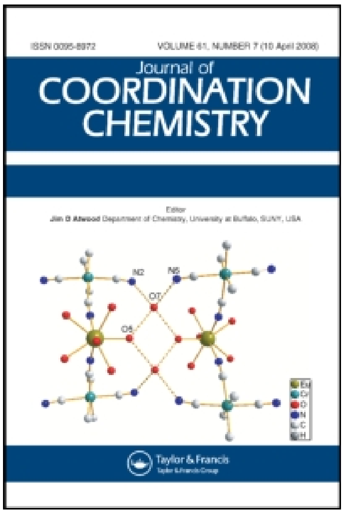

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NEW DINUCLEAR ASYMMETRIC COMPLEXES OF RUTHENIUM AND RHENIUM

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New dinuclear asymmetric complexes of ruthenium and rhenium, of formula $[(bpy)(CO)_3Re^{I}(4,4'\text{-bpy})Ru^{II/III}(NH_3)_5]^{3+/4+}$ have been prepared and characterized by spectroscopic and electrochemical techniques. In the mixed-valent species $[Re^{I}, Ru^{III}]$, the back electron transfer reaction $Ru^{II} \rightarrow Re^{II}$, that occurs after light excitation, is predicted to be in the Marcus inverted region. This fact is consistent with the observed quenching of the luminiscence of the Re chromophore in $[(bpy)(CO)_3Re^{I}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{4+}$, when compared to the parent complex $[(bpy)(CO)_3Re^{I}(4,4'\text{-bpy})]^{+}$. A theoretical treatment due to Creutz, Newton and Sutin has been successfully applied to predict the electronic coupling element in the mixed-valent complex.

Keywords: Mixed-valence; Electron transfer; Asymmetric complexes

INTRODUCTION

Interest in mixed-valence complexes arises from their use as models for testing current electron transfer theories [1] and for designing molecular devices for solar energy conversion [2]. In this work, we report the syntheses and characterization of new dinuclear asymmetric complexes derived from $Re(CO)_3(bpy)^+$ ($bpy = 2,2'$-bipyridine) as a photosensitizing unit bridged by 4,4′-bpy (4,4′-bpy = 4,4′-bipyridine) to $Ru(NH_3)_5^{n+}$ as electron donor ($n = 2$) or acceptor ($n = 3$) units.

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A related work by Lin and Guarr [3] on bimetallic complexes containing a (α-diimine)$(CO)_3Re^I$ chromophore covalently attached to a ruthenium pentaammine moiety has evidenced that, in spite of a very weak metal-metal interaction in these systems, the emission from the Re → α-diimine ^{3}MLCT excited state is quenched by both Ru^{II} and Ru^{III}, thus pointing to the occurrence of rapid photoinduced intramolecular electron transfer processes. We address in this work the changes in photophysical behavior that can be obtained by separating the α-diimine moiety from the electron relay groups by shorter chemical bridges, such as that formed by 4,4′-bpy.

For the mixed-valent species $[(bpy)(CO)_3Re(4,4'\text{-}bpy)Ru(NH_3)_5]^{4+}$, we have attempted to test, for the first time in an asymmetric system, a recent theoretical formula developed by Creutz, Newton and Sutin [4] that predicts the electronic metal-to-metal coupling element from metal-to-ligand charge transfer (MLCT) absorption data, and to compare this calculated value to that determined from metal-to-metal charge transfer (MMCT) absorption data, by Hush's well-known formula [5]. Encouraging results on the applicability of this formalism have been recently reported by Crutchley *et al.* [6] for symmetric mixed-valent ruthenium complexes. The prediction of intramolecular electron transfer parameters is relevant to the design of efficient photoconverters [7].

EXPERIMENTAL

Syntheses

The previously reported hexafluorophosphate salts of the complexes $[Re(CO)_3(bpy)(4,4'\text{-}bpy)]^+$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ were prepared and purified as in previous Refs. [8, 9].

The new binuclear PF_6^- salt of the complex $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{II}(NH_3)_5]^{3+}$, (**I**), was prepared as a tetrahydrate by stirring $[Re(CO)_3(bpy)(4,4'\text{-}bpy)](PF_6)$ (80 mg, 0.1 mmol) in Me_2CO (10 mL) under Ar and adding, after 1 h, $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (54 mg, 0.1 mmol), followed by continuous stirring under Ar for 2 h in the dark. 100 mL of ether was then added to precipitate the complex. The solid was dissolved in MeOH (2 mL) and sorbed onto a column of Sephadex LH-20 (3 × 10 cm) and eluted with MeOH. The 2nd fraction was collected, rotoevaporated to 5 mL, cooled to room temperature and precipitated with ether (100 mL). The solid was filtered, washed with ether and dried *in vacuo* over P_4O_{10}. *Yield*: 100 mg

(78%). *Anal.* Calc.: C, 21.65%, H, 3.08%; N, 9.88%. Found: C, 21.14%; H, 2.92%; N, 10.42%.

The mixed-valent ion $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{4+}$, (II), was generated by adding 100 times in excess Br_2 (0.5 mL) to an acetonitrile solution (10 mL) of $(I)(PF_6)_3$ (50 mg, 0.04 mmol) with a stoichiometric amount of $Bu_4{}^nPF_6$ (11.8 mg). After 10 min of reaction, 100 mL of ether was added to precipitate the complex. The solid was filtered, washed with ether and dried *in vacuo* over P_4O_{10}. *Yield:* 43 mg (75%). *Anal.* Calc.: C, 20.48%, H, 2.32%; N, 9.34%. Found: C, 20.86%; H, 2.76%; N, 9.73%.

Materials, Instrumentation and Techniques

Acetonitrile was distilled from $KMn0_4$ and dried over molecular sieves. Tetrakis(*n*-butyl)ammonium hexafluorophosphate (TBAH) was recrystallized four times from EtOH and dried at 150°C for 72 h. All other chemicals were reagent grade and used without further purification.

IR spectra were recorded, as KBr pellets, on a double-beam Perkin-Elmer 983G spectrophotometer. UV-visible spectra were obtained with a double-beam Shimadzu UV-160A spectrophotometer in 1-cm cells. Cyclic voltammetry experiments were carried out in MeCN, 0.1 M TBAH, with an EQMAT-Sl cyclic voltammetry equipment, controlled by a IBM-compatible computer. A standard three electrode compartment cell was used with Ag/AgCl (3 M KCl) as a reference electrode and Pt as auxiliary and working electrodes. Ar was bubbled through the solutions prior to measurements. Luminiscence spectra were recorded with a spectrofluorometer Shimadzu RF-5301 PC, provided with 1-cm fluorescence cells. Samples were bubbled with Ar prior to measurements. Chemical analyses were performed at INQUIMAE, University of Buenos Aires, Argentina.

RESULTS

Figures 1 and 2 show the IR spectra (as KBr pellets) of the PF_6^- salts of complexes (I) and (II) respectively. Table I displays the UV-visible absorption data in MeCN at 22°C for both complexes. Figure 3 shows the UV-visible spectrum of (I) in MeCN. A spectrophotometric titration of complex (I) with Br_2 in MeCN is recorded in Figure 4. The cyclic voltammogram of complex (I) is shown in Figure 5, at v = 200 mV/s. Finally, Figure 6 shows the emission spectra in MeCN solution ($\lambda_{ex} = 350$ nm) of the

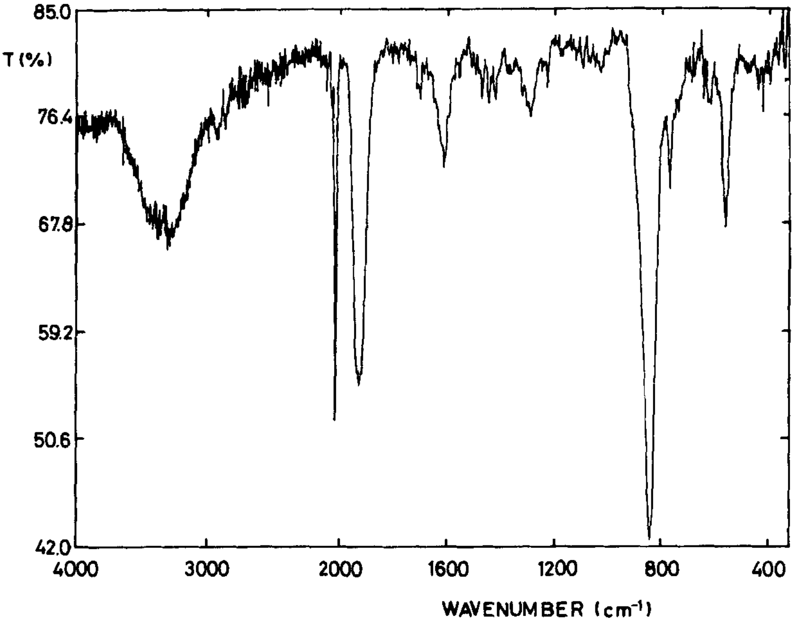


FIGURE 1 IR spectrum of $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{II}(NH_3)_5](PF_6)_3 \cdot 4H_2O$ (KBr pellet).

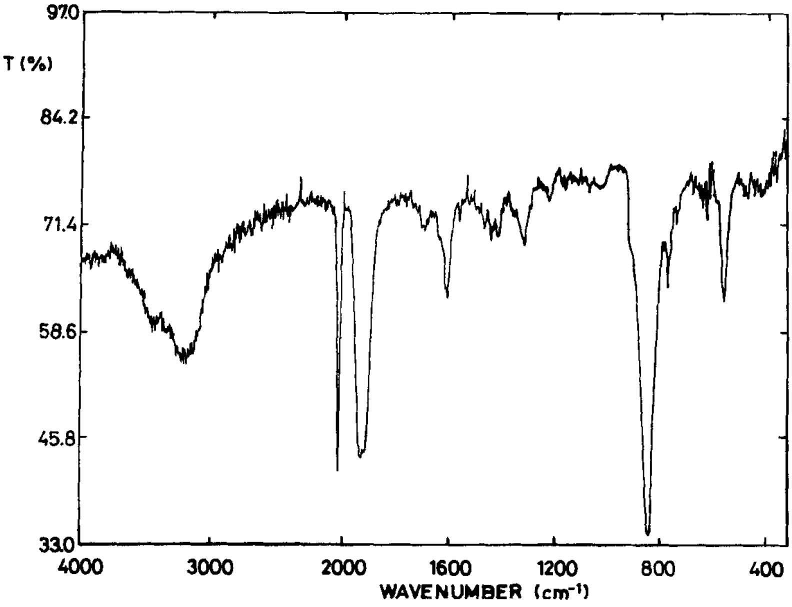


FIGURE 2 IR spectrum of $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{III}(NH_3)_5](PF_6)_4$ (KBr pellet).

TABLE I Electronic absorption spectral data in MeCN

Complex	λ_{max}, *nm* (10^{-3} ε_{max}, M^{-1} cm^{-1})[a]
(I), $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{II}(NH_3)_5]^{3+}$	534 (4.5), 346 (6.1), 319 (13), 309 (12), 268 (13), 245 (17)
(II), $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{4+}$	480 (1.0), 343 (10), 319 (21), 304 (17), 273 (sh), 236 (29)

[a] At 22°C. Errors: ± 2 nm in λ_{max}, ± 5% in ε_{max}.

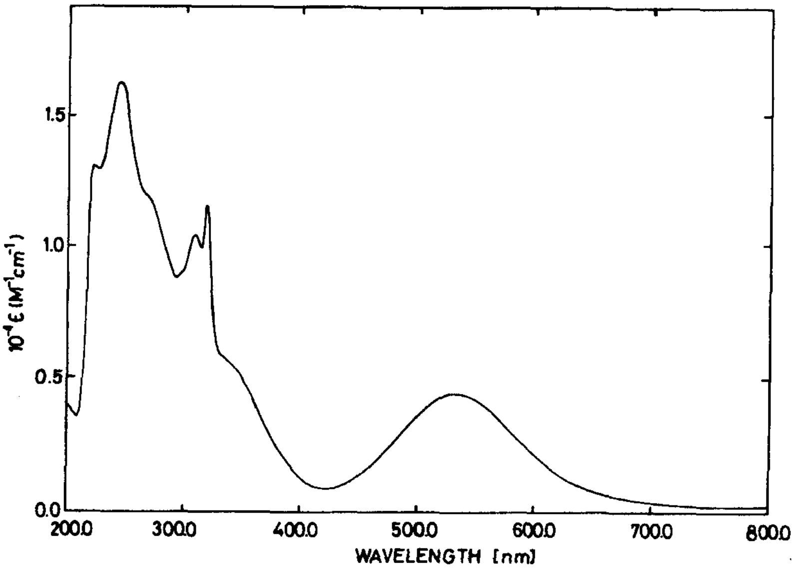


FIGURE 3 UV-visible spectrum of $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{II}(NH_3)_5]^{3+}$ in MeCN.

mononuclear species $[Re(CO)_3(bpy)(4,4'\text{-}bpy)]^+$ and of the dinuclear complex (II).

DISCUSSION

IR Spectra

As shown in Figures 1 and 2, characteristic carbonyl stretching frequencies [10] $\nu(CO)$ are exhibited at 2033 and 1927 cm^{-1} for complex (I) and at 2034 and 1924 cm^{-1} for complex (II). The main differences arise when comparing the ammonia deformation frequencies $\delta_{sym}(NH_3)$ that appear at 1289 cm^{-1} for complex (I) and at 1319 cm^{-1} for complex (II), a clear indication of

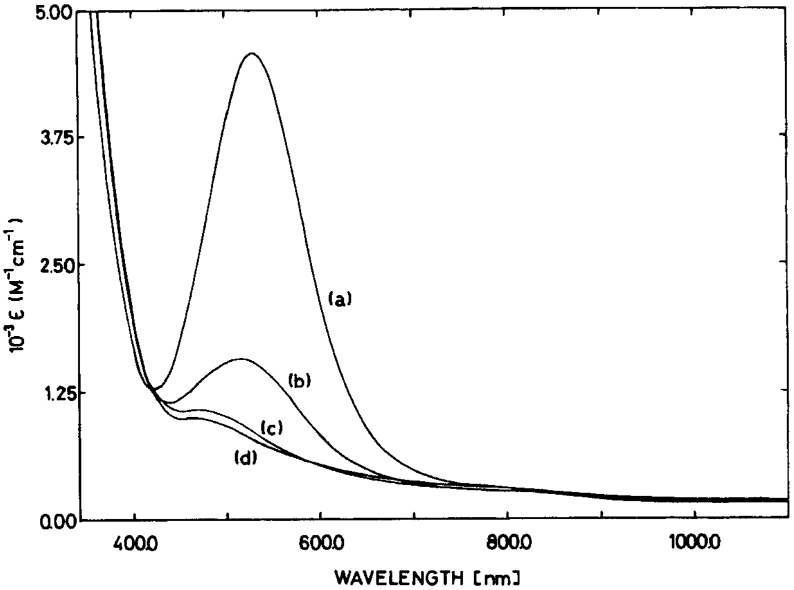


FIGURE 4 Spectrophotometric titration of $[(bpy)(CO)_3Re^{I}(4,4'\text{-bpy})Ru^{II}(NH_3)_5]^{3+}$, (I), by Br_2 in MeCN. Molar ratios [(I)]/[Br_2] are: (a) 1 : 0; (b) 1 : 0.5; (c) 1 : 1; (d) 1 : 1.25.

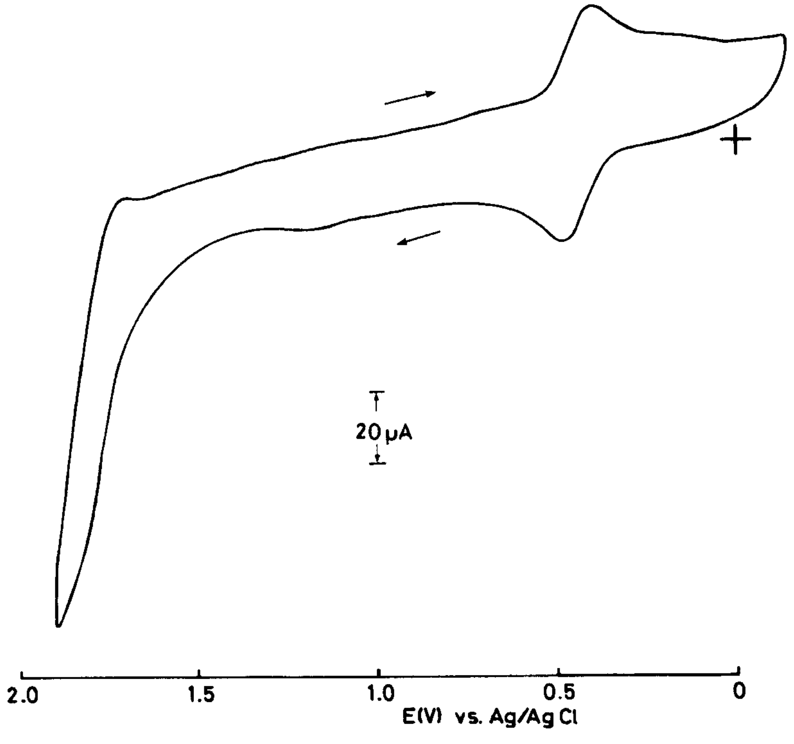


FIGURE 5 Cyclic voltammogram of complex (I) in MeCN, 0.1 M TBAH, v = 200 mV/s.

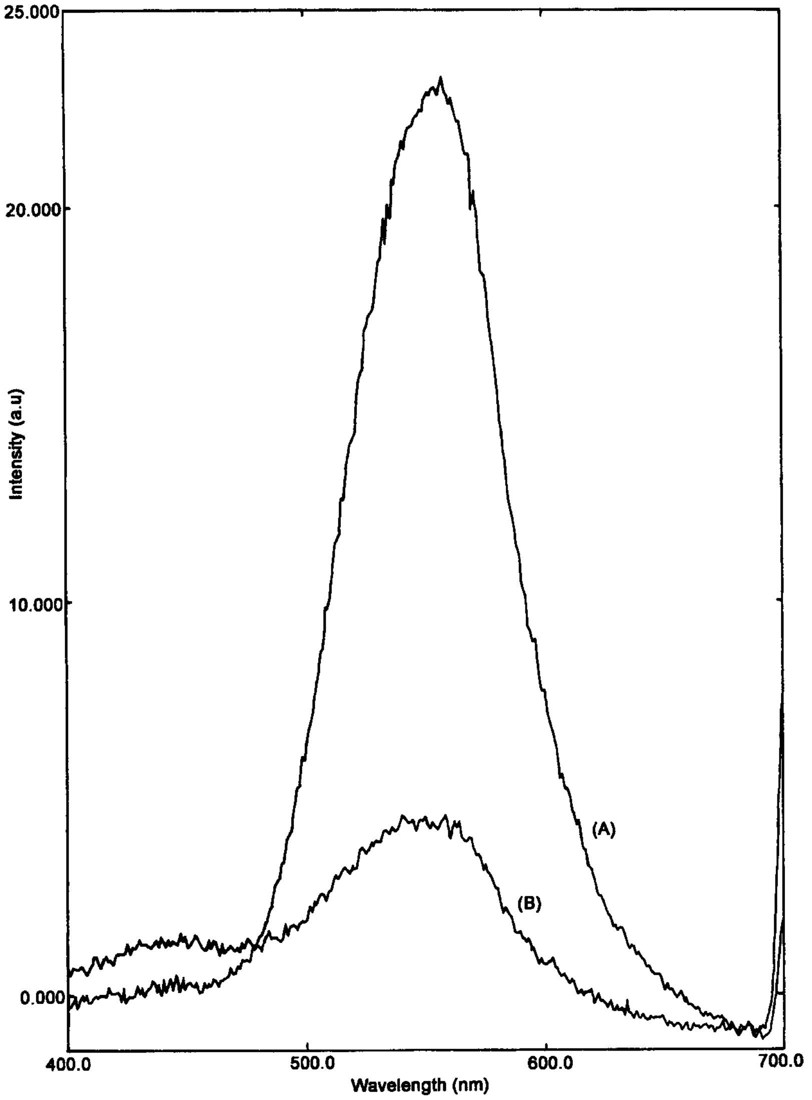


FIGURE 6 Emission spectra, in MeCN, at 22°C, of (A): $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)]^+$ and (B): $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{4+}$ ($\lambda_{ex} = 350$ nm).

localized oxidation states +2 and +3 for ruthenium in complexes (I) and (II), respectively [11].

UV-vis Spectra

The electronic spectral data shown in Table I include UV absorptions between 200 and 300 nm, that can be assigned to characteristic intraligand

π-π^* transitions of the pyridinic ligands [8]. The absorptions at $\lambda_{max} = 346$ and 534 nm for complex (I), shown in Figure 3, correspond to metal-to-ligand charge transfer transitions (MLCT) d_π (Re) $\rightarrow \pi^*$(bpy) and d_π (Ru) $\rightarrow \pi^*$(4,4′-bpy) respectively, by comparison with the spectra of the mononuclear parent complexes [8, 12]. The latter band is red-shifted when compared to the same band in $[Ru(NH_3)_5(4,4\text{-bpy})]^{2+}$ ($\lambda_{max} = 470$ nm), indicating considerable metal-metal π-interaction between Re and Ru through the 4,4′-bpy bridge. A spectrophotometric redox titration of complex (I) with Br_2 in MeCN is shown in Figure 4. When the molar ratio of $[(I)]/[Br_2] \geq 1$, the band at 534 nm disappears, while that at *ca.* 340 nm is left almost unchanged, clear evidence of formation of complex (II). The new band at $\lambda_{max} \approx 480$ nm ($\varepsilon_{max} \approx 980\,M^{-1}cm^{-1}$) can be assigned to a metal-to-metal charge transfer (MMCT) transition Re(I) → Ru(III), which has not been previously detected in similar systems [3].

Electrochemistry

Figure 5 shows the cyclic voltammogram in the oxidative range of complex (I), in MeCN at 22°C, 0.1 M TBAH and scan rate v = 200 mV/s. The two observed waves can be assigned to the couples Re^{II}/Re^{I}($E_{1/2} = 1.84$ V) and Ru^{III}/Ru^{II}($E_{1/2} = 0.44$ V). The value obtained for $\Delta E_{1/2} = E_{1/2}(Re^{II}/Re^{I}) - E_{1/2}(Ru^{III}/Ru^{II}) = 1.40$ eV.

From a Hush treatment of the MMCT spectrum [5], the reorganization energy λ for the intramolecular electron transfer through the 4,4′-bpy bridge can be calculated as:

$$\lambda = E_{op} - \Delta G^o - \Delta E_{exc} \qquad (1)$$

where E_{op} (maximum of the MMCT absorption) = 2.58 eV, $\Delta G^o = \Delta E_{1/2} =$ 1.40 eV, and $\Delta E_{exc} = 0.25$ eV [13]. Thus, $\lambda \approx 1$ eV, a value comparable to that obtained by Lin and Guarr for a similar complex [3]. Since $\lambda < -\Delta G^o$ for the reverse electron transfer process $Ru^{II} \rightarrow Re^{II}$, we predict that this back reaction will fall in the Marcus inverted region [14].

Luminescence Properties

Figure 6 shows the emission spectra of the mononuclear species $[(bpy)(CO)_3Re(4,4'\text{-bpy})]^+$, (**A**), and of the dinuclear complex $[(bpy)(CO)_3Re(4,4'\text{-bpy})Ru(NH_3)_5]^{4+}$, (**B**). The emission of the former complex at $\lambda_{max} = 559$ nm ($\lambda_{ex} = 350$ nm) is quenched by a factor of 6.4 in the latter complex, evidencing an electron transfer process in the excited state, as shown in Scheme I.

This possibility has also been addressed by Lin and Guarr in a similar complex [3]. In this case, with a shorter metal-to-metal distance, the quenching of the emission is not complete, as expected from the distance dependence of the reorganization energy.

Calculations of H_{AB}

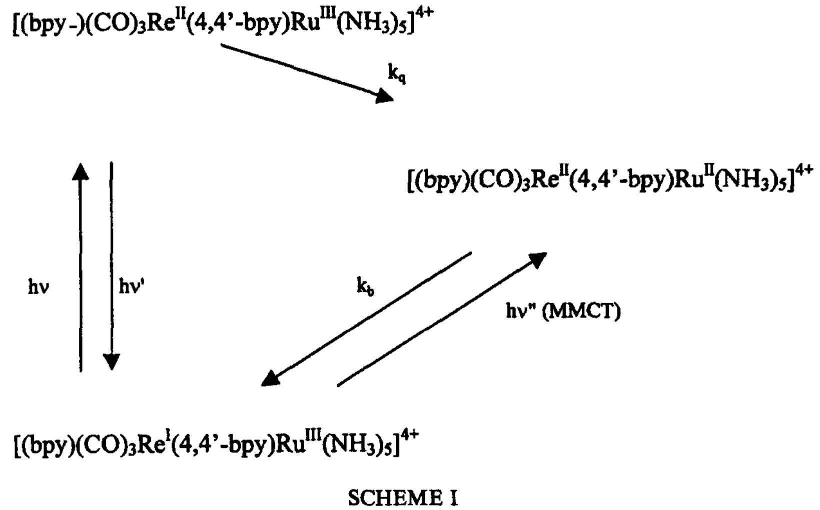
According to Creutz, Newton and Sutin [4], the electronic coupling element H_{AB} for intramolecular electron transfer reactions in mixed-valent systems can be calculated by assuming a superexchange mechanism. For a metal-to-metal coupling $H_{AB} = H_{MM'}$ and can be derived as follows:

$$H_{MM'} = \frac{H_{ML}H_{M'L}}{2\Delta E_{ML}} \tag{2}$$

where H_{ML} and $H_{M'L}$ are the two metal-ligand coupling elements ($M = Re$ and $M' = Ru$ in this study) and ΔE_{ML} can be computed from the energy maxima of the MLCT and MMCT bands through the formula:

$$\frac{1}{\Delta E_{ML}} = \frac{1}{2}\left(\frac{1}{\Delta E_{MLCT}} + \frac{1}{\Delta E_{MLCT} - \Delta E_{MM'CT}}\right) \tag{3}$$

We neglect in this case LMCT interactions.



SCHEME I

On the other hand, we can derive H_{AB} from spectral data of the mixed-valent species by using Hush formula [5]:

$$H_{AB} = \frac{2.06 \times 10^{-2}}{r}(\varepsilon_{\max} \cdot \Delta\tilde{\nu}_{1/2} \cdot \tilde{\nu}_{\max})^{1/2} \tag{4}$$

where H_{AB} is the donor-acceptor coupling element, r is the metal-to-metal distance and $\varepsilon_{\max}$, $\Delta\tilde{\nu}_{1/2}$ and $\nu_{\max}$ are the molar absorptivity (in $M^{-1}\,cm^{-1}$), bandwith at half-height (in cm^{-1}) and energy maximum of the MMCT band (in cm^{-1}), respectively.

We can determine ΔE_{ML} with Eq. (3) by using spectral data of Meyer *et al.*, on the Re → bpy MLCT transition [15], and our own data on the Re → Ru MM′CT transition (Tab. I). By introducing this value into Eq. (2), with the previously calculated values of H_{ML} and $H_{M'L}$ through Eq. (4), we obtain a "calculated" value of $H_{MM'} = 674\,cm^{-1}$. With the same formula (4), and using our own spectral data, we determine an "experimental" value of $H_{MM'} = 736\,cm^{-1}$. Both values compare very well and thus we infer that the Creutz, Newton and Sutin theoretical treatment is also applicable to asymmetric mixed-valent species, as well as to symmetric systems, such as those studied by Crutchley *et al.* [6].

CONCLUSIONS

New dinuclear complexes derived from the photosensitizing unit $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)]^+$ have been obtained, using capping $[Ru(NH_3)_5]^{n+}$ units as electron donor (n = 2) or electron acceptor (n = 3) relay groups, and characterized by spectroscopic and electrochemical techniques. The new mixed-valent complex, of formula $[(bpy)(CO)_3Re^I(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{4+}$, presents a MMCT transition $Re^I \rightarrow Ru^{III}$ at $\lambda_{\max} \approx 480\,nm$; in this species, the high asymmetry between both redox sites ($\Delta E_{1/2} = 1.40\,eV$) and the quenching of the emission (by a factor of 6.4) of the Re^I chromophore (when compared to the mononuclear Re species) point to the fact that the reverse intramolecular electron transfer $Ru^{II} \rightarrow Re^{II}$ falls in the Marcus inverted region. Besides, the value of the electronic coupling element between the donor (Re) and acceptor (Ru), H_{AB}, as deduced by Hush theory, can be calculated from spectroscopic data of the parent complexes through a theoretical treatment due to Creutz, Newton and Sutin, which seems to work very well for these asymmetric mixed-valent complexes. Thus, this and similar systems [3] can be used as models to test current theories of electron transfer and to help in designing efficient schemes for energy conversion.

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