bonds a conformation is achieved whereby the coordination spheres of the metal centers come in contact as illustrated in 2.



2

For the closed conformation 2, it is suggested that "outer sphere" electron transfer across the cyanide and ammonia coordination shells obtains. For BPM, where the two pyridine rings are connected by a single CH_2 group, the two metal centers cannot come closer to each other than 10 A, too large a distance for outer sphere electron transfer (contact between cyanide and ammonia coordination shells gives a distance of 8.0 A between iron and cobalt centers). Thus, it is suggested that coupling of the metal centers via bridging ligands with uninterrupted conjugation is necessary for net electron transfer and for transmission of electron withdrawing effects. When conjugation between the pyridine rings is interrupted, then electron withdrawing effects are not transmitted and net electronn transfer through the ligand is precluded. However, with interrupted conjugation net electrons transfer is still possible by an outer sphere pathway, e.g., a bridging ligand bypass mechanism, provided that the bridging ligand is sufficiently flexible to allow for contact between the coordination shells of the metal ions.

Some additional evidence for the suggestion of an "outer sphere" mechanism in the complexes bridged by BPEa and BPP comes from measurements of the rate constants for outer sphere electron transfer in the ion pairs $Co(NH_3)_5BPEa^{3+}$ $Fe(CN)_6{}^{4-}$ (Ref.22) and $Co(NH_3)_5BP^{3+}$ $Fe(CN)_5BPEa^{3-}$ (Ref.23). The observed values are 1.0×10^{-2} and 9.0×10^{-3} s^{-1} which compare favorably with the values 2.1×10^{-3} and 4.6×10^{-3} for the binuclear complexes bridged by BPEa and BPP, respectively. (The value 1.0×10^{-2} s^{-1} for the ion pair with $Fe(CN)_6{}^{4-}$ becomes 9.0×10^{-3} s^{-1} when corrected for free energy and self exchange rate utilizing the Marcus cross relation).

COUPLING OF METAL CENTERS BY BRIDGING LIGANDS: ADIABATICITY AND THE ROLE OF DISTANCE IN ELECTRON TRANSFER

The electron transfer mechanism for the ligands which feature uninterrupted conjugation is considered to be the resonance mechanism, (Ref.24) the bridge serving to couple the two metal centers. For these ligands, it is found that a plot of the free energy of activation for electron transfer vs. the inverse of the distance between the metal centers is linear (cf. Fig.1).

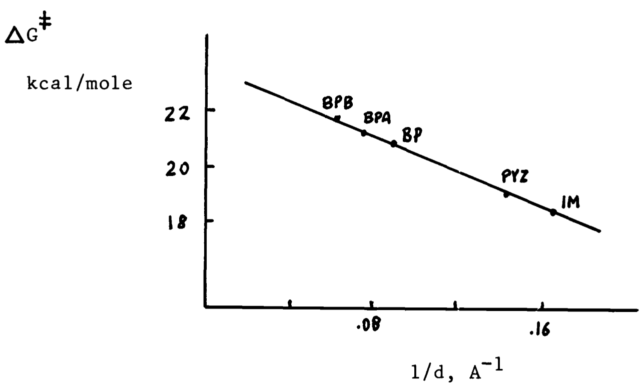


Fig. 1. Free energy of activation for intramolecular electron transfer vs inverse of distance between metal centers.

This is the anticipated behavior if all that is changing along the series is the outer sphere reorganization energy. According to current concepts in electron transfer (Ref.25), the barrier to electron transfer is made up of two terms: the electronic and the nuclear factors. The former is a measure of the probability of electron transfer once the intersection region has been reached, e.g., it is a measure of adiabaticity. The nuclear factor consists of inner and outer shell reorganization terms. In analytical form, the Marcus free energy barrier for intramolecular electron transfer in a bridged binuclear complex is given by eq. 5.

$$\Delta G^{*} = \frac{\lambda i + \lambda o}{4} + \frac{\Delta G\overset{o}{r}}{2} + \frac{(\Delta G\overset{o}{r})^2}{4(\lambda i + \lambda o)} \qquad (5)$$

λ_i and λ_o are the energy terms related to the reorganization of the inner and outer coordination shells of the reactants, and ΔG^* is the standard free energy change for internal electron transfer within the binuclear complex. The solvent reorganization term is given by eq. 6 (Ref.12).

$$\lambda_o = e^2\left|\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right|\left|\frac{1}{D_{op}} - \frac{1}{D_s}\right| \qquad (6)$$

a_1 and a_2 are the radii of the reactants (assumed to be spherical), r is the distance between the metal centers in the transition state, and D_{op} and D_s are the optical and static dielectric constants of the medium. Since the inner sphere reorganization energies, standard free energy changes, and the radii of the reactants are likely to be fairly constant along the present series of closely related nitrogen heterocyclic ligands, eq. 5 can be simplified to $\Delta G^{\ddagger}$ = int - slope/d, with $\Delta G^{\ddagger} = \Delta G^{*} + RT\ln(hk/k_Bt)$ and slope = 45 kcal.A. Experimentally, it is found that the slope is 31 kcal.A. Considering the approximations and assumptions, the agreement between experimental and theoretical slopes is considered acceptable. Since the reactivity trends can be accounted for by invoking only nuclear factors, it is inferred that the electronic factors are constant throughout the series of ligands, presumably because the adiabatic limit has been reached for all the ligands. Some support for this suggestion comes from calculations of the coupling parameters from the observed intervalence bands (Ref.26) in a series of mixed valence compounds $(NH_3)_5Ru\ L\ Ru(NH_3)_5^{5+}$ where L is a nitrogen heterocyclic ligand. Values of $2H_{12}$, the interaction energy or energy splitting at the intersection region, are 2.2, 1.8 and 1.1 kcal for BP, BPEy and DMBP, respectively. It has been estimated on theoretical grounds (Ref.27) that a value of ≃ 1 kcal is sufficient for electron transfer to be in the adiabatic regime. Since the calculated values of $2H_{12}$ for the above ligands are larger than the estimated lower limit of ≃ 1 kcal, it follows that adiabatic electron transfer obtains for these ligands acting as bridges.

Additional evidence in favor of the suggestion of adiabatic electron transfer comes from a comparison between BP and DMBP as bridging ligands. For the former, the two pyridine rings are free to adopt a coplanar conformation. For DMBP, the steric constraints associated with the methyl groups in the 3,3 positions result in a favorable conformation with the rings perpendicular to each other. The coupling between the pyridines is smaller for DMBP than for BP. Reference has already been made to the values of $2H_{12}$, 2.2 and 1.1 kcal, respectively. Additional evidence to show the decreased coupling in DMBP as compared to BP comes from examining the positions of the MLCT bands of various pyridine complexes of $Fe(CN)_5^{3-}$. The MLCT bands of $Fe(CN)_5Py^{3-}$, $Fe(CN)_5BP^{3-}$ and $Fe(CN_5DMBP^{3-}$ occur at 362, 432 and 383 nm, respectively. Even taking into account the inductive effects of the methyl groups, it is evident that the transmission of the electronic withdrawing effect of the remote pyridine is much less efficient for the dimethyl derivative than for the unsubstituted ligand. Moreover, addition of $Co(NH_3)_5^{3+}$ to the remote N of $Fe(CN)_5BP^{3-}$ results in a large bathochromic shift (432 to 505 nm), whereas the shift is rather small (383 to 405 nm) for coordination of $Co(NH_3)_5^{3+}$ to $Fe(CN)_5DMBP^{3-}$. The evidence points to a substantially smaller degree of coupling in DMBP as compared to BP. In spite of this difference, the rate constants for intramolecular electron transfer in $(NC)_5FeBPCo(NH_3)_5$ and $(NC)_5FeDMBPCo(NH_3)_5$ (2.6×10^{-3} and 2.3×10^{-3} s^{-1}) are almost equal, and therefore it is reasonable to infer that both reactions are occurring in the adiabatic regime.

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