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Synthesis and Characterization of New Binuclear Electron-Transfer Models Containing Rigid Aromatic Spacers

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A series of new binuclear ruthenium electron-transfer models has been prepared. The ruthenium centers are linked via rigid aromatic spacers that allow the metal–metal separation to be varied between 8 and 20 Å. Visible spectra recorded for the series of Ru(II)–spacer–Ru(II) complexes show a blue-shift in the MLCT transition with increasing metal–metal distance. Cyclic voltammograms of these model compounds exhibit peak to peak separations that are larger than expected for a reversible one-electron process. The peak to peak separations also decrease with increasing metal separation. In addition, broad intervalence absorptions are observed for the mixed-valence species, although no well-defined peaks are detected. These results suggest that the ruthenium centers interact weakly in these new models and that aromatic spacers alone are not sufficient to promote strong electronic coupling.

Introduction

Long-range electron-transfer reactions (eq 1) are currently the focus of intense study because of their key role in important biological processes such as photosynthesis and respiration.[1]

$$D\text{–spacer–}A \rightarrow D^{+}\text{–spacer–}A^{-} \qquad (1)$$

Particularly relevant to the study of biological systems is understanding how the nature of the intervening protein medium or spacer (SPA) (e.g., aliphatic vs aromatic amino acids) affects the magnitude of the electronic coupling between a donor (D) and an acceptor (A).[2] For example, fast electron-transfer rates in the photosynthetic reaction center and in metalloprotein systems have been attributed to enhanced donor–acceptor electronic coupling mediated by aromatic groups lying between the electron-transfer centers.[3-5]

One approach that has been utilized to probe the mechanism of donor–acceptor electronic coupling involves evaluating the distance dependence of electron transfer in model complexes.[6-16] Studies of organic donor–acceptor pairs bridged by rigid aliphatic[6] and aromatic[7] spacers suggest that direct or "through-bond" interactions with the spacer enhance the electronic coupling relative to an isotropic medium.[9] The distance dependence of long-range electron transfer has also been investigated for inorganic models that consist of two metal centers bridged by aliphatic spacers,[10] polypeptides,[11] and other groups.[12-16] The effect of the spacer on electronic coupling is not, however, well-understood for systems in which the metal centers are separated by large (<10 Å) distances. To understand better the importance of the spacer, we have initiated studies on a series of new binuclear ruthenium complexes in which the metal centers are bridged by rigid variable-length aromatic groups (Figure 1). An attractive feature of these new systems is that the metal–metal separation is well-defined and variable over a wide range of distances. For example, in the Ru–4SPA*n*–Ru system the metal-metal separation varies from 11 to 20 Å for n = 0–2, respectively. Herein we report the preparation and characterization of these new binuclear ruthenium complexes as well as preliminary studies of the intervalence charge-transfer transition in the mixed-valence complexes.

Experimental Section

Materials. The 3SPA*n* and 4SPA*n* (n = 1, 2) bifunctional ligands (figure 1) were prepared via a palladium-catalyzed coupling of 2 equiv of 3-(trimethylstannyl)pyridine or 4-(trimethylstannyl)pyridine with 1 equiv of 1,4-dibromobenzene or 4,4′-dibromobiphenyl as described elsewhere.[17-19] The water used in all experiments was purified by using a Barnstead Nanopure ion-exchange system. Acetonitrile used for the spectroscopic measurements was HPLC grade. All other materials were reagent grade and used without further purification.

Preparation of Metal Complexes. The binuclear pentaammineruthenium(II) complexes were prepared by the reaction of 2 equiv of $[(NH_3)_5Ru(H_2O)](PF_6)_2$ with the appropriate ligand in acetone. The method of Meyer and co-workers was used to prepare $[(NH_3)_5Ru(H_2O)](PF_6)_2$.[15] For example, 0.25 g of $[Ru(NH_3)_5Cl]Cl_2$[20] in 15 mL of degassed 0.1 M H_2SO_4 was reduced under argon with zinc amalgam.

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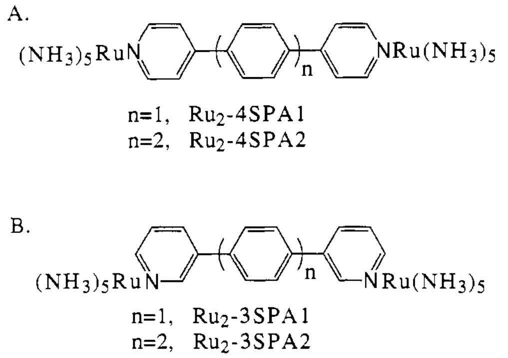

Figure 1. Schematic view of the (a) $(NH_3)_5Ru$–4SPA*n*–$Ru(NH_3)_5$ and (b) $(NH_3)_5Ru$–3SPA*n*–$Ru(NH_3)_5$ model systems.

The ruthenium(II) aquo complex was precipitated by the addition of 5 mL of a saturated aqueous ammonium hexafluorophosphate solution. The yellow product (stored in vacuo) was used within a week of its preparation.

The typical procedure used to prepare the binuclear complexes is described for the case of the 4SPA1 bridging ligand. First, 0.04 g (0.17 mmol) of 4SPA1 was dissolved in 30 mL of argon-degassed acetone. Under a steady flow of argon, 0.18 g (0.35 mmol) of solid $[(NH_3)_5Ru(H_2O)](PF_6)_2$ was added, and the substitution reaction was allowed to proceed with stirring in the dark for 48 h. After 15 mL of the solvent was evaporated under an argon flow, the crude product was precipitated from solution by the addition of 30 mL of degassed ether. This reaction product, which contained some monomer species, was recrystallized twice from acetonitrile–toluene as described previously.[21] The final yield of pure complex was 0.14 g (68%). Anal. Calcd for $[(NH_3)_5Ru$–4SPA1–$Ru(NH_3)_5](PF_6)_4$: C, 16.22; H, 3.55; N, 14.19; Ru, 17.06; F, 38.51; P, 10.47. Found: C, 16.29; H, 3.76; N, 13.61; Ru, 16.86; F, 38.69; P, 9.03.

The other new binuclear pentaammineruthenium(II) complexes were also prepared by using the above procedure. Satisfactory elemental analyses were obtained in all cases. Anal. Calcd for $[(NH_3)_5Ru$–3SPA1–$Ru(NH_3)_5](PF_6)_4$: C, 16.22; H, 3.55; N, 14.19; Ru, 17.06. Found: C, 16.62; H, 3.62; N, 13.26; Ru, 17.21. Anal. Calcd for $[(NH_3)_5Ru$–3SPA2–$Ru(NH_3)_5](PF_6)_4$: C, 20.96; H, 3.68; N, 13.33. Found: C, 21.78; H, 4.03; N, 12.49. Anal. Calcd for $[(NH_3)_5Ru$–4SPA2–$Ru(NH_3)_5](PF_6)_4$: C, 20.96; H, 3.68; N, 13.33. Found: C, 20.54; H, 3.89; N, 12.94. All microanalytical analyses were done by Galbraith Laboratories.

Instrumentation and Methods. Cyclic voltammetry and differential-pulse polarography measurements were made by using a PAR Model 273 potentiostat/galvanostat and a PAR Model 174 polarographic analyzer, respectively. All of the electrochemical experiments were carried out by using an argon-purged three-electrode cell with a gold-button working electrode, platinum-wire counter electrode, and saturated calomel (SCE) reference electrode. The concentration of the ruthenium complex in these electrochemical experiments was typically 1 mM. UV-visible and near-infrared (near-IR) spectra were recorded on a computer-controlled (IBM-XT) Perkin-Elmer λ9 spectrophotometer in 1–10 cm quartz cells. Solid ceric ammonium nitrate was added to DMSO-d_6 solutions of the $[(NH_3)_5Ru^{II}$–SPA*n*–$Ru^{II}(NH_3)_5]^{4+}$ ions (in optical cells) to oxidize the complexes in situ. Oxidation in acetonitrile or using bromine caused the complexes to precipitate from solution.

Results and Discussion

The UV–visible spectra of the new ruthenium(II)–ruthenium(II) binuclear complexes (Ru^{II}–4SPA*n*–Ru^{II} and Ru^{II}–3SPA*n*–Ru^{II}; $n = 1, 2$) exhibit π–π^* and metal to ligand charge-transfer (MLCT) absorptions that are characteristic of pentaammineruthenium(II)–(π-acceptor) complexes.[22] These results, which are summarized in Table I, give a qualitative measure of the magnitude of electronic coupling through the aromatic spacers. For example, in the series of 4-substituted compounds (Figure 2), we observe a 36-nm blue-shift in the $d\pi \rightarrow \pi^*$ MLCT transition when the first phenyl group is added ($n = 0$–1, $\Delta d = 4.3$ Å), and an additional 18-nm blue-shift when the second phenyl spacer is added ($n = 1$–2; $\Delta d = 4.3$ Å). In contrast, the 3-substituted compounds exhibit a much smaller blue-shift: 12 nm for $n = 0$–1 and 2 nm for $n = 1$–2. These shifts in the MLCT energy can be attributed to changes in the π^*-pyridine energy levels since the $d\pi$-ruthenium energy levels are the same (to first order) in the Ru^{II}–4SPA*n*–Ru^{II} and Ru^{II}–3SPA*n*–Ru^{II} complexes. Specifically, electronic coupling between the two terminal pyridine π-systems will split the π^* levels energetically, and therefore the MLCT transition will blue-shift as this electronic coupling decreases.[16] Our data indicate that the pyridine–pyridine coupling decreases more in the Ru^{II}–4SPA*n*–Ru^{II} complexes than in the Ru^{II}–3SPA*n*–Ru^{II} complexes as *n* increases from 0 to 2 and that for a given value of *n* (or spacer length), the interaction is stronger in the 4-substituted system.

Table I. Spectroscopic[a] and Electrochemical Properties of Ru^{II}–4SPA*n*–Ru^{II} and Ru^{II}–3SPA*n*–Ru^{II} Complexes

L	*n*	λ, nm (log ε) π–π^*	λ, nm (log ε) MLCT	$E_{1/2}$,[b] V	*d*(M–M), Å
4,4′-bipyridine[c]	0	249 (4.18)	521 (4.42)	0.128	11.3
4SPA1	1	281 (4.36)	485 (4.31)	0.089	15.6
4SPA2	2	301 (4.13)	467 (4.02)	0.074	19.9
3,3′-bipyridine	0	236 (4.22) 258 (4.11)	429 (4.24)	0.120	7.8–9.7 (cis–trans)
3SPA1	1	280 (4.51)	417 (4.24)	0.093	12.1–13.5
3SPA2	2	298 (4.62)	415 (4.17)	0.089	16.4–17.5

[a] All spectra were recorded in acetonitrile by using the PF_6^- salts of the compounds. [b] Versus SCF; aqueous solution, 0.1 M NaCl supporting electrolyte. [c] Reference 16.

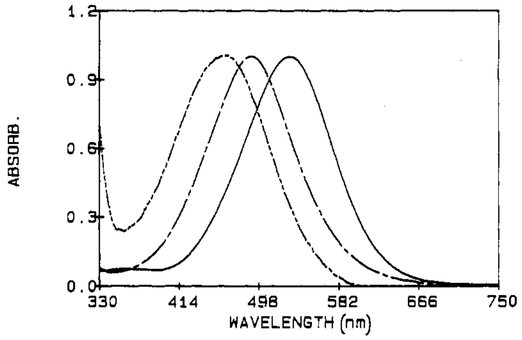

Figure 2. Visible spectra of the Ru^{II}–4SPA*n*–Ru^{II} complexes recorded in acetonitrile: $n = 0$ (—); $n = 1$ (- - -); and $n = 2$ (– – –). The spectra were normalized by using the absorbance at the MLCT maxima of the complexes.

Cyclic voltammograms of the Ru^{II}–4SPA*n*–Ru^{II} and Ru^{II}–3SPA*n*–Ru^{II} complexes exhibit single oxidation–reduction waves. The anodic–cathodic peak separations in the voltammograms are, however, greater than expected for an ideal 1-electron reversible redox couple (Table I).[23] The increases in peak to peak separations are 14 ($n = 1$) and 7 mV ($n = 2$) for the Ru–4SPA*n*–Ru complexes and 14 ($n = 1$) and 6 mV ($n = 2$) for the Ru–3SPA*n*–Ru models.[24] Deviations from ideality are also observed in differential-pulse polarograms of the compounds. The deviations observed in the voltammograms and polarograms indicate that oxidation of the two ruthenium centers does not occur independently.

In principle, the electronic interaction between the two metal sites can be determined from the stability of the mixed-valence Ru^{II}–SPA*n*–Ru^{III} complex relative to the fully reduced and oxidized species Ru^{II}–SPA*n*–Ru^{II} and Ru^{III}–SPA*n*–Ru^{III}, respectively (eq 2).[25] The stability of the mixed-valence product, as measured

$$\mathrm{Ru^{II}\text{–}SPA}n\text{–}\mathrm{Ru^{II}} + \mathrm{Ru^{III}\text{–}SPA}n\text{–}\mathrm{Ru^{III}} \rightleftharpoons 2\mathrm{Ru^{II}\text{–}SPA}n\text{–}\mathrm{Ru^{III}} \quad (2)$$

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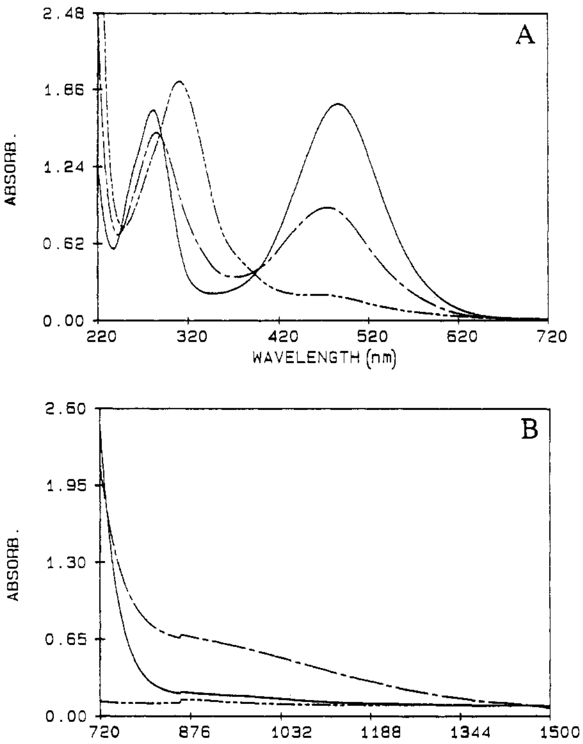

Figure 3. (A) UV-visible spectra recorded in acetonitrile by using a 5 cm cell for the Ru^{II}–4SPA1–Ru^{II} (—), Ru(II)-4SPA1-Ru(III) (- - -), and Ru^{III}–4SPA1–Ru^{III} (- --- -) complexes. The total concentration was 1 × 10^{-5} M. (B) Near-IR spectra recorded in situ in a 5-cm cell as the Ru^{II}–4SPA1–Ru^{II} complex was oxidized in DMSO-d_6 with Ce(IV). The total concentration was 6 × 10^{-4} M.

by the comproportionation constant for eq 2, is directly related to the difference in the Ru^{II}–Ru^{II}/Ru^{II}–Ru^{III} and Ru^{II}–Ru^{III}/Ru^{III}–Ru^{III} redox potentials.[25] The broadening observed in the cyclic voltammograms suggests that the mixed-valence state may be weakly stabilized in these new compounds. It is difficult, however, to attribute this small stabilization to electronic delocalization since statistical and electrostatic factors also contribute to the stability of the mixed-valence state.[25]

The most direct measure of the metal–metal electronic coupling in a mixed-valence system is the intensity and band shape of the intervalence transition since these spectral properties can be used to directly calculate the electronic matrix element.[25,26] The mixed-valence state of the Ru^{II}–SPA–Ru^{II} dimers was prepared via chemical oxidation using Ce(IV). Typical examples of the UV-visible and near-infrared (near-IR) spectra for the reduced, mixed-valence, and oxidized states of the Ru–4SPA1–Ru system are shown in Figure 3. The mixed-valence ion does not exhibit an intervalence peak, although there is a well-defined increase in absorbance in the near-IR region that is lost when the complex is oxidized to the Ru^{III}–4SPA1–Ru^{III} state. The ϵ_{max} calculated[27] from the absorbance increase at 830–850 nm (160 M^{-1} cm^{-1}) was found to be independent of concentration between 5 × 10^{-4} and 5 × 10^{-3} M indicating that intermolecular effects do not give rise to this broad NIR absorption. Visible–near-IR spectra of the mixed-valence Ru^{II}–4SPA2–Ru^{III} also exhibit a broad absorption in the near-IR region, although the ϵ_{max} for this species (16 M^{-1} cm^{-1}) is smaller than that for the Ru^{II}–4SPA1–Ru^{III} complex (Figure 4). Similar spectra were also observed for the Ru^{II}–3SPA1–Ru^{III} mixed-valence complex (ϵ_{max} = 0.40 M^{-1} cm^{-1}); however, the Ru^{II}–3SPA2–Ru^{III} ion does not show any detectable increase in absorbance (above background) in this spectral region.

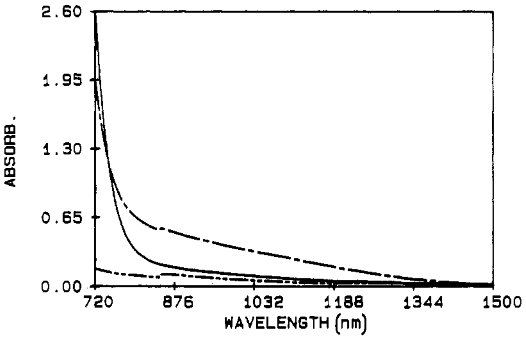

Figure 4. Near-IR spectra of the Ru^{II}–4SPA2–Ru^{II} (—), Ru^{II}–4SPA2–Ru^{III} (- - -), and Ru^{III}–4SPA2–Ru^{III} (- --- -) complexes recorded in a 5-cm cell. The total concentration of complex was 4 × 10^{-3} M.

Our observations are somewhat surprising in light of recent studies of intervalence transitions in binuclear ruthenium complexes containing rigid aliphatic and olefinic spacers.[10a,12] In the aliphatic dithiaspiro complexes reported by Lewis and co-workers,[10a] well-defined intervalence peaks were observed for metal–metal separations comparable to those studied here. It is believed that the ruthenium centers couple via the sulfur ligands to the uninterrupted σ-system in these compounds.[28] More recently, relatively intense intervalence transitions observed in ruthenium–alkene systems have been attributed to favorable π-interaction through the alkene bridging group.[12,29] The weak, broad near-IR absorptions that we observe in the mixed-valence Ru^{II}–SPA*n*–Ru^{III} complexes imply that electronic coupling is weak in these aromatic systems. Alternatively, broad absorptions would be observed if the Ru^{II}–SPA*n*–Ru^{III} complexes have several distinct conformations in solution (each with a different λ_{max}), although we believe that this is unlikely.[30] Weak coupling in these aromatic systems is not unexpected (even though the ruthenium centers have a strong charge-transfer interaction with the π-systems of the pyridine end groups) because the pyridine–phenyl and phenyl–phenyl π-system coupling is weak.[31] It is interesting to note that strong coupling has been reported with similar bridging groups that link organic donor–acceptor pairs.[7] The electronic interaction in these systems is believed, however, to be transmitted through the σ-system.

In summary, we have prepared and characterized a new series of long-range ET models based on variable-length aromatic spacers. Our spectroscopic and electrochemical measurements show that the ruthenium centers in these models interact only weakly. Hence, these results suggest that aromatic groups do not necessarily promote an unusually strong electronic coupling between redox centers.[5] Further studies designed to quantify the electronic interaction in these new systems and to probe the orientation dependence of the coupling are in progress.

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(27) The calculated value was not corrected by the comproportionation constant; hence, the actual value of ϵ for the mixed-valence species may be up to 2 times greater.

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(29) The intensities and positions of the near-IR peaks reported in this work[12] exhibit surprisingly little variation with distance.

(30) We note that the full width at half-maximums (fwhm) for the MLCT transitions in the Ru–SPA*n*–Ru compounds are comparable to that found for (NH$_3$)$_5$Ru^{II}py, a rigid system. Since it is known that λ_{max} (MLCT) will blue-shift as the pyridine–pyridine orientation approaches 90°,[16] we believe that distinct rotomers are unlikely because a superposition of their MLCT bands would lead to larger fwhms than are observed.

(31) Although the relative orientation of the aromatic rings is not fixed, previous studies[32] indicate that adjacent rings will be rotated ca. 40° relative to each other. Hence, the π–π overlap between rings will be weak.

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