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Intramolecular electron transfer from $Ru^{II}(EDTA)^{2-}$ to $Co^{III}(NH_3)_5{}^{3+}$ via nitrogen heterocycle bridging ligands

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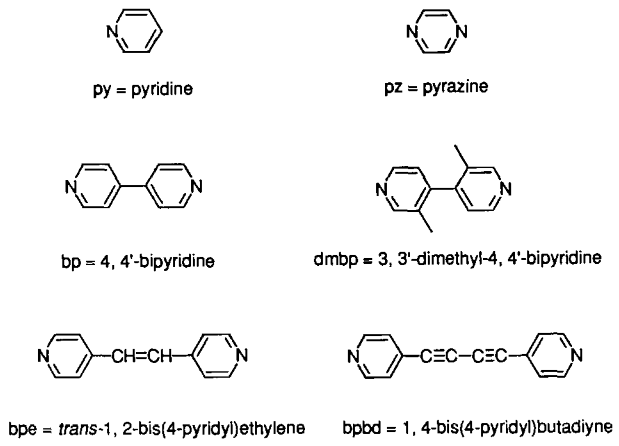
Abstract

A series of binuclear complexes of formula $(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+}$ (EDTA = ethylenediaminetetraacetate, L = pyrazine, 4,4′-bipyridine, 3,3′-dimethyl-4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,4-bis(4-pyridyl)butadyne) were prepared in aqueous solution by reaction of $Ru^{III}(EDTA)OH_2{}^-$ with $Co(NH_3)_5L^{3+}$. The reduction potentials of the binuclear complexes were measured. Reactions of the binuclear complexes with ascorbic acid or dithionite result in the preferential reduction of Ru(III) to Ru(II) and produce $(EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+$. The latter undergo intramolecular electron transfer from Ru(II) to Co(III) with rate constants (25.0 °C, $I = 0.20$ M) 22.7 ± 0.4, 0.64 ± 0.02, 0.067 ± 0.002, 0.21 ± 0.01 and 0.039 ± 0.001 s^{-1} (in the same order as above). The decrease in rate constant with increasing distance between metal centers is ascribed to the increase in solvent reorganization energy with increasing metal to metal distance. The reorganization energies corrected for the solvent contribution (ellipsoidal cavity model) have values of 10.6, 10.5, 11.8, 10.5 and 10.9 kcal mol^{-1}. Except for 3,3′-dimethyl-4,4′-bipyridine, it is suggested that the electron transfer is adiabatic. The results are compared with results from previous studies with $(NC)_5Fe^{II}LCo^{III}L(NH_3)_5$.

Keywords: Intramolecular electron transfer; Ruthenium complexes; Cobalt complexes; Heterocyclic ligand complexes

1. Introduction

The measurement of intramolecular rather than intermolecular electron transfer offers distinct advantages for investigating the details of the mechanism of electron transfer. Complications arising from the assembly of the reactants are absent and the transition state has a relatively well-defined geometry. In this manner it is possible to evaluate the relative contributions of inner-sphere, outer-sphere and thermodynamic barriers to the free energy of activation [1]. Unfortunately, there are few systems with the requisite properties which make them amenable to systematic studies of intramolecular electron transfer [1]. One such system involves $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ (**I**), where L represents one of the nitrogen heterocycles shown in Scheme 1. In previous work [2,3], we showed that the free energy of activation for internal electron transfer in **I** is inversely proportional to the Fe–Co distance. Moreover, when the free energies of activation are corrected for the solvent reorganization energies, the resulting values fall in the narrow range 13.5 ± 0.5 Kcal. We inferred that the electron transfer in these compounds lies in the limiting adiabatic regime [3].



Scheme 1.

In the present work, we extend our intramolecular electron transfer studies to binuclear complexes formulated as **II**: $(EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+$. The strategy employed here is based on that devised by Taube and

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co-workers [4–6] for the analogous $(H_2O)(NH_3)_4Ru^{II}LCo^{III}(NH_3)_5^{5+}$ systems. An $Ru^{III}LCo^{III}$ binuclear complex is first assembled in solution and the intramolecular electron transfer reaction is then triggered via the preferential reduction of the Ru(III) center by an external reducing agent. In contrast with the rather elaborate procedure [4] required for the assembly of the $(H_2O)(NH_3)_4Ru^{III}LCo^{III}(NH_3)_5^{6+}$ binuclear complexes, their $(EDTA)Ru^{III}LCo^{III}(NH_3)_5^{+}$ counterparts can be readily prepared via Eq. (1) by mixing the pentadentate EDTA aquo complex $Ru^{III}(EDTA)OH_2^-$ [7] with $Co(NH_3)_5L^{3+}$, where L is a ligand containing an exposed aromatic nitrogen. This straightforward procedure is a consequence of the demonstrated high lability of the water ligand in $Ru^{III}(EDTA)OH_2^-$ and the high affinity of the Ru(III) center for nitrogen heterocycles [7]. Following Eq. (1), the preferential reduction of the Ru(III) center is accomplished with the appropriate reductant, Eq. (2), and the sequence is then completed with the intramolecular electron transfer step, Eq. (3). We report herein values of k_{et} for the reactions of the ligands shown in Scheme 1, as well as ancillary measurements for Eqs. (1) and (2). The mechanism of intramolecular electron transfer is discussed in the light of the spectroscopic and electrochemical properties of the binuclear complexes **II**.

$$Ru^{III}(EDTA)OH_2^- + Co^{III}(NH_3)_5L^{3+} = \underset{\textbf{III}}{(EDTA)Ru^{III}LCo^{III}(NH_3)_5^{2+}} + H_2O \quad k_f, k_r \qquad (1)$$

$$(EDTA)Ru^{III}LCo^{III}(NH_3)_5^{2+} + R = (EDTA)Ru^{II}LCo^{III}(NH_3)_5^{+} + R^+ \quad k_{red} \qquad (2)$$

$$(EDTA)Ru^{II}LCo^{III}(NH_3)_5^{+} = (EDTA)Ru^{III}LCo^{II}(NH_3)_5^{+} \quad k_{et} \qquad (3)$$

2. Experimental

2.1. Materials

Sodium *p*-toluenesulfonate, bp, bpe and lithium perchlorate were recrystallized from hot water. The water and argon used were purified as described previously [8]. $[Co(NH_3)_5LH](ClO_4)_4 \cdot H_2O$ (L = pz, bp) were prepared according to literature procedures [9,10]. The analogous compounds with L = dmbp and bpbd were from a previous study [3]. $Ru(HEDTA)OH_2 \cdot 4H_2O$ was prepared as described in Ref. [11]. Solutions of $Ru^{II}(EDTA)OH_2^{2-}$ were prepared by reduction of the corresponding Ru(III) complex with amalgamated zinc under argon in acetate buffer. All other materials were reagent grade and used as received.

2.2. Physical measurements

Electronic spectra and slow kinetic measurements were obtained in a Cary 17 or 118 spectrophotometer. Fast kinetic measurements were carried out with a Durrum-Gibson stopped-flow instrument connected to a Nicolet digital oscilloscope model 204A. Cyclic voltammetric measurements were carried out with a Princeton Applied Research model 170 electrochemical system. The built-in XY recorder was used to record voltammograms at scan rates up to 500 mV s^{-1}. For faster scan rates oscillographic recording was used. The electrochemical cell was a conventional three-electrode type with an aqueous saturated calomel electrode as the reference electrode and pieces of platinum wire for the working and auxiliary electrodes. Formal reduction potentials are reported to ±0.01 V versus the normal hydrogen electrode. Ionic strength was adjusted to 0.200 M with sodium chloride. pH measurements were carried out with a Radiometer model 26 and an Orion model 801 pH meter. All solutions utilized for the measurements were adjusted to the desired pH with acetate or tris buffers. The temperature was 25.0 °C.

2.3. Kinetic measurements

Reaction conditions were adjusted to yield pseudo-first-order processes in every case, with one of the reactants kept in at least ten-fold excess. When the infinite time absorbance was constant, a two-parameter least-squares fit was carried out according to $(A_t - A_\infty) = (A_0 - A_\infty)\exp(-k_{obs}t)$. When subsequent secondary reactions resulted in a drift in the absorbance at long times, A_∞ was also floated. Absorbances were measured at wavelength maxima for reactants or products. The temperature was 25.0 °C and the ionic strength was 0.20 M adjusted with sodium *p*-toluenesulfonate.

3. Results

The electronic spectra of the mononuclear $Ru^{II}(EDTA)L^{2-}$ complexes (L = pz, bp, bpe, dmbp, bpbd) are summarized in Table 1. The visible spectra of these complexes are dominated by an intense metal to ligand charge transfer band [7]. Measurements were carried out at low (2.0–3.8) and at high (7.9–8.0) pH where the remote nitrogen of the aromatic heterocycle is protonated or deprotonated, respectively. Protonation of the remote nitrogen results in a bathochromic shift, as observed with the analogous pentaammineruthenium(II) [12] and pentacyanoferrate(II) [13] complexes.

In Table 2 the reduction potentials for the $Ru^{III/II}(EDTA)L^{-/2-}$ and $(EDTA)Ru^{III/II}LCo^{III}$-

Table 1
Electronic spectra of $Ru^{II}(EDTA)L^{2-}$ and $Ru^{II}(EDTA)LH^{-}$ complexes in aqueous solution[a]

L	λ_{max} (nm) (10^{-3} A (M^{-1} cm^{-1}))
py	382 (6.8)[b]
pz	463 (12)[c]
pzH^+	540 (10)[d]
bp	465 (7.0)[c]
bpH^+	560 (10)[e]
dmbp	405 (4.1)[c]
$dmbpH^+$	430 (6.2)[e]
bpe	495 (10)[c]
$bpeH^+$	568 (12)[e]
bpbd	502 (14)[c]
$bpbdH^+$	523 (16)[e]

[a] Ionic strength 0.20 M controlled with sodium p-toluenesulfonate; [Ru] = 5.0E–5 M; L = 2.0×10^{-3} M.
[b] Ref. [7].
[c] pH 7.9–8.0, tris buffer.
[d] 0.010 M HCl.
[e] pH 3.8, acetate buffer.

Table 2
Formal reduction potentials of $Ru^{III}(EDTA)L^{2-}$ and $(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+}$ complexes[a]

L	E° [b] (V)	ΔE° [c] (mV)
pz	0.24 ± .01	60
$pzCo^{III}(NH_3)_5{}^{3+}$ [d]		
bp	0.15 ± .01	70
$bpCo^{III}(NH_3)_5{}^{3+}$	0.13 ± .01	62
dmbp	0.13 ± .01	63
$dmbpCo^{III}(NH_3)_5{}^{3+}$	0.12 ± .01	67
bpe	0.13 ± .01	60
$bpeCo^{III}(NH_3)_5{}^{3+}$	0.11 ± .01	65
bpbd	0.14 ± .01	70
$bpbdCo^{III}(NH_3)_5{}^{3+}$	0.15 ± .01	72

[a] At 25 °C, pH 4.7 (acetate), ionic strength 0.20 M (sodium chloride).
[b] Average of oxidation and reduction peaks vs. NHE, uncorrected for junction potential.
[c] Separation between anodic and cathodic peaks in cyclic voltammogram.
[d] The anodic peak was not observed.

$(NH_3)_5{}^{2+/+}$ couples are given. The values reported represent the average of the potentials for the anodic and cathodic peaks, the peak separation being 60–70 mV except for the pyrazine-bridged binuclear complex where the anodic peak was not observed.

Reaction (1) was studied in detail only for bp and bpe. An excess of $Co(NH_3)_5L^{3+}$ was mixed with $Ru^{III}(EDTA)OH_2{}^-$ at pH 4.7 (acetate buffer). This pH was chosen to ensure that the dangling carboxylate is deprotonated ($pK_a = 2.4$) and the water is protonated ($pK_a = 7.6$) [7]. Plots of k_{obs} versus the concentration of the cobalt complex for bp and bpe are given in Fig. 1. According to the reaction in Eq. (1), $k_{obs} = k_f[Co] + k_r$.

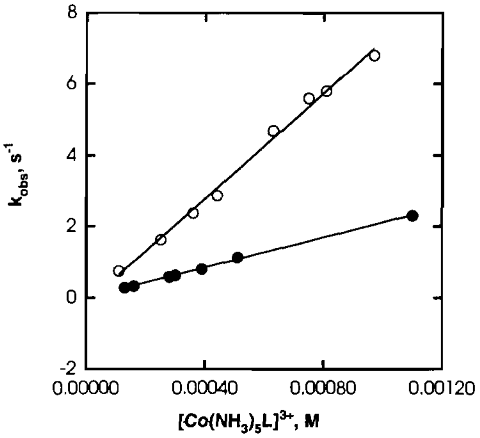

Fig. 1. Observed rate constants for reaction (1) at 25.0 °C, $I = 0.20$ M, pH = 4.7: ○, L = bp; ●, L = bpe.

The solid lines in Fig. 1 are the least-squares fits and yield values of $k_f = (7.4 \pm 0.3) \times 10^3$ and $(2.1 \pm 0.1) \times 10^3$ M^{-1} s^{-1} and $k_r = -0.17 \pm 0.2$ and $(8.4 \pm 0.9) \times 10^{-2}$ s^{-1} for bp and bpe, respectively. The intercepts are too small to be determined accurately from these plots. Therefore, values of k_r for bp and bpe were measured directly by studying the dissociation of the binuclear complexes in the presence of excess pyridine. Values of k_{obs} were independent of pyridine concentration in the range 0.010–0.20 M, as expected from a mechanism whereby the reverse of Eq. (1) is rate-determining and is followed by the fast reaction ($k = 6.3 \times 10^3$ M^{-1} s^{-1} [7]) shown in Eq. (4). Values of k_{-1} were 0.139 ± 0.003

$$Ru^{III}(EDTA)OH_2{}^- + py = Ru^{III}(EDTA)py^- + H_2O \qquad (4)$$

(average of 5 measurements) and $(3.82 \pm 0.04) \times 10^{-2}$ s^{-1} (average of 3 measurements) for bp and bpe, respectively. From the forward and reverse reactions, the value of the formation constants for the bp and bpe binuclear complexes are estimated at $(5.2 \pm 0.3) \times 10^4$ and $(5.5 \pm 0.1) \times 10^4$ M^{-1}, respectively. A cursory examination of the kinetics of reaction (1) for pz yielded values of $k_f = 4 \times 10^4$ M^{-1} s^{-1} and $k_r = 1$ s^{-1}, respectively. These values compare favorably with the values $k_f = 2.7 \times 10^4$ M^{-1} s^{-1} and $k_r = 0.90$ s^{-1} for the reaction of $Ru^{III}(EDTA)OH_2{}^-$ with $Ru(NH_3)_5pz^{2+}$ [14].

In order to assess the feasibility of ascorbic acid as a preferential and rapid reductant of the Ru(III) center in $(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+}$, a brief study of the kinetics of reduction of $Ru^{III}(EDTA)L^-$ (L = bp, bpe, pz) by ascorbic acid was carried out at 25.0 °C, $I = 0.200$ M (NaPTS) and pH 8.0 (tris buffer) with $[Ru(III)] = (2–8) \times 10^{-5}$ M and $[AA] = 4.00 \times 10^{-2}$ M. Under these conditions, ascorbic acid is present predominantly as HA^- (the pK_a of H_2A is 4.08 [15] at 25.0 °C and $I = 0.100$ M). Based on our previous work [16] on the ascorbic acid reduction of $Ru(NH_3)_5L^{3+}$

(L = pyrazine, pyridine, isonicotinamide), and on general considerations regarding reductions of transition metal complexes by ascorbic acid [17], we formulate the corresponding reductions of $Ru^{III}(EDTA)L^-$ as sequences of two one-electron transfer steps, Eqs. (5) and (6)[1]. Second-order rate constants k_5 are $(1.42 \pm 0.02) \times 10^2$, $(1.32 \pm 0.04) \times 10^2$ and $(6.5 \pm 0.2) \times 10^2$ M^{-1} s^{-1} for bp, bpe and pz, respectively. The reductions of the corresponding mononuclear $Co(NH_3)_5L^{3+}$ complexes by ascorbic acid have time scales of the order of hours [8,18].

$$Ru^{III}(EDTA)L^- + HA^- = Ru^{II}(EDTA)L^{2-} + HA \qquad k_5 \qquad (5)$$

$$Ru^{III}(EDTA)L^- + A^- = Ru^{II}(EDTA)L^{2-} + A \qquad \text{fast} \qquad (6)$$

When the binuclear complexes $(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+}$ are mixed with an excess of ascorbic acid in the stopped-flow apparatus, an absorbance increase is followed by an absorbance decrease at 500–650 nm. This is the wavelength region where the binuclear complexes $(EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+$ exhibit their characteristic Ru(II) to N-heterocycle transfer bands and therefore we identify the intermediates produced in the ascorbic acid reductions as Ru(II)–Co(III) binuclear complexes formulated as **II**. The increase in absorbance corresponds to the formation of the intermediate according to Eqs. (7) and (8) and the decrease in absorbance corresponds to the disappearance of **II** according to Eq. (3). In all cases the formation was found to be 20–100 times faster than the disappearance. We focused our attention on the kinetics of the disappearance of $(EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+$ but also obtained some information about the kinetics of Eq. (7) for bp and bpe. With ascorbic acid in the $(1.0–10.0) \times 10^{-2}$ M range, pH 8.1, $I = 0.20$ M and 25.0 °C, reaction (7) was found to be first-order in ascorbic acid with $k_7 = (1.8 \pm 0.2) \times 10^3$ and $(6.1 \pm 0.5) \times 10^2$ M^{-1} s^{-1} for bp and bpe, respectively. For pz, the formation reaction was at the limit of resolution of the stopped flow apparatus and only the disappearance was measured.

$$(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+} + HA^- = (EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+ + HA \qquad k_7 \qquad (7)$$

$$(EDTA)Ru^{III}LCo^{III}(NH_3)_5{}^{2+} + A^- = (EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+ + A \qquad \text{fast} \qquad (8)$$

The observed rate constants for the disappearance of the Ru(II)–Co(III) binuclear complexes, with the exception of pz, were found to exhibit a typical saturation behavior. Observed first-order rate constants are plotted versus the concentration of ascorbic acid in Fig. 2. Limiting values were estimated from plots of $1/k_{obs}$ versus 1/[AA] and are listed in column 2 of Table 3. Qualitatively, the dependence of k_{obs} upon [AA] is consistent with a mechanism where the sum of Eqs. (7) and (8) represents a rapid, reversible equilibrium and Eq. (3) is rate-determining. The limiting values are taken to be good estimates of k_{et} for Eq. (3)[2].

In order to obtain independent evidence about the reliability of the k_{et} measurements obtained by the extrapolation procedure, a different set of measurements was performed. The reduction of **III** was carried out with dithionite ion. Dithionite being a stronger and faster reductant than ascorbic acid, the yield of **II** is quantitative. With $[S_2O_4{}^{2-}] = (0.10–4.5) \times 10^{-3}$ the reduction of Ru(III) to Ru(II) is outside of the stopped-flow time scale, and thus only one reaction was observed, namely the disappearance of **II**. However, a complication arose. The disappearance of **II** was found to proceed by two parallel paths, one independent of and one first-order in dithionite concentration. The term dependent on $[S_2O_4{}^{2-}]$ is attributed to reduction of the cobalt(III) center by the external reductant [19]. The values of k_{et} obtained from the intercepts of plots of the observed first-order rate constants for disappearance of **II** versus $[S_2O_4{}^{2-}]$ are 0.65 ± 0.02 and 0.19 ± 0.02 s^{-1} for bp and bpe, respectively, well in agreement with the values obtained from the studies with ascorbic acid.

Direct evidence that the reactions corresponding to the disappearance of the intermediate formed when the Ru(III) center of **III** is reduced by external reductants are real intramolecular electron transfer processes was obtained in the study of the reactions of $Ru^{II}(EDTA)OH_2{}^{2-}$ with $Co(NH_3)_5L^{3+}$ (L = pz, bp). Because of the lability of the water in $Ru^{II}(EDTA)OH_2{}^{2-}$, **II** is formed rapidly by Eq. (9)

$$Ru^{II}(EDTA)OH_2{}^{2-} + Co^{III}(NH_3)_5L^{3+} = (EDTA)Ru^{II}LCo^{III}(NH_3)_5{}^+ + H_2O \qquad (9)$$

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[1] At the pH 8.1 utilized in our measurements, deprotonation of HA is extremely rapid [17].

[2] The differential equations corresponding to the mechanism represented by the forward and reverse reactions in Eqs. (7) and (8), the equilibrium between HA, H^+ and A^-, and Eq. (3) were integrated numerically for various concentrations of ascorbic acid. The disappearance of **II** was first-order with a first-order rate constant that exhibited a dependence upon [AA] identical to that found experimentally. The values of k_{et} obtained from the $1/k$ vs. 1/[AA] plots were within 1% of the input values. The independence of k_{obs} with respect to [AA] is consistent with a larger reduction potential for **III** with L = pz. Although we were unable to obtain the reduction potential because the anodic wave was not seen, it is likely that **III** with L = pz is a stronger reductant than the remaining complexes. Note that the reduction potential of $(EDTA)Ru^{III}pzRh^{III}(NH_3)_5{}^{2+}$, a good model for the corresponding Co(III) complex, is 0.37 V [14].

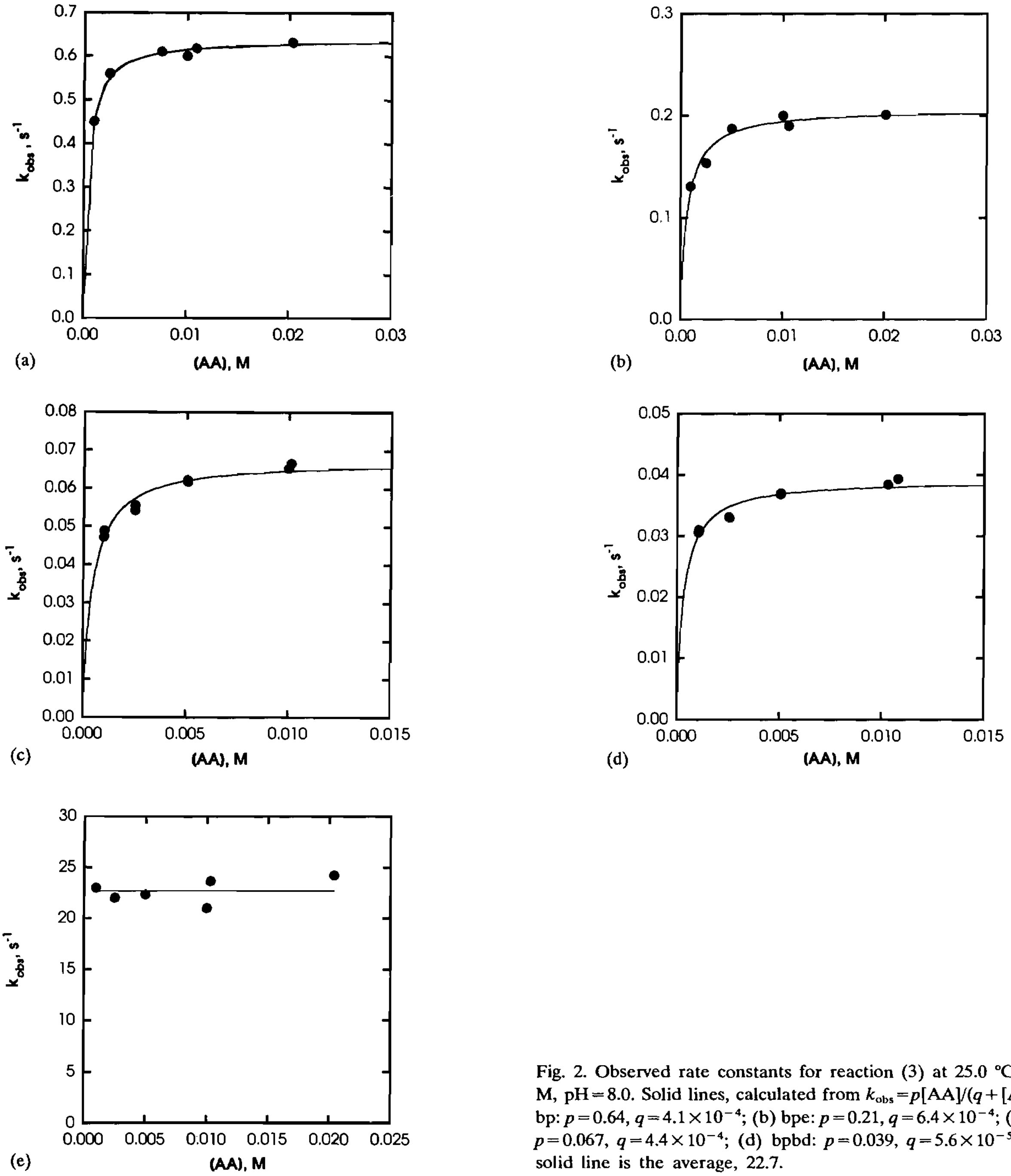

Fig. 2. Observed rate constants for reaction (3) at 25.0 °C, $I=0.20$ M, pH = 8.0. Solid lines, calculated from $k_{obs}=p[AA]/(q+[AA])$. (a) bp: $p=0.64$, $q=4.1\times10^{-4}$; (b) bpe: $p=0.21$, $q=6.4\times10^{-4}$; (c) dmbp: $p=0.067$, $q=4.4\times10^{-4}$; (d) bpbd: $p=0.039$, $q=5.6\times10^{-5}$; (e) pz: solid line is the average, 22.7.

and this is followed by its disappearance according to reaction (3). The reactions were followed at 600 and 500 nm for pz and bp, respectively, with $[Co(III)]=(1–2.5)\times10^{-3}$, $[Ru(II)]=5.0\times10^{-4}$, pH 8.0, $I=0.20$ M and 25 °C. The increases in absorbance, which corresponded to the formation of **II**, were at the limit of the time resolution of the stopped-flow apparatus. The decreases in absorbance were governed by first-order processes with rate constants 21 ± 3 and 0.69 ± 0.03 s^{-1} for pz and bp, respectively, in acceptable agreement with the values of k_{et} derived from the ascorbic acid studies.

Of all the methods employed to measure rates of intramolecular electron transfer the most reliable and convenient seems to be the one based on the reduction of **III** by ascorbic acid. No secondary reactions are encountered as is the case with dithionite. The method based on the direct mixing of Ru(II) and Co(III) is rather inconvenient because of the extreme sensitivity of $Ru^{II}(EDTA)OH_2^{2-}$ toward dioxygen.

Table 3
Rate constants for intramolecular electron transfer in binuclear complexes at 25 °C

L[a]	$(EDTA)Ru^{II}LCo^{III}(NH_3)_5^+$	$(NC)_5Fe^{II}LCo^{III}(NH_3)_5^+$ [b]	$(H_2O)(NH_3)_4Ru^{II}LCo^{III}(NH_3)_5^{5+}$ [c]
pz (6.8)	22.7±0.4	5.5×10^{-1}	3.0×10^{-1}
bp (11.0)	0.64±0.02	2.0×10^{-3}	4.4×10^{-2}
dmbp (11.5)	0.067±0.02	2.3×10^{-3}	5.5×10^{-3}
bpe (13.5)	0.21±0.01	1.4×10^{-3}	1.9×10^{-2}
bpbd (16.1)	0.039±0.001	6.9×10^{-4}	

[a] Value in parentheses is the metal to metal distance in Å.
[b] Ref. [3].
[c] Refs. [4–6].

4. Discussion

Much of the chemistry of $Ru^{II}(EDTA)^{2-}$ complexes with nitrogen heterocycles is dominated by the π back-bonding interaction between the filled t_{2g} (dπ) metal center orbitals and the unoccupied π* orbitals of the aromatic nitrogen heterocycle. The electronic spectra of these species exhibit low-energy metal to ligand charge transfer (MLCT) bands analogous to those found in other systems containing aromatic nitrogen heterocycles bound to metal centers in low-spin d^6 octahedral configurations such as $Ru^{II}(NH_3)_5L^{2+}$ [12], $Fe^{II}(CN)_5L^{3-}$ [13], $W^0(CO)_5L$ [20], $Re^I(\eta^5\text{–}C_5H_5)L$ [21]. A linear relationship was obeyed [13] between the energy maxima of $Ru^{II}(NH_3)_5L^{2+}$ and $Fe^{II}(CN)_5L^{3-}$ complexes. Similarly, we find a linear relationship of nearly unit slope between the energy maxima of $Fe^{II}(CN)_5L^{3-}$ and $Ru^{II}(EDTA)L^{2-}$ complexes (Fig. 3). The MLCT bands for Ru lie at lower energies than those for Fe because, as a comparison between the reduction potentials indicates, it is easier to remove an electron from Ru(II) than from Fe(II).

It has been shown that the energies of the MLCT bands of the $Fe^{II}(CN)_5L^{3-}$ complexes are very sensitive to substituent changes on L and that these effects provide information about the extent of communication between the Fe and Co centers in **I** [3]. This in turn is of considerable value in shedding light on the intramolecular electron transfer processes that take place in these species. Therefore, we examined the substituent effects on the MLTC bands of $Ru^{II}(EDTA)L^{2-}$ in order to assess the extent of communication between Ru and Co centers. Although all the ligands studied in the present work feature uninterrupted conjugation between the pyridine rings bound to the two different metal centers and are therefore capable of transmitting electron-withdrawing effects, they do so with different degrees of efficiency. Thus, when the H in the *para* position of the pyridine ring in $Ru^{II}(EDTA)py^{2-}$ is replaced by the electron-withdrawing group C_5H_4N (resulting in the net change of py to bp), the MLCT band shifts from 26.2 to 21.5 kK. However, on going from py to dmbp, the band shifts only to 24.7. Even when the inductive effects of the methyl group are considered, it is apparent that transmission of electronic effects is much less efficient for dmbp than for bp. Moreover, the coordination of $Co^{III}(NH_3)_5^{3+}$ to the remote N of $Ru^{II}(EDTA)bp^{2-}$ results in a 3.6 kK shift whereas the shift is rather modest, 1.4 kK, for coordination of $Co^{III}(NH_3)_5^{3+}$ to the remote N of $Ru^{II}(EDTA)dmbp^{2-}$. Clearly, coupling between the metal centers is considerably smaller for dmbp than for bp as expected because for dmbp the pyridine rings are far from coplanar, whereas coplanarity is possible for bp. Diminished coupling between metal centers in the mixed valence compounds $(NH_3)_5Ru^{II}LRu^{III}(NH_3)_5^{5+}$ for dmbp as compared to bp has also been reported [5]. Turning to the role of distance between metal centers, we note that bathochromic shifts in the MLCT maxima of the $Ru^{II}(EDTA)L^{2-}$ complexes which occur upon coordination of $Co^{III}(NH_3)_5^{3+}$ to the remote N of the L ligands pz, bp, bpe and bpbd have values of 3.1, 3.6, 2.6 and 0.8 kK, respectively. Except for pz, this trend is the same as that observed previously [3] for the $Fe^{II}(CN)_5L^{3-}$ complexes and it is apparent that an increase in bridge length (the metal to metal distances for pz, bp, bpe and bpbd are 6.8, 11.0, 13.5 and 16.1

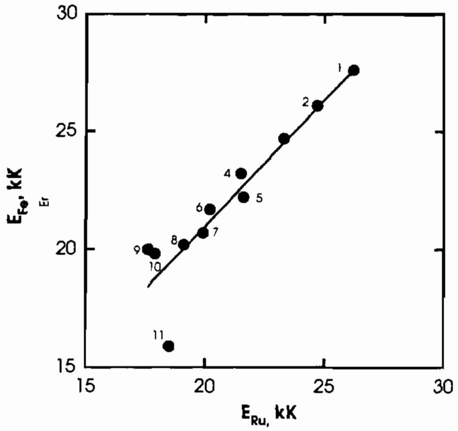

Fig. 3. Energy of MLCT maximum for $Fe^{II}(CN)_5L$ vs. energy of MLCT maximum for $Ru^{II}(EDTA)L$ in kK. Solid line is $E_{Fe} = -0.44 + 1.07\ E_{Ru}$. 1, py; 2, dmpb; 3, dmpb$Co(NH_3)_5$; 4, bp; 5, pz; 6, bpe; 7, bpbd; 8, bpbd$Co(NH_3)_5$; 9, bpe$Co(NH_3)_5$; 10, bp$Co(NH_3)_5$; 11, pz$Co(NH_3)_5$.

A, respectively) attenuates the communication between metal centers.

Now we turn to the rate constants for intramolecular electron transfer in **II**. As will be seen by comparing columns 1 and 2 of Table 3, as the length of the bridge increases, the rate constant decreases. Almost identical trends were observed previously for the intramolecular electron transfer reactions of **1** and $(H_2O)(NH_3)_4Ru^{II}LCo^{III}(NH_3)_5^{5+}$ (see columns 3 and 4 of Table 3). Since these trends parallel the spectroscopic trends discussed above, one might be tempted to ascribe the decrease in rate with increasing distance to the decrease in coupling between the metal centers and therefore to non-adiabaticity effects. However, as the following analysis will show, we believe that the coupling between metal centers, even for bpbd, is sufficiently strong that all the reactions, with the exception of the reaction of the dmbp complex, lie in the adiabatic regime. Our analysis follows closely that presented earlier [3] for the reactions of **1**. According to electron transfer theory [22], rate constants for intramolecular electron transfer between donor and acceptor in a binuclear complex (inner sphere) or a reactant pair (outer sphere) are given by Eq. (10) where ν_n is an effective nuclear frequency (taken to be 10^{13} s^{-1}), κ_e is the electronic factor (equal to 1 for adiabatic reactions and less than 1 for non-adiabatic reactions) and ΔG^* is the

$$k_{et} = \nu_n \kappa_e \exp(-\Delta G^*/RT) \tag{10}$$

reorganization free energy. The latter is related to ΔG^*_{in} and ΔG^*_{out}, the inner- and the outer-shell (solvent) reorganization energies, respectively, and to $\Delta G°_{et}$, the standard free energy change for intramolecular electron transfer, by Eq. (11). The expression for ΔG^*_{out} on the basis of the two-sphere continuum dielectric model is given by Eq. (12) where Δe is the charge

$$\Delta G^* = \Delta G^*_{in} + \Delta G^*_{out} + 0.5\ \Delta G°_{et} + (\Delta G°_{et})^2/16(\Delta G^*_{in} + \Delta G^*_{out}) \tag{11}$$

$$\Delta G^*_{out} = 0.25(\Delta e)^2\{(1/2r_1) + (1/2r_2) - (1/d)\}\{(1/D_{op}) - (1/D_s)\} \tag{12}$$

transferred in the reaction, D_{op} and D_s are the optical and static dielectric constants of the solvent, respectively, r_1 and r_2 are the radii of the reactants (assumed to be spherical), and d is the distance between the metal centers.

The rate constants for internal electron transfer in **II** depend on the standard free energy change for reaction (3), the inner-sphere reorganization energy, the solvent reorganization energy and the electronic factor. The standard free energy changes are fairly constant since the reduction potentials for **III** fall in the narrow range 0.10–0.15 V and the reduction potentials of the Co(III) centers in **II** are expected [23] to be insensitive to the details of the substituents in the nitrogen heterocycle. In fact, with a value of 0.10 V as a reasonable estimate of the reduction potential of the cobalt(III) center [24], the reactions of **II** are essentially ergoneutral. The inner-sphere reorganization energies are expected to be rather constant as the bridge is varied [3]. Thus, we only need to consider two factors: the solvent reorganization energy and the electronic factor. Plots of the reorganization energy ΔG^* versus $1/d$ (the inverse of the distance between metal centers) are linear (see Fig. 4) with slopes of 31, 40 and 33 kcal mol^{-1} for the Fe, edta and ammine systems, respectively. The predicted slope based on Eqs. (10)–(12) with the provisos stipulated above is 45 kcal mol^{-1}. In view of the approximations involved, the agreement, in particular for the edta system, is remarkably good. We infer that, with the exception of the reactions mediated by dmbp in the ruthenium ammine and edta systems, the electronic factors must be constant throughout the series of ligands for each of the three systems. Barring an unusual coincidence, it seems clear that the limiting adiabatic regime has been attained. Similar conclusions for the ruthenium ammine system [5,6] have been advanced on the basis of somewhat different considerations.

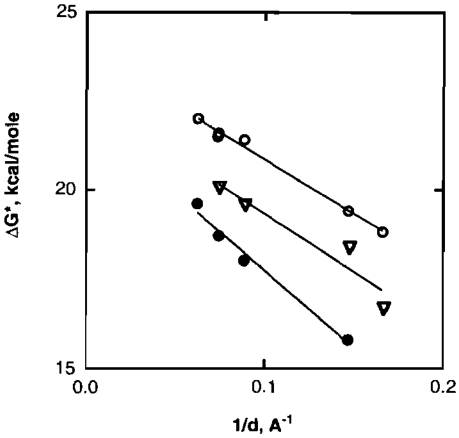

Fig. 4. Reorganization free energies for intramolecular electron transfer vs. the inverse of the distance between metal centers: ○, $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$. ∇, $(H_2O)(NH_3)_4Ru^{II}LCo^{III}(NH_3)_5^{5+}$; ●, $(EDTA)Ru^{II}LCo^{III}(NH_3)_5^{+}$.

An alternative analysis of solvation effects can be carried out with the more realistic [25] ellipsoidal cavity model[3]. The values of ΔG^* for pz, bp, bpe, bpbd and dmpb calculated from Eq. (10) assuming $\kappa_e = 1$ are 15.8, 17.9, 18.6, 19.6 and 19.3 kcal mol^{-1}, respectively. The values corrected for the outer-sphere contribution, $\Delta G^* - \Delta G^*_{out}$, are 10.5, 10.4, 10.5, 10.9 and 11.8 kcal mol^{-1} in the same order. It will be seen that once the solvent reorganization energy is factored out, the rates

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[3] For a comparison between the two-sphere and the ellipsoidal cavity models, see Ref. [3].

of electron transfer, except for the dmbp complex, are independent of donor–acceptor separation. Since the coupling between the metal centers decreases with increasing distance [26], we infer that the adiabatic limit $\kappa_e = 1$ has been reached in all but the dmpb complex. For the latter, non-adiabatic electron transfer is indicated with $\kappa_e = 0.1$. It is noteworthy that for the electron transfer from $Fe^{II}(CN)_5{}^{3-}$ to $Co(NH_3)_5{}^{3+}$ mediated by dmbp, the rate comparisons [3] led us to suggest that electron transfer was adiabatic. The reasons for the difference between the $Fe^{II}(CN)_5{}^{3-}$ and $Ru^{II}(EDTA)^{2-}$ systems are not immediately apparent. However, since a splitting energy of only ≈1 kcal [27] appears to provide sufficient coupling between metal centers for electron transfer to proceed in the adiabatic limit, small energy differences in the extent of coupling provided by a bridging ligand bound to different metal centers may result in transitions from the non-adiabatic to the adiabatic regime.

Finally, we analyze the relative rates of electron transfer in **I** and **II**. The reorganization energies corrected for the outer-sphere contributions for **I** and **II** are 13.5 and 10.5 kcal mol^{-1}, respectively. On the basis of Eq. (11), the difference between the corrected values for Fe and Ru is given by Eq. (13) where f represents the last term in Eq. (11). From the oxidation

$$\begin{aligned}(\Delta G^* - \Delta G^*{}_{\mathrm{out}})_{\mathrm{Fe}} - (\Delta G^* - \Delta G^*{}_{\mathrm{out}})_{\mathrm{Ru}} \\ = \Delta G^*{}_{\mathrm{in(Fe)}} - \Delta G^*{}_{\mathrm{in(Ru)}} \\ + 0.5(\Delta G^\circ{}_{\mathrm{et(Fe)}} - \Delta G^\circ{}_{\mathrm{et(Ru)}}) + f_{\mathrm{Fe}} - f_{\mathrm{Ru}} \qquad (13)\end{aligned}$$

potentials of **I** and **II** (≈ −0.5 [3] and ≈ −0.15 V, Table 2, respectively), we estimate $0.5(\Delta G^\circ{}_{\mathrm{et(Fe)}} - \Delta G^\circ{}_{\mathrm{et(Ru)}}) \approx 4$ kcal mol^{-1}. Estimates of f_{Fe} and f_{Ru} are ≈0.5 [3] and ≈0 (reaction (3) is ergoneutral). Estimates of rate constants for electron transfer in the ion pairs $Ru^{II}(EDTA)L^{2-}/Ru^{III}(EDTA)L^{-}$ and $Fe^{II}(CN)_5L^{3-}/Fe^{III}(CN)_5L^{2-}$ are 8×10^6 [28] and 7×10^7 [29] s^{-1}, respectively, for a difference in reorganization energies $\Delta G^*{}_{\mathrm{in(Fe)}} - \Delta G^*{}_{\mathrm{in(Ru)}} \approx -1.3$ kcal mol^{-1}. Therefore, $(\Delta G^* - \Delta G^*{}_{\mathrm{out}})_{\mathrm{Fe}} - (\Delta G^* - \Delta G^*{}_{\mathrm{out}})_{\mathrm{Ru}} = -1.3 + 4 + 0.5 = 3.2$ kcal mol^{-1}, is in remarkable agreement with the value 3.0 (13.5 − 10.5) calculated from the intramolecular studies in the present and earlier [3] work. The fact that Franck–Condon factors are sufficient to account for the reactivity differences between the Ru and Fe systems reinforces our suggestion, based on the analysis of solvation effects, that, except for dmbp in **II**, the intramolecular electron transfer reactions of **I** and **II** lie in the adiabatic regime.

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