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DISTANCE DEPENDENCE OF INTRAMOLECULAR ELECTRON TRANSFER PARAMETERS IN MIXED-VALENCE ASYMMETRIC COMPLEXES OF RUTHENIUM†

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Abstract—New mixed-valence complexes of the type $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}\text{-L-Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (terpy = 2,2′:6′,2″-terpyridine, bipy = 2,2′-bipyridine) with L = pz and BPE (pz = pyrazine; BPE = *trans*-1,2-bis(4-pyridyl)ethylene) exhibit metal-to-metal ($\text{Ru}_\text{b}^{\text{II}} \rightarrow \text{Ru}_\text{a}^{\text{III}}$; Ru_b = Ru bonded to bipyridine, Ru_a = Ru bonded to ammine) charge transfer transitions in the visible region, due to the strong asymmetry of the redox sites. Although the electronic coupling element of the pz-bridged complex is higher than that of the BPE analogue, both complexes are considered partially delocalized (Robin and Day class II). From a comparison of these data and those from closely related compounds, the distance dependence of intramolecular electron transfer parameters has been determined over a range of metal-to-metal distances r from 5 to ≅ 14 Å, good correlations being obtained, the electronic coupling H_{AB} and the molar absorptivity ε_{max} decreasing exponentially with r. The bridging ligands appear to behave as electronic π mediators with intermediate conducting properties ($\beta = 0.40$ Å^{-1}). The reorganization energy λ increases with r, but for $r > 9$ Å, the intramolecular electron transfer back reactions $\text{Ru}_\text{a}^{\text{II}} \rightarrow \text{Ru}_\text{b}^{\text{III}}$ fall in the barrierless regime, where the nuclear factor shows small distance dependence. In order to slow charge recombination after photoexcitation, it may be possible to combine more asymmetric redox sites, and by manipulation of the distance between them, generate intermediate values of H_{AB}, thereby causing Marcus "inverted" behaviour.

The distance dependence of intramolecular electron transfer parameters in mixed-valence complexes is an important issue,[1,2] especially in connection to studies of long-range electron transfer in metalloproteins[3] and to artificial photosynthesis.[4] In this work, we address this subject by analysing the optical data corresponding to metal-to-metal charge transfer (m.m.c.t.) transitions of a series of ligand-bridged mixed-valence asymmetric ruthenium complexes of the type $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}\text{-L-Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (terpy = 2,2′:6′,2″-terpyridine, bipy = 2,2′-bipyridine), with L = CN^-, pz, 4-CNpy, 4,4′-bipy and BPE (pz = pyrazine, 4-CNpy = 4-cyanopyridine, 4,4′-bipy = 4,4′-bipyridine, BPE = *trans*-1,2-bis(4-pyridyl) ethylene). Terpyridyl ruthenium(II) complexes are interesting as photosensitizing units in covalently-linked donor–acceptor assemblies that can be involved in efficient photoinduced charge separation processes.[5] We have herein extended our previous studies on mixed-valence complexes with L = CN^-,[6] 4-CNpy[7] and 4,4′-bipy[8] with the previously unreported dinuclear species with L = pz and BPE; their syntheses and spectroscopic and electrochemical properties being also described. The distance dependence of those parameters relevant to intramolecular electron transfers in these systems has been determined over a range of metal-to-metal distances from 5 to almost 14 Å.

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EXPERIMENTAL

Syntheses

The previously reported[9, 10] PF_6^- salts of the ions $[Ru(terpy)(bipy)(pz)]^{2+}$, **1**, and $[Ru(terpy)(bipy)(BPE)]^{2+}$, **2**, were prepared and purified using the same method described for the 4,4′-bipy analogue.[8a] For $(\mathbf{1})(PF_6)_2 \cdot Me_2CO$, the yield obtained was 77%. (Found: C, 41.6; H, 4.0; N, 11.0. Calc.: C, 41.8; H, 3.2; N, 10.7%.) Crystals of this complex were obtained from MeCN/toluene and are being currently studied by X-ray diffraction techniques.[8b]

The new dinuclear PF_6^- salt of the complex $[(terpy)(bipy)Ru^{II}(pz)Ru^{II}(NH_3)_5]^{4+}$, **3**, was synthesized as a trihydrate by stirring $[Ru(terpy)(bipy)(pz)](PF_6)_2 \cdot Me_2CO$ (81 mg, 0.09 mmol) in Me_2CO (8 cm^3) for 1 h under Ar. $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (52 mg, 0.1 mmol), prepared as in Ref. 11, was then added and the mixture was stirred for 6 h under Ar in the dark; 100 cm^3 of ether were used to precipitate the complex, which was then dissolved in Me_2CO (5 cm^3) and sorbed onto a column of SP-Sephadex C-25 (3 × 10 cm). Mononuclear species were eluted with 0.2 and 0.3 M LiCl in acetone–water solution (1 : 1 v/v). The desired species was eluted with 1 M LiCl in the same solvent mixture, rotoevaporated to 5 cm^3, cooled to room temperature and precipitated with NH_4PF_6 (1.5 g in 1 cm^3 of water). The solid was filtered, washed with cold water and dried *in vacuo* over P_4O_{10}. It can be further purified by recrystallizing from acetone–ether. Yield: 68 mg (54%). (Found: C, 25.0; H, 3.2; N, 12.8. Calc.: C, 25.0; H, 3.2; N, 12.1%.)

The mixed-valence ion $[(terpy)(bipy)Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+}$, **4**, was generated *in situ* by adding Br_2 vapour to an acetonitrile solution of **3**. A PF_6^- salt can be obtained as described for similar polynuclear compounds.[12]

The dinuclear species $[(terpy)(bipy)Ru^{II}(BPE)Ru^{II}(NH_3)_5]^{4+}$, **5**, was unstable in the air. Therefore, it was prepared by reduction *in situ* of the mixed-valence complex $[(terpy)(bipy)Ru^{II}(BPE)Ru^{III}(NH_3)_5]^{5+}$, **6**. The PF_6^- salt of **6** could be synthesized by stirring the corresponding mononuclear species **2** in Me_2CO (10 cm^3) for 1 h under Ar and then adding a stoichiometric amount of $[Ru(NH_3)_5(H_2O)](PF_6)_2$. The mixture was stirred for 6 h under Ar in the dark; 100 cm^3 of ether were used to precipitate the complex, which was then dissolved in MeCN (10 cm^3) and oxidized by I_2 in MeCN. The oxidized species was precipitated with ether, dissolved in Me_2CO and reprecipitated with excess Bu^n_4NBr in Me_2CO. The Br^- salt was collected by filtration, washed with cold acetone and air-dried. It was then dissolved in HCl 0.2 M (5 cm^3) and sorbed on to a column of SP-Sephadex C-25 and eluted with HCl at different concentrations. The desired complex was eluted with HCl 1 M, rotoevaporated to 5 cm^3, cooled to room temperature and precipitated with excess NH_4PF_6. It was then filtered off, washed with cold water and dried under vacuum over P_4O_{10}. It was finally recrystallized twice from acetone–ether. For the species $(\mathbf{6})(PF_6)_5 \cdot 2\ Me_2CO$ the yield was 20%. (Found: C, 30.8; H, 3.6; N, 11.1; Calc.: C, 30.4; H, 3.3; N, 9.9%.)

The PF_6^- salt of the monoprotonated species $[Ru(terpy)(bipy)(BPEH)]^{3+}$, **7**, was obtained as a monohydrate as a subproduct of the chromatographic separation of **6**. It was eluted from the column with HCl 0.6 M, before the mixed-valence dimeric species. (Found: C, 39.2; H, 3.2; N, 9.8. Calc.: C, 39.4, H, 2.9; N, 8.7%.)

Materials, instrumentation and techniques

Acetonitrile was distilled from $KMnO_4$ 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 Perkin–Elmer 983G spectrophotometer. UV/vis spectra were obtained with a Shimadzu UV-160A spectrophotometer. Cyclic voltammetry experiments were carried out in MeCN, 0.1 M TBAH, with a potentiostat/galvanostat EQMAT-S1, made at Instituto de Química de Materiales, Medio Ambiente y Energía (INQUIMAE), Universidad de Buenos Aires, Argentina. An H-type conventional cell was used, with Pt as working and auxiliary electrodes and Ag/AgCl (3 M) as a reference electrode. All potentials are referred to the SCE (standard calomel electrode) by subtracting 36 mV to the measured values. The ferrocene/ferrocinium couple ($Fc^{+/o}$) has a value of $E_{1/2}$ = 0.40 V (vs SCE), under the same conditions. Ar was bubbled through the solutions prior to measurements.

For pK_a determinations, the equipment and conditions used were the same as those described before.[8] Chemical analyses were done at Unidad de Microanálisis y Métodos Físicos en Química Orgánica (UMYMFOR) and at INQUIMAE, Universidad de Buenos Aires, Argentina.

Table 1. Values of pK_a for pz and BPE as free and coordinated ligands

L	pK_{a1} (free)	$[Ru(NH_3)_5(L)]^{2+}$	$[Ru(terpy)(bipy)(L)]^{2+}$
pz	0.6 ± 0.2[a]	2.6 ± 0.1[a]	1.0 ± 0.2[b]
BPE	5.9 ± 0.1[a]	5.0 ± 0.1[a]	5.5 ± 0.1[b]

[a] Ref. 13.
[b] This work.

RESULTS AND DISCUSSION

pK_a determinations

pK_a values for coordinated pz and BPE in complexes **1** and **2** respectively were determined by spectrophotometric titrations, and are shown in Table 1, together with the corresponding data for the free ligands and the ammineruthenium analogues.[13] A numerical method already described[14] was used for the calculation of pK_a of **1** (1.0) in water, at 22°C. Figure 1 shows a plot of the ratios of absorbances at 425 nm (λ_{max} for the non-protonated form of **2**) and at 445 nm (λ_{max} for the protonated form of **2**) vs pH, from which the value of pK_a of **2** (5.5) was determined in water, at 22°C, $\mu = 0.5$ M (KCl). Both values of pK_a are similar to those of the free ligands. It is worth noting the considerable reduction in pK_a for **1**, when compared to the pK_a of $[Ru(NH_3)_5(pz)]^{2+}$ (2.6); Ru → pz back-bonding is greatly diminished in **1**, due to competition of terpy and bipy for the metal π-electron density.

IR spectra

IR spectra of the PF_6^- salts of **1** and **2** show characteristic ligand (terpy, bipy, pz or BPE) vibrations between 1600 and 600 cm^{-1}.[8] For complex **3**, a new band appears at 1285 cm^{-1}, which is assigned to $\delta_{sym}(NH_3)$, and indicates oxidation state (II) for Ru of the capping pentaammineruthenium group.[15] Instead, complex **6** shows the corresponding absorption at 1325 cm^{-1}, a clear indication of oxidation state (III) for the same ruthenium.[15]

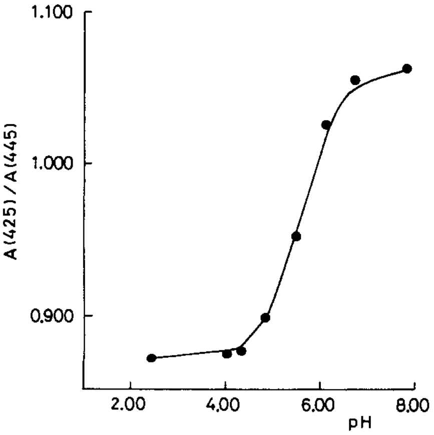

Fig. 1. Plot of ratio of absorbances of [Ru(terpy)(bipy)(BPE)]$^{2+}$ and [Ru(terpy)(bipy)(BPEH)]$^{3+}$ vs pH, in aqueous solutions, at 22°C, $\mu = 0.5$ M (KCl). The solid curve is calculated for pK_a = 5.5.

UV/vis spectra

Table 2 shows the complete UV/vis spectral data in MeCN at 22°C for the mononuclear complexes **1**, **2** and **7**, the dinuclear species **3** and **5** and the mixed-valence complexes **4** and **6**. The UV absorptions between 200 and 300 nm can be assigned to characteristic intraligand $\pi \rightarrow \pi^*$ transitions (terpy, bipy, pz or BPE).[8] The intense bands at 428 and 464 nm in **1** and those at 425 and 479 nm in **2** can be assigned to metal-to-ligand charge transfer (m.l.c.t.) transitions $d_\pi(Ru) \rightarrow \pi^*$ (bipy) and $d_\pi(Ru) \rightarrow \pi^*$ (terpy) respectively, by comparison with analogous systems.[7, 8] Bands at 360 nm in **1** and 379 nm in **2** can be ascribed to $d_\pi(Ru) \rightarrow \pi^*(pz)$ and $d_\pi \rightarrow \pi^*(BPE)$ m.l.c.t. respectively. All these bands show small solvent dependence. In strong acid media (pH = 0), the band at 428 nm for complex **1** is shifted to higher energies and decreases in intensity, while the intensity of the shoulder at 530 nm is enhanced. This can be attributed to protonation of the free N of coordinated pz. At pH = 2.0, the bands of complex **2** at 425 and 379 nm are shifted to the red (445 nm) in complex **7**, due to protonation of the free N of coordinated BPE.

The dinuclear complexes **3** and **5** exhibit, in MeCN, new and intense absorptions at 543 and 540 nm respectively, both of which disappear upon Br_2 vapour addition, and are sensitive to the donor number of the solvent. These bands are assigned to m.l.c.t. transitions from d_π orbitals of ammine ruthenium (Ru_a) to π^* orbitals of the bridging ligands (pz or BPE). Br_2 is capable of oxidizing Ru_a but not the polypyridyl ruthenium (Ru_b).[8] When comparing these values to the λ_{max}

Table 2. Electronic absorption spectral data[a]

Complex	λ_{max}(nm) [$10^{-3}\varepsilon_{max}$($dm^3\ mol^{-1}\ cm^{-1}$)][b]
1 $[Ru(terpy)(bipy)(pz)]^{2+}$	232 (26.9), 244 (28.3), 275 (36.8), 285 (42.4), 310 (38.4), 333 (sh), 360 (sh), 428 (11.3), 464 (10.1), 531 (sh), 580 (sh)
2 $[Ru(terpy)(bipy)(BPE)]^{2+}$	243 (sh), 254 (29.2), 274 (sh), 289 (53.7), 311 (44.6), 333 (sh), 379 (10.1), 425 (12.8), 479 (8.82), 537 (sh), 586 (sh)
3 $[(terpy)(bipy)Ru^{II}(pz)Ru^{II}(NH_3)_5]^{4+}$	235 (17.4), 243 (18.1), 255 (16.7), 275 (23.7), 285 (25.8), 311 (23.4), 333 (sh), 360 (sh), 465 (8.87), 543 (18.0)
4 $[(terpy)(bipy)Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+}$	429 (11.8), 455 (11.6), 470 (11.4), 570 (sh), 832 (0.8)
5 $[(terpy)(bipy)Ru^{II}(BPE)Ru^{II}(NH_3)_5]^{4+}$	258 (40.0), 275 (sh), 310 (sh), 380 (sh), 432 (7.01), 487 (7.81), 540 (8.16)
6 $[(terpy)(bipy)Ru^{II}(BPE)Ru^{III}(NH_3)_5]^{5+}$	231 (16.8), 243 (15.2), 274 (sh), 289 (27.2), 311 (26.3), 350 (sh), 380 (sh), 435 (9.40), 480 (sh), 540 (sh), 600 (sh)
7 $[Ru(terpy)(bipy)(BPEH)]^{3+}$	228 (21.3), 274 (sh), 291 (43.2), 302 (44.3), 305 (45.2), 311 (45.1), 333 (sh), 380 (sh), 445 (13.1), 479 (sh), 537 (sh), 586 (sh)

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

of the corresponding m.l.c.t. transitions in $[Ru(NH_3)_5(pz)]^{2+}$ (455 nm in MeCN)[15] and $[Ru(NH_3)_5(BPE)]^{2+}$ (500 nm in MeCN),[15] we deduce that a stronger metal–metal π interaction between Ru_a and Ru_b occurs through the pz bridge ($\Delta\nu = 3600\ cm^{-1}$) than through the 4,4′-bipy ($\Delta\nu = 2700\ cm^{-1}$)[8] and the BPE ($\Delta\nu = 1500\ cm^{-1}$) bridges.

In the mixed-valence complex **4**, a new and relatively intense and broad band appears at $\lambda_{max} = 832$ nm in MeCN ($\varepsilon_{max} = 797\ dm^3\ mol^{-1}\ cm^{-1}$, $\Delta\nu_{1/2} = 4540\ cm^{-1}$), which is securely assigned to the m.m.c.t. transition $Ru_b^{II} \rightarrow Ru_a^{III}$, since it is not present neither in the corresponding [II,II] nor in the [III,III] dinuclear species, as shown in Fig. 2, where we represent the spectrophotometric titration of the [II,II] ion (complex **3**) with added aliquots of Ce^{IV} in 1 M H^+. This m.m.c.t. band is shifted to the blue in DMF ($\lambda_{max} = 686$ nm, $\varepsilon_{max} = 304\ dm^3\ mol^{-1}\ cm^{-1}$, $\Delta\nu_{1/2} = 6480\ cm^{-1}$), indicating a correlation of the absorption maximum with the solvent donor number, as already known for similar asymmetric mixed-valence species of Ru.[16]

For the mixed-valence ion **6**, it is not possible to observe clearly the m.m.c.t. band in MeCN, probably because it is masked under the strong m.l.c.t. bands. In $MeNO_2$, however, as shown in Fig. 3, a shoulder is observed at $\lambda_{max} = 575$ nm, with $\varepsilon_{max} = 163\ dm^3\ mol^{-1}\ cm^{-1}$ and $\Delta\nu_{1/2} = 4956\ cm^{-1}$ (values obtained after gaussian deconvolution of ε/ν vs ν), which can be ascribed to the m.m.c.t. transition $Ru_b^{II} \rightarrow Ru_a^{III}$. Indeed, a new absorption feature, extending from 600 to 900 nm is observed in this dinuclear species, but not in the mononuclear complex $[Ru(terpy)(bipy)(BPE)]^{2+}$, whose spectrum in $MeNO_2$ is also included in Fig. 3.

Electrochemistry

Table 3 gives the results for the voltammetric studies of the mono- and di-nuclear complexes in MeCN, 0.1 M TBAH, $v = 200\ mV\ s^{-1}$ and $T = 22°C$. In complexes **1** and **2**, only one reversible oxidation wave is observed, corresponding to the $Ru_b^{3+/2+}$ couple. The values are similar to those of other $[Ru(terpy)(bipy)(L)]^{2+}$ (L = substituted pyridine) species.[7, 10, 17] As expected,[15] for the BPE-dimer (as well as for the $BPEH^+$-monomer), contrasting to the pz-dimer, electrostatic effects are small and the $E_{1/2}$ values are almost unchanged. The dinuclear complexes **3**–**6** present an additional reversible oxidation wave at 0.66 V for pz and 0.31 V for BPE, corresponding to the $Ru_a^{3+/2+}$ couples. These values compare reasonably well to the $E_{1/2}$ ($Ru^{3+/2+}$) values for the $[Ru(NH_3)_5(L)]^{2+}$ ions (0.55 V for pz, 0.37 V for BPE).[15] As already discussed before[15] for $[(NH_3)_5Ru\text{-}L\text{-}Ru(Cl)(bipy)_2]^{3+/4+}$ couples, there is a small increase when pz is the bridging ligand, but almost no changes when BPE is connecting both metals. The values for the $L^{0/-}$ couples are assigned, in decreasing order, to terpy, bipy and pz (or BPE) reductions.[8, 17]

Intramolecular electron transfer

The Marcus–Hush formalism can be applied to optical data of m.m.c.t. transitions in mixed-val-

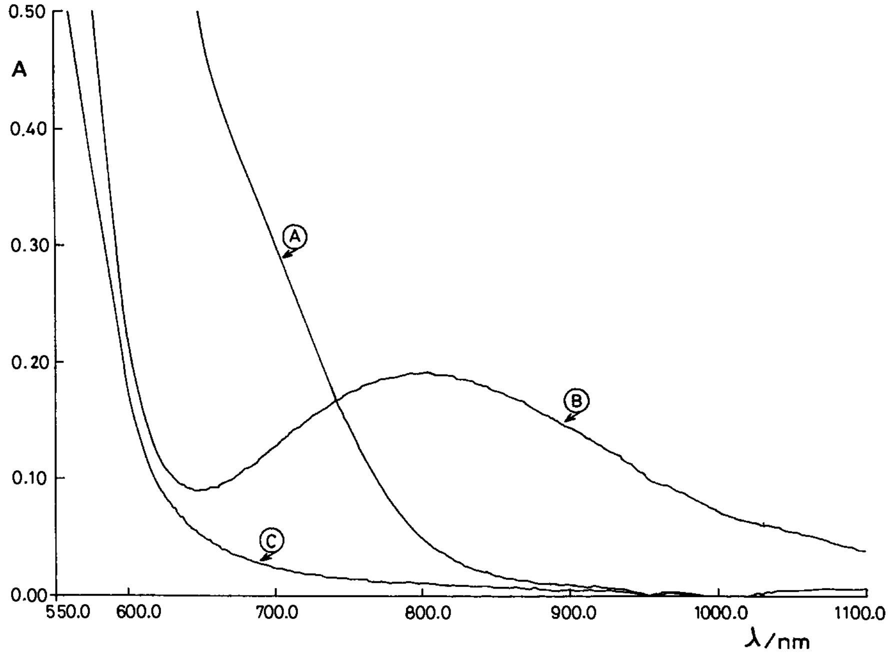

Fig. 2. Spectrophotometric titration of $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru}^{\mathrm{II}}(\mathrm{pz})\mathrm{Ru}^{\mathrm{II}}(\mathrm{NH_3})_5]^{4+}$ ($C = 2.88 \times 10^{-4}$ mol dm^{-3}) in aqueous solution with $\mathrm{Ce^{IV}}$ in 1 M $\mathrm{H^+}$. Molar ratios $[\mathrm{complex}]/[\mathrm{Ce^{IV}}]$ are: **A**, 1 : 0; **B**, 1 : 1; **C**, 1 : 2.

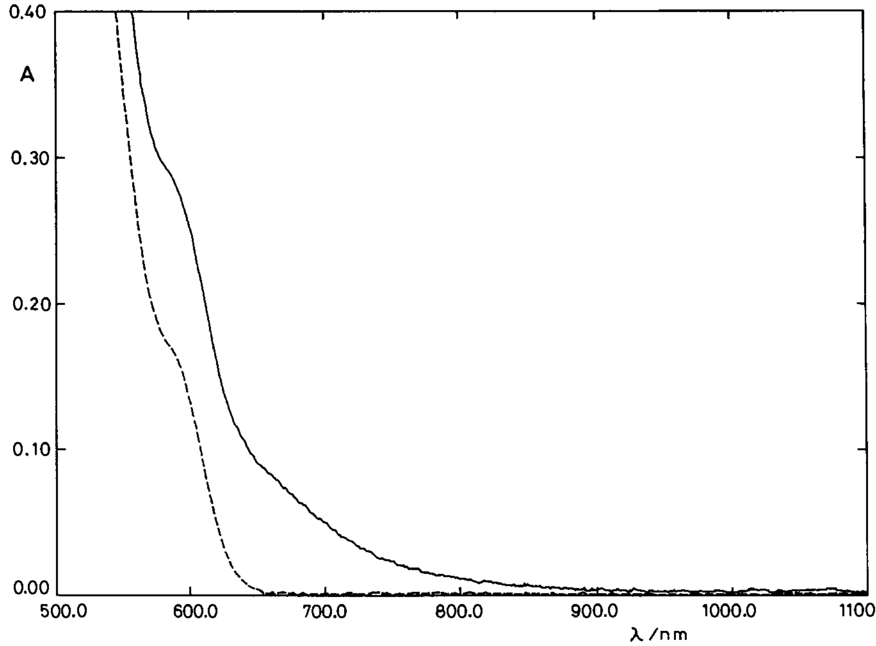

Fig. 3. Visible spectra in $\mathrm{MeNO_2}$ of: (—) $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru}^{\mathrm{II}}(\mathrm{BPE})\mathrm{Ru}^{\mathrm{III}}(\mathrm{NH_3})_5]^{5+}$ ($C = 1.88 \times 10^{-4}$ M), and (---) $[\mathrm{Ru}^{\mathrm{II}}(\mathrm{terpy})(\mathrm{bipy})(\mathrm{BPE})]^{2+}$ ($C = 3.3 \times 10^{-4}$ M).

ence complexes in order to determine parameters relevant to the corresponding thermal intramolecular electron transfer processes.[1] Table 4 shows values of E_{op}, the absorption maximum, $\Delta\nu_{1/2}$, the bandwidth at half-height (taken as twice the value obtained on the low-energy side) and $\varepsilon_{\max}$, the molar absorptivity of m.m.c.t. bands in the mixed-valence species $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru}^{\mathrm{II}}\text{-L-}\mathrm{Ru}^{\mathrm{III}}(\mathrm{NH_3})_5]^{5+}$ ($\mathrm{L} = \mathrm{CN}^-$, pz, 4-CNpy, 4,4′-bipy and BPE) in MeCN at 22°C. A range of metal-to-metal distances r of $\simeq 10$ Å is encompassed when going from $\mathrm{L} = \mathrm{CN}^-$ to L = BPE. Previously, for L = 4-

Table 3. Electrochemical potentials (vs SCE) at 22°C[a]

Complex	$E_{1/2}$(V) [ΔE_p (mV)][b]
1	+1.34 (75), −1.22 (60), −1.53 (120), −1.75 (160)
2	+1.29 (70), −1.33 (65), −1.62 (85), −1.80[c]
3–**4**	+1.48 (80), +0.66 (70), −1.29 (60), −1.68[c]
5–**6**	+1.20 (60), +0.31 (80), −1.41,[c] −1.74[c]
7	+1.22 (60), −1.21 (60), −1.46,[c] −1.62[c]

[a] In MeCN, 0.1 mol dm^{-3} TBAH, v = 200 mV s^{-1}.

[b] $E_{1/2} = (E_a + E_c)/2$, $\Delta E_p = E_a - E_c$, estimated error in $E_{1/2}$: ±0.01 V. Couples are considered reversible when ΔE_p = 60–80 mV.

[c] Irreversible; only the peak potential is informed.

CNpy,[7] the m.m.c.t. band could not be detected in dilute Br_2 solutions. We could now observe it by adding Br_2 vapour to a concentrated solution of the corresponding [II,II] ion, as shown in Fig. 4.

The electronic coupling element H_{AB} (A = donor, B = acceptor) between the donor Ru(terpy) (bipy)$^{2+}$ and the acceptor Ru(NH$_3$)$_5^{3+}$ moieties has been determined by using the following equation:[1]

$$H_{AB}\ (\mathrm{cm}^{-1}) = 2.06 \times 10^{-2}(\varepsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}(1/r) \tag{1}$$

with ν_{max} and $\Delta\nu_{1/2}$ in cm^{-1}, ε_{max} in dm^3 mol^{-1} cm^{-1} and r in Å. On the other hand, the reorganization energy for electron transfer λ is calculated as:[18]

$$\lambda = E_{op} - \Delta G^\circ - \Delta E_{ex} \tag{2}$$

where ΔG° is the free energy difference between both redox sites [obtained approximately[18] as the difference in redox potentials $\Delta E_{1/2} = E_{1/2}(\mathrm{Ru_b^{3+/2+}}) - E_{1/2}(\mathrm{Ru_a^{3+/2+}})$] and ΔE_{ex} is an excited-state energy difference, taken as 0.25 eV for ruthenium complexes.[18]

The delocalization parameter α^2 can be calculated as:[1]

$$\alpha^2 = (H_{AB}/\nu_{max})^2. \tag{3}$$

Experimental values of $\Delta\nu_{1/2}$ are ≃20% higher than those calculated by Hush formula:

$$\Delta\nu_{1/2}\ (\mathrm{cm}^{-1}) = [2310(\nu_{max} - \Delta G^\circ)]^{1/2} \tag{4}$$

as normally observed for partially delocalized mixed-valence species. This fact and the determined values of α^2 allow us to describe these systems as Robin and Day Class II.[1]

In covalently-linked donor–acceptor assemblies, the thermal first-order electron transfer rate constant can be expressed as:[19]

$$k\ (\mathrm{s}^{-1}) = \kappa_{el}\nu_n\kappa_n \tag{5}$$

where κ_{el} is the electronic transmission coefficient, ν_n is a nuclear vibration frequency and κ_n is the nuclear factor, which depends upon λ and ΔG° as follows:

$$\kappa_n = \exp(-\Delta G^*/RT) \tag{6}$$

$$\Delta G^* = [(\lambda + \Delta G^\circ)^2/4\lambda] - H_{AB}. \tag{7}$$

Figure 5 shows that the reorganization energy λ decreases with the inverse of the donor–acceptor separation, $(1/r)$, as expected by Marcus theory, if we take into account the distance dependence of the solvent (outer-sphere) reorganization barrier λ_{out}.[20] Moreover, the experimental slope (−7.1 eV Å) is very close to the theoretical one (−7.6 eV Å). If we consider that λ is the same for the reverse reaction $\mathrm{Ru_a^{II}} \rightarrow \mathrm{Ru_b^{III}}$, then, when $r > 9$ Å, the thermal reactions are essentially barrierless ($\Delta G^* \simeq 0$) and the dependence of the nuclear factor with r is small.[21]

Figure 6 shows the dependence of 2 ln H_{AB} on distance r. A slope of $\beta = 0.40$ Å^{-1} is obtained, which is intermediate between those values for polyene-bridged ruthenium ammines (0.20 Å^{-1})[22] and for polyproline-bridged ruthenium and osmium

Table 4. Optical and thermal m.m.c.t. parameters in [(terpy)(bipy)Ru^{II}-L-Ru^{III}(NH$_3$)$_5$]$^{5+}$ complexes, in MeCN, at 22°C

L	r (Å)	E_{op} (eV)	$\Delta\nu_{1/2}$ (cm^{-1})	ε_{max} (M^{-1} cm^{-1})	H_{AB} (cm^{-1})	ΔG° (eV)	λ (eV)	Ref.
CN$^-$	5.0	1.77	3600	2000	1300	1.19	0.33	6
pz	7.0	1.49	4540	807	614	0.82	0.42	t.w.
4-CNpy	9.3	1.81	6200	403	421	0.63	0.93	t.w.
4,4-bipy[a]	11.3	1.91	7826	266	325	0.86	0.80	8
BPE[b]	13.8	2.48	4956	163	189	0.89	1.34	t.w.

[a] Values of E_{op}, ε_{max} and $\Delta\nu_{1/2}$ were corrected with respect to Ref. 8 by gaussian deconvolution.

[b] Corrected by the effect of solvent donor number, as in Ref. 16.

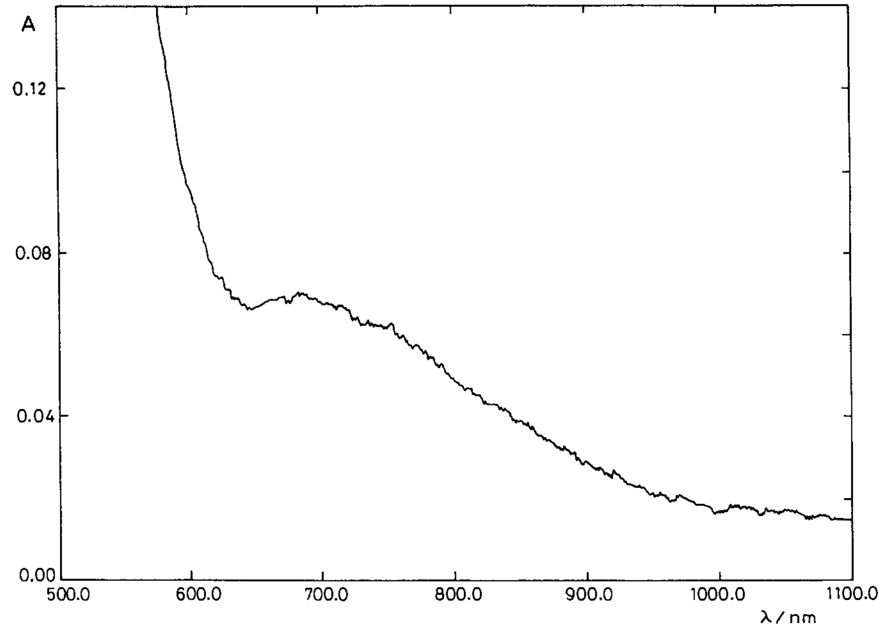

Fig. 4. Metal-to-metal charge transfer band in MeCN of $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru^{II}}\text{-}(4\text{-CNpy})\mathrm{Ru^{III}}(\mathrm{NH_3})_5]^{5+}$ ($C = 1.76 \times 10^{-4}$ M).

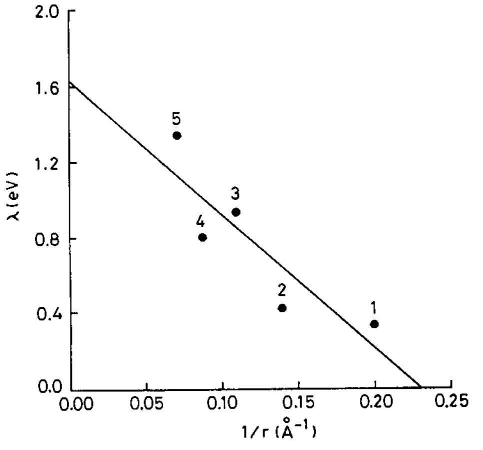

Fig. 5. Plot of the reorganization energy λ for the intramolecular electron transfer vs the inverse of the metal-to-metal distance, $(1/r)$, in $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru^{II}}\text{-L-}\mathrm{Ru^{III}}(\mathrm{NH_3})_5]^{5+}$ complexes. L: **1**, $\mathrm{CN^-}$; **2**, pz; **3**, 4-CNpy; **4**, 4,4′-bipy; **5**, BPE.

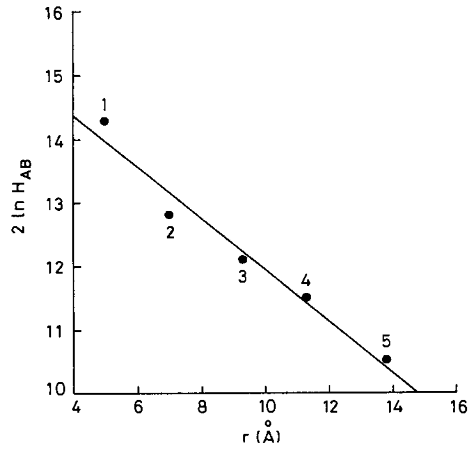

Fig. 6. Logarithmic plot of the square of the electronic coupling element H_{AB} vs metal-to-metal distance r in $[(\mathrm{terpy})(\mathrm{bipy})\mathrm{Ru^{II}}\text{-L-}\mathrm{Ru^{III}}(\mathrm{NH_3})_5]^{5+}$ complexes. L: **1**, $\mathrm{CN^-}$; **2**, pz; **3**, 4-CNpy, **4**, 4,4′-bipy; **5**, BPE.

ammines (0.60 Å^{-1}).[21] β is a measure of the attenuation with distance of the electronic overlap of donor and acceptor with the bridge.[23a,b] We then deduce that aromatic nitrogen heterocycles behave as electron π-mediators with intermediate properties between pure σ- and pure π-connectors between similar donors and acceptors. That the ligands used in this work do not behave as "molecular wires"—like the polyenes—can be adscribed to electron density being more delocalized over space.

Figure 7 shows a plot of ln $\varepsilon_{\max}$ for the m.m.c.t. transitions against r. The variations follow those observed in H_{AB}, with a lesser slope. According to the values of H_{AB}, the thermal reactions are considered adiabatic.[1] In this case, the distance dependence of the electronic factor is also small.[21] For $\mathrm{L = CN^-}$ and pz, however, the reverse processes $\mathrm{Ru_a^{II}} \rightarrow \mathrm{Ru_b^{II}}$ fall in the inverted regime ($\lambda < |\Delta G^\circ|$) and they are necessarily non-adiabatic.[20] In these two cases of relatively strong electronic coupling, solvent dynamics and quantization of vibrations become important.[24] Since in some cases, as already pointed out,[25] it is not possible to relate optical and thermal reactions in a simple way, we have not

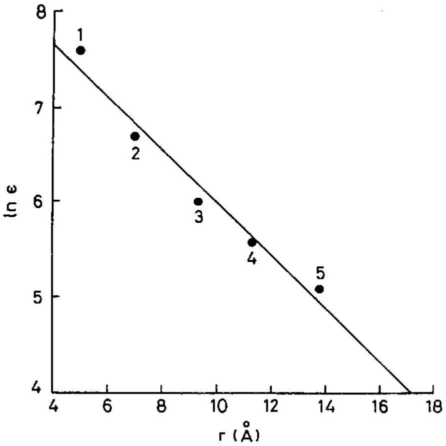

Fig. 7. Plot of the logarithm of the molar absorptivity ε_{max} of the m.m.c.t. bands vs metal-to-metal distance r in $[(terpy)(bipy)Ru^{II}\text{-}L\text{-}Ru^{III}(NH_3)_5]^{5+}$ complexes. L: **1**, CN^-; **2**, pz; **3**, 4-CNpy; **4**, 4,4′-bipy; **5**, BPE.

attempted to calculate the thermal rate constants for the back reactions with the semi-classical formalism. Besides, one must consider that electronic couplings H_{AB} of optical electron transfers may differ from those of thermal electron transfers,[26] and that they may be underestimated with the Marcus–Hush formalism.[27] Anyway, one can predict, as a main contribution of this analysis, that at separation distances where the coupling element is not so high as in CN^- or pz, a higher asymmetry of the redox sites could eventually lead to slow charge recombination (Marcus "inverted" behaviour) after light excitation. Work is in progress to prove this assertion.

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REFERENCES

1. C. Creutz, *Prog. Inorg. Chem.* 1983, **30**, 1.
2. N. S. Hush, *Coord. Chem. Rev.* 1985, **64**, 135.
3. S. S. Isied, M. Y. Ogawa and J. F. Wishart, *Chem. Rev.* 1992, **92**, 381.
4. T. J. Meyer, *Acc. Chem. Res.* 1989, **22**, 163.
5. J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. DeCola, L. Flamigni and V. Balzani, *Inorg. Chem.* 1991, **30**, 4230.
6. A. Ben Altabef, S. B. Ribotta de Gallo, M. E. Folquer and N. E. Katz, *Transition Met. Chem.* 1993, **18**, 319.
7. A. Ben Altabef, S. B. Ribotta de Gallo, M. E. Folquer and N. E. Katz, *Inorg. Chim. Acta* 1991, **188**, 67.
8. (a) F. Fagalde and N. E. Katz, *J. Chem. Soc., Dalton Trans.* 1993, 571; (b) D. J. Szalda, F. Fagalde and N. E. Katz, unpublished data.
9. J. D. Petersen, L. W. Morgan, I. Hsu, M. A. Billadeau and S. E. Ronco, *Coord. Chem. Rev.* 1991, **111**, 319.
10. J. M. Calvert, R. H. Schmehl, B. P. Sullivan, J. S. Facci, T. J. Meyer and R. W. Murray, *Inorg. Chem.* 1983, **22**, 2151.
11. J. E. Sutton and H. Taube, *Inorg. Chem.* 1981, **20**, 3125.
12. M. J. Powers, R. W. Callahan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.* 1976, **15**, 894.
13. D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.* 1972, **94**, 2583.
14. C. R. Johnson and R. E. Shepherd, *Inorg. Chem.* 1983, **22**, 1117.
15. R. W. Callahan, G. M. Brown and T. J. Meyer, *Inorg. Chem.* 1975, **14**, 1443.
16. J. P. Chang, E. Y. Fung and J. C. Curtis, *Inorg. Chem.* 1986, **25**, 4233.
17. R. M. Berger and D. R. McMillin, *Inorg. Chem.* 1988, **27**, 4245.
18. N. E. Katz, C. Creutz and N. Sutin, *Inorg. Chem.* 1988, **27**, 1687.
19. N. Sutin, B. S. Brunschwig, C. Creutz and J. Winkler, *Pure Appl. Chem.* 1988, **60**, 1817.
20. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* 1985, **811**, 265.
21. N. Sutin, *Adv. Chem. Series* 1991, **228**, 25.
22. S. Woitellier, J. P. Launay and C. W. Sprangler, *Inorg. Chem.* 1989, **28**, 758.
23. (a) P. Siddarth and R. A. Marcus, *J. Phys. Chem.* 1990, **94**, 2985; (b) M. D. Newton, *Chem. Rev.* 1991, **91**, 767.
24. D. A. V. Kliner, K. Tominaga, G. C. Walker and P. F. Barbara, *J. Am. Chem. Soc.* 1992, **114**, 8323.
25. J. T. Hupp, G. A. Neyhart, T. J. Meyer and E. M. Kober, *J. Phys. Chem.* 1992, **96**, 10820.
26. M. H. Chou, C. Creutz and N. Sutin, *Inorg. Chem.* 1992, **31**, 2318.
27. J. T. Hupp, Y. Dong, R. L. Blackbourn and H. Lu, *J. Phys. Chem.* 1993, **97**, 3278.