Forbidden π–σ donor–acceptor electronic coupling in linked transition metal complexes: contrasting behavior of ruthenium(II) donors with ruthenium(III) and cobalt(III) acceptors

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Abstract

The metal-to-metal charge transfer (MM′CT) spectroscopy is compared to the variations in $Ru(NH_3)_5^{3+,2+}$ half-wave potentials for several complexes of the type $LM(CNRu(NH_3)_5)$ in which L=polypyridyl or tetraazamacrocyclic ligand and M = Ru, Fe, Co, Rh or Cr. In general, there are bigger variations in $E_{1/2}^{obs}$ than expected on the basis of a simple analysis of MM′CT spectra. The exception appears to occur for the complexes with M = Co, for which the value of $E_{1/2}^{obs}$ appears to be very close to that expected in the absence of any electron delocalization through the mixing of MM′CT excited state character into the ground state wavefunction. These observations are consistent with symmetry selection rules, which constrain the mixing of σ and π type orbitals in rigid linear systems. The implications for electron transfer processes are discussed.

Keywords: π–σ Donor–acceptor electronic coupling; Ruthenium complexes; Cobalt complexes

1. Introduction

The experimental evaluation and theoretical description of the electronic coupling between donors and acceptors in electron transfer systems have been of increasing interest during the past decade [1–11]. The strength of donor–acceptor electronic coupling is conveniently expressed in terms of an electronic matrix element, H_{DA}, as in Eq. (1); Ψ_D° and Ψ_A° are the wave functions of the electronic states with the electron predominantly on the donor or acceptor, respectively.

$$H_{DA} = \langle \Psi_D^\circ | H | \Psi_A^\circ \rangle \tag{1}$$

In general, one expects simple symmetry issues to be important in determining the magnitude of integrals such as H_{DA}, and Orgel long ago speculated [12] that symmetry contributions could be important in electron transfer processes. However, the relevance of the symmetries of the donor and acceptor orbitals to observed electron transfer rates has been very difficult to establish. Much of the experimental difficulty in probing H_{DA} derives from the fact that the observed rate constant, k_{elt}, is a product of electronic and nuclear factors, conveniently represented as retardation factors (or

transmission coefficients) as in Eqs. (2)–(4) [13–15], and H_{DA} is expected to contribute to variations in k_{elt} only when $\kappa_{el} \ll 1$ so that an expression such as in Eq. (5) may be used ($\Delta G^\ddagger$ is the activation free energy; ΔG° is the free energy change for the electron transfer step; λ is a nuclear reorganizational parameter). The

$$k_{elt} = \nu_{eff} \kappa_{el} \kappa_{nu} \tag{2}$$

$$\ln \kappa_{nu} = -\Delta G^\ddagger / RT \tag{3}$$

$$\Delta G_{classical}^\ddagger \cong (\lambda/4)(1 + \Delta G^\circ/\lambda)^2 \tag{4}$$

$$\nu_{eff} \kappa_{el} \cong \frac{H_{DA}^2}{\hbar} \left(\frac{\pi^3}{k_B T \lambda} \right)^{1/2} \tag{5}$$

experimental uncertainties in the evaluations of λ (or other parameters contributing to κ_{nu}) are usually large enough to obscure any contributions of κ_{el} to k_{elt} (in most thermal electron transfer processes (ln $\nu_{eff}\kappa_{nu}$)/ (ln k_{elt}) ≥ 0.8, with uncertainties of the order of 10–25%). Strategies for circumventing this problem have involved approaches such as: (a) the examination of the response of k_{elt} to variations in parameters which should alter H_{DA} but have little effect on κ_{nu} (e.g. separation distance or charge transfer perturbations) [1–6]; (b) the generation of reactant systems in which $\kappa_{nu} \sim 1 (|\Delta G^\circ| \sim \lambda)$ [1–3]. Our recent work has involved the absorption of

light by covalently linked donors and acceptors in order to achieve the latter condition [16–19].

One of the most basic symmetry issues arises in a rigidly linked donor–acceptor complex in which the donor orbital wave function has largely π symmetry with respect to a linear D–L–A linkage, and the acceptor orbital has predominantly σ symmetry. Such a situation can be achieved in cyanide bridged ruthenium(II)–cobalt(III) complexes, and we have found that back electron transfer, Eq. (6), is consistently slower by factors of 10–10^4 than predicted on the basis of κ_{nu} [16–19] (where for $L = (NH_3)_5$ and $[14]aneN_4$, $L' = (bpy)_2$ and $(NH_3)_5$, respectively). This contrasts

$$LCo^{II}(CN^-)Ru^{III}L' \longrightarrow LCo^{III}(CN^-)Ru^{II}L' \qquad (6)$$

dramatically to the back electron transfer behavior reported for the isostructural (when $L = (NH_3)_5$ and $L' = (bpy)_2$) $L'Ru^{II}(CN^-)Ru^{III}L$ complex [16], or for the related complexes with $L' = (CN)_6^{6-}$ [20–23], in which $k_{elt}(obs.) \geqslant \nu_{nu}\kappa_{nu}$, and for which k_{elt} is even larger than the rate constant for vibrational equilibration. Some of the electronic retardation manifested in the back electron transfer rate constant for the $LCo^{II}(CN^-)Ru^{III}L'$ complexes can be attributed to the spin and orbital forbiddeness of the process when the cobalt(II) center has three unpaired electrons (quartet spin state) [16] and some of the retardation appears to derive from the intrinsic orthogonality of σ and π orbitals [19]. The present study was undertaken to examine the question of σ/π orthogonality in linked donor–acceptor complexes from the independent perspectives of spectroscopic and thermodynamic measurements.

The ground state wave functions can be formulated as in Eq. (7) (where $\beta_g = H_{DA} - S_{DA}E_D^\circ$, S_{DA} is an overlap integral, E_D° is the ground state energy in the absence of donor–acceptor coupling, and ΔE_{DA} is the vertical energy difference between the unperturbed ground and charge transfer excited state [24]). The

$$\Psi_D = \Psi_D^\circ + (\beta_g/\Delta E_{DA})\Psi_A^\circ \qquad (7)$$

oscillator strength for the optically induced transition from D to A is related to H_{DA} by Eq. (8) in the limit that the dipole length of the transition moment is given by r_{DA}, and where ϵ_{max}, $\Delta\nu_{1/2}$ and ν_{max} are the molar absorptivity, the bandwidth at half maximum and the frequency of the absorption maximum, respectively, for the donor–acceptor charge transfer (DACT) absorption [24,25]. Furthermore, the mixing described by Eq. (7)

$$\beta_g/\Delta E_{DA} \cong \frac{0.0205}{r_{DA}}\left(\frac{\epsilon_{max}\Delta\nu_{1/2}}{\nu_{max}}\right)^{1/2} \qquad (8)$$

gives rise to a contribution to the stabilization energy of the ground state, ϵ_s, which is given by Eq. (9) when $|\Delta E_{DA}| > |\beta_g|$, and the fraction of charge delocalized is

given by $(\beta_g/\Delta E_{DA})^2 = \epsilon_s/\Delta E_{DA}$ [24]. The thermodynamic contribution, ϵ_s', can in principle be determined

$$\epsilon_s = \beta_g^2/\Delta E_{DA} \qquad (9)$$

from electrochemical measurements using Eq. (10) [11,17–19], provided other CT and solvational contributions can be ignored (the sign of ϵ_s' in Eq. (10) depends on which component of the redox couple is CT stabilized). This is somewhat crucial in the present study, because ϵ_s' can be readily related to the amount of charge delocalized, and thus to the coupling pertinent to the electron transfer process, while electronic selection rules can lead to some ambiguity about the meaning of the electronic coupling parameter inferred from normal spectroscopic measurements using Eq. (8). Thus, an optically induced σ–π transition in a rigidly

$$E_{1/2}^{obs} \cong E_{1/2}^{ref} \pm \epsilon_s' \qquad (10)$$

coupled system is formally allowed only orthogonal (x,y-allowed) to the actual electron transfer axis (the z-axis). Our efforts to address this issue, in what is generally a very complicated class of compounds, have led us to examine the ruthenates of several $Co(MCL)(CN)_2^+$ complexes (MCL, a macrocyclic ligand) and $Co(bpy)_2(CN)_2^+$. Ruthenation of the latter complex turns out to compete with its reduction and substitutional equilibration, so that this is the most complicated system that we have attempted. In this report we describe our observations on this system and how they relate to the issue of σ and π coupling in a rigidly linked donor–acceptor complex.

2. Experimental

The syntheses of several of the complexes used in this study are described elsewhere as noted: $(bpy)_2M(CNRu(NH_3)_5)_2^{n+}$ for M = Ru [26] and Rh [18]; $trans$-M($[14]aneN_4$)$(CNRu(NH_3)_5)_2^{5+}$ for M = Co and Rh [18]; $trans$-CoMe$_6$($[14]dieneN_4$)$(CNRu(NH_3)_5)_2^{5+}$ [18]; ($[14]aneN_4 = 1,4,8,11$-tetraazacyclotetradecane; $Me_6[14]dieneN_4 = 5,7,7,12,14,14$-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). New complexes synthesized for this study are listed below.

2.1. $[(bpy)_2Cr(CNRu(NH_3)_5)_2](PF_6)_5$

A 0.05 g sample of $[Cr(bpy)_2(CN)_2]Cl$ [27] was dissolved in 2.5 ml H_2O and the solution was deaerated with Cr^{2+} scrubbed Ar. A 0.1 g sample of $[Ru(NH_3)_5Cl]Cl_2$ (Strem Chemicals) was suspended in 2.5 ml H_2O. After deaeration with Ar this mixture was reduced and dissolved over Zn(Hg) for 1 h. A stoichiometric excess of the ruthenium(II) solution was

transferred to the deaerated chromium(III) solution, and the mixture was stirred in the dark at room temperature for 3–6 h. The blue reaction product was precipitated by the addition of NH_4PF_6 in an Ar atmosphere in a glove box. The solid was washed with water, ethanol and ether and dried in vacuo.

2.2. [(bpy)$_2$Fe(CNRu(NH$_3$)$_5$)$_2$](PF$_6$)$_4$

The [Fe(bpy)$_2$(CN)$_2$] complex [28] was ruthenated in a slight modification of the procedure for [(bpy)$_2$Cr(CNRu(NH$_3$)$_5$)$_2$](PF$_6$)$_5$: the two reactants were mixed anaerobically over Zn(Hg) in the dark at room temperature. The reaction products are very air sensitive. Air oxidation resulted in unidentified products. Oxidation with Fe^{3+}(aq.) did produce a (bpy)$_2$Fe(CNRu(NH$_3$)$_5$)$_2$$^{6+}$ complex, and this could be separated from other reaction products on a Sephadex SP-C25 resin in the Na^+ form (use of this resin in the acid form resulted in product decomposition). The chromatographic elution had to be performed with concentrated NaCl solutions, and we were unable to separate the products eluted from the excess NaCl. We did use this approach to obtain materials for spectroscopic analysis. For most purposes the purple reaction product was precipitated under Ar by adding NH_4PF_6 to the reaction mixture.

2.3. [(phen)$_2$Fe(CNRu(NH$_3$)$_5$)$_2$](PF$_6$)$_4$

This complex was prepared using the procedure described above for the bipyridine analog.

2.4. [Trans-Co(Me$_4$[14]tetraeneN$_4$)(CN)$_2$](PF$_6$)

A 0.75 g sample of NaCN was added to a solution of 0.350 g [trans-Co(Me$_4$[14]tetraeneN$_4$)Cl$_2$]PF$_6$ [29] in about 40 ml of H_2O (Me$_4$[14]tetraeneN$_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and heated to about 40 °C for 1 h. When the solution had become orange, its volume was reduced by rotary evaporation and the orange solid which formed was removed by filtration. Yellow crystals of the product were obtained after exchanging the counter-ion on a Dowex 1-X8 (Cl$^-$ form) resin.

2.5. [Trans-Co(Me$_4$[14]tetraeneN$_4$)(CNRu(NH$_3$)$_5$)$_2$]-(PF$_6$)$_5$

The procedure described above for ruthenating Cr(bpy)$_2$(CN)$_2$$^+$ was also used for this complex.

2.6. [(phen$_2$)Rh(CNRu(NH$_3$)$_5$)$_2$](PF$_6$)$_5$

The [Rh(phen)$_2$(CN)$_2$]Cl complex [30] was ruthenated using the procedure for [(bpy)$_2$Cr(CNRu-(NH$_3$)$_5$)$_2$](PF$_6$)$_5$.

2.7. [(bpy)$_2$(CN)$_{2-n}$Co(CNRu(NH$_3$)$_5$)$_n$](PF$_6$)$_{2n+1}$

The [CO(bpy)$_2$(CN)$_2$]Cl complex [31] was ruthenated using a modification of the above procedure. In order to repress an autocatalytic Ru(II) initiated reduction of (bpy)$_2$Co(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ the synthesis had to be carried out in solutions ~0.05 M in NaClO$_4$. ClO$_4$$^-$ was used to repress the Ru(NH$_3$)$_5$OH$_2$$^{2+}$ initiated electron transfer reduction of the ruthenated complexes (see Eqs. (11)–(13) below). The desired product was orange–brown in color, while side reactions resulted in a purple product with an intense 900 nm absorbance and a brown product absorbing at 510 nm. In order to optimize formation of the bis-ruthenate, the syntheses were performed with an excess of Ru(NH$_3$)$_5$OH$_2$$^{2+}$. It seems likely that the product obtained was always a mixture of mono- and bis-ruthenates ($n = 1$ and 2, respectively). As a consequence of this and of the large impurity absorptivities, there is considerable uncertainty about the absorption bandwidth. Ruthenation was monitored using IR, as well as Vis–UV spectra, since the CN$^-$ stretch characteristically shifts to lower frequencies ($\Delta\nu_{CN} \cong 7$ cm^{-1} in this case) in compounds with MM'CT absorptions [18]. Other 1900–2100 cm^{-1} absorptions were used as criteria for the presence of impurities.

The compounds were characterized by IR and UV–Vis spectra, redox titrations, electrochemistry and elemental analysis (Midwest Microanalytical Laboratories).
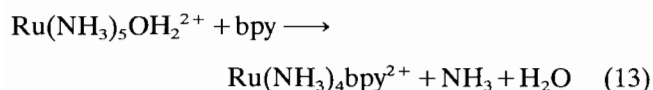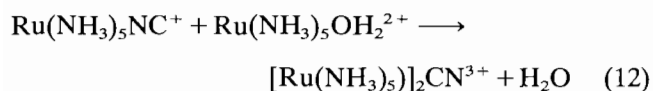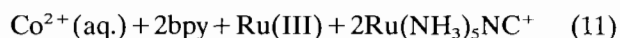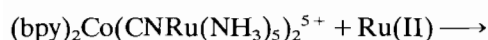
The redox titrations were performed by dissolving a sample of ruthenated complex in 10 ml of Ar-purged H_2O in an all glass apparatus fused to a 1 cm cuvette. The complex concentration was adjusted to give about a 1.0 absorbance for the dominant spectral features in the visible or/and near-IR regions; typical concentrations were between 10^{-3} and 10^{-4} M. Approximately 10 μl aliquots of a standard solution of oxidant, Fe^{3+}(aq.) or Ce^{4+}(aq.) for Ru(NH$_3$)$_5$$^{2+}$ complexes, or standard solution of reductant, Ru(NH$_3$)$_6$$^{2+}$ for Ru(NH$_3$)$_5$$^{3+}$ complexes, were added through a septum by means of a syringe. The solutions were mixed, then transferred to the cuvette end of the apparatus and spectra determined after each addition.

UV, Vis and near-IR absorption measurements were performed on either an OLIS modified Cary 14 spectrophotometer or an HP-8452 diode array spectrophotometer. Spectral deconvolution was performed with Spectracalc software from Galactic, Inc. IR spectra were recorded on a Nicolet 20 DXM FT-IR spectrometer using KBr pellets.
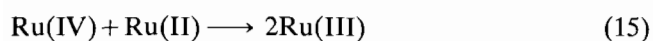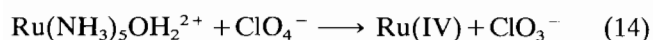
The voltammetric measurements were performed on a Princeton Applied Research electrochemical system in acetonitrile as described previously [18]. All of the cyclic voltammograms were referenced to ferrocene or diacetylferrocene dissolved in the sample solutions (the potentials of these couples were taken to be 0.367 and 0.827 V, respectively, versus SCE).

3. Results

The ruthenated complexes prepared for this study have turned out to be relatively fragile and reactive. It has been our experience that most of the metal cyanide complexes coordinate $Ru(NH_3)_5{}^{2+}$ moieties reasonably readily, somewhat reminiscent of the affinity of Ru(II) for N_2, but syntheses from Ru(III) starting materials have only succeeded with $Ru(bpy)_2(CN)_2$. Conversely, oxidation of the $Ru(NH_3)_5{}^{2+}$ moiety in these complexes leads to products which generally dissociate in solution: (a) often in seconds if air oxidized; or (b) in hours if chemically oxidized and kept in an oxygen free environment. The exceptions to this behavior were complexes with Ru(II) or Fe(II) central metals for which the $Ru(NH_3)_5{}^{3+}$ cyano-metalates were reasonably stable. Overall, the ruthenated complexes were stable as powders for weeks to months if kept at 0 °C in an Ar atmosphere. The most difficult of the syntheses reported in this paper was that of $(bpy)_2Co(CNRu(NH_3)_5)_2{}^{5+}$. We were only able to obtain this complex in the presence of an appreciable excess of $ClO_4{}^-$. What might be regarded as more rational synthetic approaches, in the absence of any substance known to oxidize $Ru(NH_3)_5OH_2{}^{2+}$, failed to produce cobalt containing cyano-ruthenates; rather they resulted in the formation of Co^{2+} and substances such as $Ru(bpy)(NH_3)_4{}^{2+}$ and $[Ru(NH_3)_5]_2CN^{4+}$ in what appears to be an autocatalytic reduction of the cobalt(III) complexes. Eqs. (11)–(13) describe the kinds of reactions which appear to complicate the synthesis and study of this complex; the Ru(II) reductant in Eq. (11) could be $Ru(NH_3)_5OH_2{}^{2+}$, $Ru(NH_3)_5NC^+$ or $[Ru(NH_3)_5]_2CN^{3+}$. The one equivalent oxidation of

$$(bpy)_2Co(CNRu(NH_3)_5)_2{}^{5+} + Ru(II) \longrightarrow$$

$$Co^{2+}(aq.) + 2bpy + Ru(III) + 2Ru(NH_3)_5NC^+ \quad (11)$$

$$Ru(NH_3)_5NC^+ + Ru(NH_3)_5OH_2{}^{2+} \longrightarrow$$

$$[Ru(NH_3)_5]_2CN^{3+} + H_2O \quad (12)$$

$$Ru(NH_3)_5OH_2{}^{2+} + bpy \longrightarrow$$

$$Ru(NH_3)_4bpy^{2+} + NH_3 + H_2O \quad (13)$$

$[Ru(NH_3)_5]_2CN^{3+}$ is expected to lead to a mixed valence complex with a very intense near IR absorbance. The 510 nm absorbance is associated with formation of $Ru(NH_3)_5bpy^{2+}$. These reactions are still under study and will be reported in detail elsewhere [32]. The role of $ClO_4{}^-$ appears to be to remove excess $Ru(NH_3)_5OH_2{}^{2+}$ before it can reduce the ruthenated Co(III) product, but not before ruthenation, Eqs. (14) and (15).

$$Ru(NH_3)_5OH_2{}^{2+} + ClO_4{}^- \longrightarrow Ru(IV) + ClO_3{}^- \quad (14)$$

$$Ru(IV) + Ru(II) \longrightarrow 2Ru(III) \quad (15)$$

In our hands many of these complexes were too unstable to be purified by conventional chromatographic techniques so that we had to rely mostly on driving the ruthenation reaction to completion and on differential solubilities or on extraction techniques to obtain pure materials. Under these circumstances coprecipitation of salts such as NH_4PF_6 was a major problem in purification. On the other hand, the spectral changes during redox titrations were very sensitive to the presence of impurities, and these titrations were useful in establishing the purity of the complexes formed from the stoichiometry of the spectral changes and from isosbestic points (in pairs for bis-ruthenates).
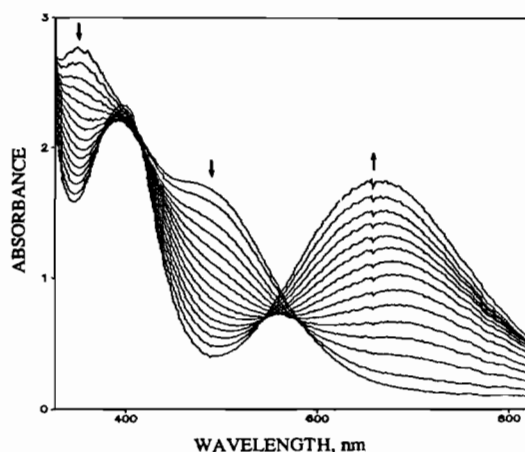
We have found that the value of $E_{1/2}$ for the $LM^{III}(CNRu^{III}(NH_3)_5)_2/LM(CNRu^{II}(NH_3)_5)_2$ couple is very sensitive to the nature of the central metal, M, and to the ligands, L, coordinated to it. The values of $E_{1/2}$ reported in this paper for these couples span a range of 350 mV (Table 1). In each instance we observe a single voltammometric wave, and when comparisons are possible, the cathodic–anodic peak separations are larger by 10–30 mV for the bis-ruthenates than for the mono-ruthenates. We have not attempted to deconvolute the bis-ruthenate waves. On the other hand, the $Ru(NH_3)_5{}^{3+,2+}$ couples of the mono- and bis-ruthenates have very similar potentials ($\Delta E_{1/2} \leqslant 20$ mV in acetonitrile) for a given central metal in this series of complexes [18,19,26]. In addition, the correlations discussed below indicate that $\epsilon_s \cong (E_{1/2}^{obs} - E_{1/2}^{ref}) \cong 0$ for the complexes with M = Co. Consequently, the ambiguity in the degree of ruthenation of $Co(bpy)_2(CN)_2{}^+$ does not affect the inferences discussed below.

The redox titrations of the cyano-ruthenates have demonstrated a very rich charge transfer spectroscopy of these complexes (Figs. 1–3). For example in the $(bpy)_2Ru(CNRu(NH_3)_5)_2{}^{6+,5+,4+}$ complexes there are CT bands that require the presence of $Ru(NH_3)_5{}^{2+}$, different bands when only $Ru(NH_3)_5{}^{3+}$ is present and a band unique to the complex containing both pentaammine ruthenium oxidation states (see Fig. 1 and Ref. [26]). Of primary interest to this study are those complexes containing cobalt(III). The cyano-ruthenates of cobalt(III) complexes in which the cobalt is coordinated to ammine (or immine) ligands all exhibit relatively weak ($\epsilon_{max} \cong 10^3$ cm^{-1} M^{-1}) MM'CT absorbances between 450 and 550 nm (Fig. 3 and Refs. [18,19,32–35]). The CT absorbances of the analogous complexes with Rh(III) centers were usually at much higher energy [18,19]. Consequently, the similarity of the $(bpy)_2(Co$ or $Rh)(CNRu(NH_3)_5)_2{}^{5+}$ spectra surprised us. This similarity, and the constrasting spectra of the corresponding tetraazamacrocyclic complexes, indicates that the principal CT absorption features shown in Fig. 2 contain only minor MM'CT contributions. A major reason for the similarity of these spectra is the $Ru(NH_3)_5{}^{2+} \rightarrow$ bpy, remote MLCT tran-

Table 1
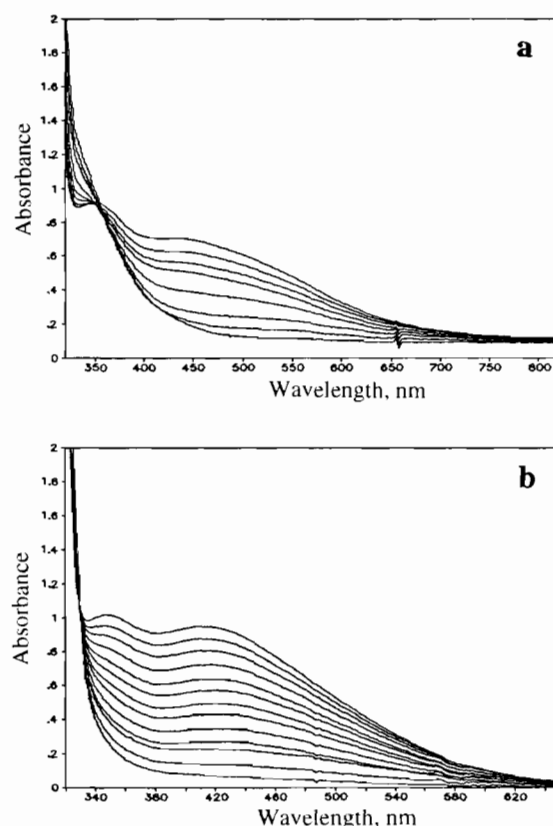Electrochemical and MM'CT absorption properties of some cyano-ruthenate complexes, $LM(CNRu(NH_3)_5)_2^{n+}$

M	L	n	$E_{1/2}^{obs}$ (V vs. SCE)[a]	λ_{max}^{b} (nm)	$\epsilon_{max}^{b} \times 10^3$ (M^{-1} cm^{-1})	$\Delta\nu_{1/2}^{b} \times 10^3$ (cm^{-1})
Ru	(bpy)$_2$	6	−0.037	656	7.8	5
Fe	(bpy)$_2$	6	0.000	875	6.6	4.8
Fe	(phen)$_2$	6	0.000	880	7.0	4.8
Co	(bpy)$_2$	5	0.140^c	~500^d	1.4	~14^d
Rh	(bpy)$_2$	5	0.215	405^e	1.5	9.2
Rh	(phen)$_2$	5	0.215	405^e	1.5	~10
Cr	(bpy)$_2$	5	0.295	650	6.0	5.6
Co	[14]aneN$_4$	5	0.267	501	1.03	7.1
Co	Me$_6$[14]dieneN$_4$	5	0.277	511	1.02	7.2
Co	Me$_4$[14]tetraeneN$_4$	5	0.215	510	1.9	7.4
Rh	[14]aneN$_4$	5	0.254	343^f	0.8	6.0

[a]In acetonitrile/TEAP with ferrocene or diacetyl ferrocene as internal reference.
[b]In water; based on redox titrations.
^{c}Solutions from preparations with significant near-IR absorptions and extraneous CN^- stretching frequencies had values of $E_{1/2}^{obs} \cong 170$ mV.
^{d}MM'CT band is convoluted with $Ru(NH_3)_5^{2+} \rightarrow bpy$ transition.
$^e Ru(NH_3)_5^{2+} \rightarrow bpy$ transition.
$^f Ru(NH_3)_5^{2+} \rightarrow CN^-$ transition.

Fig. 1. Spectroscopic changes resulting from successive oxidations of $(bpy)_2Ru(CNRu(NH_3)_5)_2^{4+}$ with 5 μl aliquots of Fe^{3+}(aq.). Arrows indicate the direction of absorbance changes with oxidation.

sition at 450–500 nm. A relatively intense transition at about 340 nm appears to be a characteristic of $MCNRu^{II}(NH_3)_5$ complexes. The apparent bandwidth of the lowest energy absorption feature of the ruthenated cobalt complex appears to be unusually large. This is the expected consequence of the convolution of $Ru(NH_3)_5^{2+} \rightarrow bpy$ and $Ru(NH_3)_5^{2+} \rightarrow Co(III)$ absorption features, but there may also be some contribution from the strongly absorbing $Ru(NH_3)_4bpy^{2+}$ product of decomposition. The smaller bandwidth of the Rh(III) complex indicates that there is no low energy $Ru(II) \rightarrow Rh(III)$ transition in this complex.

4. Discussion

In this study we have examined the pertinent thermodynamic and spectroscopic measurements for evi-

Fig. 2. Spectroscopic changes resulting from successive oxidations of $(bpy)_2M(CNRu(NH_3)_5)_2^{5+}$ with 10 μl aliquots of Ce^{4+}(aq.): (a) M = Co; (b) M = Rh. Visible absorptions decrease with oxidation in both complexes.

dence of significant contrasts in electronic coupling in $d\pi$ donor complexes with $d\pi$ acceptors and those with $d\sigma$-orbital acceptors. Our studies to date of several
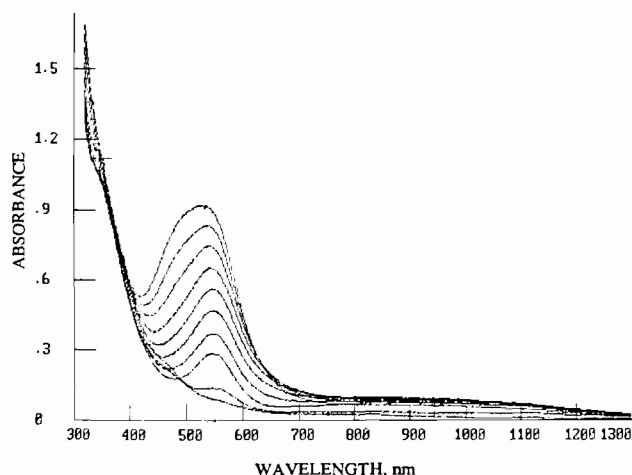
Fig. 3. Spectroscopic changes resulting from successive oxidations of trans-Co(Me$_6$[14]dieneN$_4$)(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ with 10 μl aliquots of Ce^{4+}(aq.). Absorbance between 450 and 650 nm decreases with oxidation.
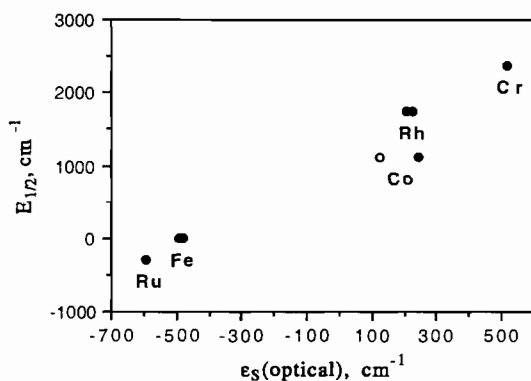

Fig. 4. Experimental correlation of $E_{1/2}^{obs}$ with $\epsilon_s^{op} = 1.53 \times 10^{-5}$ (ϵ_{max} $\Delta\nu_{1/2}$); where ϵ_{max} and $\Delta\nu_{1/2}$ are the maximum molar absorptivity and full width at half maximum of the lowest energy CT band of (PP)$_2$M(CNRu(NH$_3$)$_5$)$_2$$^{n+}$ complexes (PP = phen or bpy). Central metals are as indicated. Data for both the bpy and phen complexes of Fe and Rh are included. All other data are for bpy complexes only. ϵ_s for the open point for (bpy)$_2$Co(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ was calculated assuming $\Delta\nu_{1/2}$ to be one half the value inferred from Fig. 2.

aspects of the problem of donor–acceptor electronic coupling have shown that the issues are considerably more complex than is implicit in a simple application of Eqs. (7)–(10). Despite the overall complexity of the problem, we have found substantial evidence of much weaker electronic coupling in dπ–dσ than in dπ–dπ systems.

In accord with the predictions of Eqs. (8)–(10), we have found a strong experimental correlation between the oscillator strength of the lowest energy charge transfer (CT) absorption in (bpy)$_2$M(CNRu(NH$_3$)$_5$)$_2$$^{n+}$ complexes with the observed half-wave potentials of the M(CNRu^{III})$_2$/M(CNRu^{II})$_2$ couples (Fig. 4.). However, the slope of this correlation is much larger than predicted (see also Refs. [18,19 and 35]). Studies to

be reported elsewhere, employing complexes in which the central metal is coordinated to a macrocyclic-aliphatic-amine ligand [19,32–35], suggest that the correlation in Fig. 4 may be partly fortuitous. It seems most likely that the complexes studied actually fall into three classes which are differentiated by the central metal's electronic configuration: (a) M = Cr(III); (b) M = Rh(III), Co(III); (c) M = Ru(II), Fe(II). It is clear that a variety of intramolecular and substrate–solvent interactions contribute to $E_{1/2}^{obs}$, and that these interactions can contribute through variations in either $E_{1/2}^{ref}$ or the apparent value of ϵ_s. The rich CT spectroscopy of the ruthenated M(bpy)$_2$(CN)$_2$ complexes strongly suggests that several excited CT states may mix with the ground state, each contributing something to the apparent value of ϵ_s. In addition to the MM'CT–ground state mixing discussed above, account must be taken of CT transitions of the types: (a) CN$^-$ → M(III) (for Ru(NH$_3$)$_5$$^{3+}$, λ_{max} ~ 330 nm); (b) M(II) → CN$^-$ (for Ru(NH$_3$)$_5$$^{2+}$, λ_{max} ~ 340 nm); (c) M(II) → bpy (for Ru(NH$_3$)$_5$$^{2+}$, λ_{max} ~ 400 nm). The surprising similarity of the Ru(II) dependent CT absorbances of the polypyridyl complexes with M = Co and Rh (Fig. 2) suggests that major components of these absorptions are common to both complexes. It seems clear that one of these components is an Ru(NH$_3$)$_5$$^{2+}$ → bpy transition of about 400 nm, and that when M = Co this transition is convoluted with the Ru(NH$_3$)$_5$$^{2+}$ → Co(III) transition. When M = Rh the Ru(NH$_3$)$_5$$^{2+}$ → Rh(III) CT absorbance is probably obscured by the multitude of deeper UV absorbances. Thus, the similarity of the spectra of these two complexes leads us to assign the lowest energy transition used for the (bpy)$_2$Rh(CNRu(NH$_3$)$_5$)$_2$$^{5+}$ complex in Fig. 4 as Ru(NH$_3$)$_5$$^{2+}$ → bpy rather than MM'CT. The common relatively narrow band observed at 345 nm in both complexes probably results from a Ru(NH$_3$)$_5$$^{2+}$ → CN$^-$(dπ → π*) absorbance [36,37]. All the MCNRu^{II}(NH$_3$)$_5$ complexes which we have prepared have a strong absorbance in this region.

If there is a difference in the solvation of donor and acceptor, then the differential solvation, ΔG_s, will also contribute to $E_{1/2}^{obs}$; at the level of first-order perturbation theory, this contribution can be treated as $\epsilon_s \Delta G_s/\Delta E_{DA}$ [19–35]. The combination of these points results in Eq. (16), which is a more general form of Eq. (10); in Eq. (16) the sum is over all CT states which mix with the ground state and the choice of sign depends on which metal oxidation state is stabilized by the CT excited state mixing and on whether the charge delocalization increases or decreases the charge density of the most strongly solvated center. The various issues men-

$$E_{1/2}^{obs} \cong E_{1/2}^{ref} \pm \sum_i^{allCT} \epsilon_s(i)(1 \pm \Delta G_s(i)/\Delta E_{DA}(i)) \qquad (16)$$

tioned here will be treated in greater detail elsewhere [19,32–35]. Overall the effects of CT excited state mixing

into the ground state are to shift $E_{1/2}^{obs}$ to more positive values if the mixing stabilizes $Ru(NH_3)_5^{2+}$ and to more negative values if the mixing stabilizes $Ru(NH_3)_5^{3+}$. Thus $(bpy)_2Ru(CNRu(NH_3)_5)_2^{6+}$ and $(bpy)_2Cr(CN-Ru(NH_3)_5)_2^{5+}$, which have nearly identical MM′CT spectroscopic characteristics (Table 1), have the most negative and the most positive, respectively, values of $E_{1/2}^{obs}$ in this series of compounds; from the spectroscopy we expect that $\epsilon_s'(Ru) \cong \epsilon_s'(Cr)$ (note that primes connote effective values of ϵ_s inferred from Eq. (10)). It is a very important result of this work that $E_{1/2}^{obs}$ for $(bpy)_2Co(CNRu(NH_3)_5)_2^{5+}$ falls in the middle of this range. This implies an effective value of $\epsilon_s'(Co) \cong 0$. The inference that $\epsilon_s'(Co) \cong 0$ is not affected, at least to the level of first-order perturbation theory, by the other types of CT interactions enumerated above since these other contributions all have the same sign for the Cr(III) and Ru(II) centered complexes (in effect, the contributions amount to similar displacements of $E_{1/2}^{ref}$ in Eq. (10)). This inference is the same, regardless of whether we compare the results of our ruthenated-$Co(bpy)_2(CN)_2^+$ complex to a bis-ruthenated-polypyridyl series (Fig. 4) or to a mono-ruthenated series [32]. Our ruthenated-$Co(bpy)_2(CN)_2^+$ complex fits the correlation better when half the observed bandwidth is used (Fig. 4). This may indicate that only the $Ru(NH_3)_5^{2+} \rightarrow bpy$ component of the convoluted absorption band contributes to ϵ_s'. It is possible that other contributions of higher order perturbations could result in additional terms so that the effective stabilization energy is of the form $\epsilon_s' \cong \gamma\epsilon_s$ (where $\gamma > 1$), and this could result in a greater difference in the stabilities of the Cr(III) and Ru(II) complexes. We are currently examining this possibility, but terms of this type will not alter the inference that $\epsilon_s'(Co) \cong 0$.

The $Co(MCL)(CNRu(NH_3)_5)_2^{5+}$ ($MCL = $ a tetraazamacrocyclic ligand) complexes have much simpler CT spectra and a $Ru(NH_3)_5^{2+} \rightarrow Co(III)$ MM′CT absorbance is clearly evident as illustrated in Fig. 3. Based on Eq. (9) and the observed oscillator strengths, the contribution to ϵ_s' of MM′CT excited state–ground state mixing in these complexes is expected to be small ($\leqslant 10$ mV). The evaluation of ϵ_s' for these complexes is complicated since we currently have information for a smaller range of macrocyclic ligand complexes than for polypyridyl complexes. However, since the transition at 343 nm in trans-$Rh([14]aneN_4)(CNRu(NH_3)_5)_2^{5+}$ is probably $Ru(NH_3)_5^{2+} \rightarrow CN^-$ ($d\pi \rightarrow \pi^*$; see above discussion), there is no low energy MM′CT transition in this complex, and the observed value of $E_{1/2}$ can be taken as an approximate value for $E_{1/2}^{ref}$ for the trans-$M([14]aneN_4)(CNRu(NH_3)_5)_2^{5+}$ series of complexes. Based on this approximation for $E_{1/2}^{ref}$, $\epsilon_s'(Co) \cong 13 \pm 6$ mV per ruthenium. Based on Eqs. (8) and (9) and the oscillator strength of the Co complex we estimate $\epsilon_s(Co) \cong 7$ mV. Since neither estimate of ϵ_s is comfortably

outside the limits of our experimental uncertainties, this comparison only demonstrates that $\epsilon_s(Co)$ is small.

A comparison of the MM′CT spectroscopy and the electrochemical behavior of several $Co(MCL)(CNRu-(NH_3)_5)_2^{5+}$ complexes provides a different and useful perspective on the evaluation of ϵ_s. Thus, the values of $E_{1/2}^{obs}$ vary over more than a 60 mV range while the values of ϵ_s calculated from Eqs. (8) and (9) differ by less than 20 mV, and the variations in $E_{1/2}^{obs}$ do not correlate with the variations in MM′CT spectra. This is consistent with only very small contributions of $\epsilon_s(Co)$ to $E_{1/2}^{obs}$. It seems likely that the observed variations in $E_{1/2}$ in these macrocyclic complexes derive largely from variations in the differential solvation energies of the different macrocyclic ligand complexes.

Thus we find that the MM′CT stabilization energies based on spectroscopic and on electrochemical data are comparably small for complexes with a Co central metal, while the electrochemical values are much larger for Ru, Fe and Cr metals. A very literal interpretation of this observation is that considerably less charge is delocalized in the $Ru^{II} \rightarrow M^{III}$ MM′CT transitions in complexes with $M = Co$ and Rh than in those with $M = Ru$, Fe or Cr. This is a physically plausible inference since the $Ru^{II} \rightarrow Co^{III}$ MM′CT transition ($d\pi \rightarrow d\sigma^*$) is symmetry allowed only orthogonal ('x,y') to the Ru–Co axis, whereas charge delocalization must occur along the Ru–Co ('z') axis. In the $d\pi$-donor, $d\pi$-acceptor complexes ($M^{III} = Ru$ or Cr) the MM′CT transition is z-allowed.

At this stage the electrochemical measurements are not sufficiently sensitive (uncertainties are $\sim \pm 3$ mV in the averaged individual determinations) to allow us to estimate useful values of the electronic coupling matrix elements for thermally activated electron transfer in the Ru–Co complexes: a plausible upper limit is $H_{DA}(el) \ll 400$ cm^{-1}. However, the observations do demonstrate that the electronic coupling matrix element appropriate to electron transfer is much smaller in rigidly linked $d\pi-d\sigma$ systems than it is in $d\pi-d\pi$ systems. It is also clear that some care must be exercised in the interpretation of parameters obtained by the application of equations such as (9) and (10).

Acknowledgements

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