

Increasing transmission of electronic interaction in dinuclear unsymmetric mixed-valent ruthenium complexes

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Abstract

The preparation and characterization by spectroscopic and electrochemical techniques of new dinuclear complexes of the type [(tpm)(bpy)Ru^{II}(L)Ru^{II/III}(NH₃)₅]^{4+/5+} (bpy = 2,2'-bipyridine), tpm = tris(1-pyrazolyl)methane, L = pz (pyrazine), 4,4'-bpy (4,4'-bipyridine), BPE (*trans*-1,2-bis(4-pyridyl)ethylene) and PCA (= 4-pyridinecarboxaldehyde azine), are described in this work. The analysis of the visible spectral data for the metal-to-metal charge transfer (MMCT) bands in the corresponding mixed-valent species [Ru^{II}_b, Ru^{III}_a] (Ru_b = Ru bonded to bpy; Ru_a = Ru bonded to NH₃) allows the determination of the reorganization energies λ and electronic coupling elements H_{AB} for the intramolecular electron transfers Ru^{II}_b → Ru^{III}_a mediated by L. An increased transmission of the metal-to-metal electronic interaction is disclosed for this series, when comparing the distance dependence of H_{AB} to that of the analogous series with trpy (2,2':6',2''-terpyridine) acting as a spectator ligand instead of tpm.

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1. Introduction

The distance dependence of intramolecular electron transfer parameters in mixed-valence complexes is an important issue in connection to artificial photosynthesis [1]. The magnitude and the mechanism of the donor–acceptor electronic interactions can be tuned by changing the bridge and/or the co-ligands [2].

We have recently described the syntheses and spectroscopic, electrochemical and photophysical properties of mononuclear complexes of the type [Ru(bpy)(L)(tpm)]²⁺, with bpy = 2,2'-bipyridine, tpm = tris(1-pyrazolyl)methane, L = pz (pyrazine), 4,4'-bpy (4,4'-bipyridine) and

BPE (*trans*-1,2-bis(4-pyridyl)ethylene) [3]. These species have now been used as building blocks for new unsymmetric ruthenium complexes of formulae [(tpm)(bpy)Ru^{II}(L)-Ru^{II}(NH₃)₅]⁴⁺, with L = pz (1), 4,4'-bpy (2), BPE (3) and PCA (8), and [(tpm)(bpy)Ru^{II}(L)Ru^{III}(NH₃)₅]⁵⁺, with L = pz (4), 4,4'-bpy (5), BPE (6) and PCA (9), on which a few preliminary results were reported [3]. The additional bridging ligand PCA (4-pyridinecarboxaldehyde azine) has also been included for comparison purposes [4]. Besides, the new mononuclear complex [Ru(bpy)(PCA)(tpm)]²⁺ (7), has been synthesized and characterized. The main objective in this work is the determination of the influence of metal–metal distance on the reorganization energies and electronic coupling elements for the L-mediated intramolecular electron transfers in the mixed-valent species [Ru^{II}_b, Ru^{III}_a] (where Ru_b = Ru bonded to bpy; Ru_a = Ru bonded to NH₃).

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In a previous work [5], we have studied the series $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{II/III}}(\text{NH}_3)_5]^{4+/5+}$, with, $\text{trpy} = 2,2':6',2''\text{-terpyridine}$, $\text{L} = \text{pz}$, $4,4'\text{-bpy}$ and BPE . In this work, we report the syntheses and characterization by spectroscopic and electrochemical techniques of the analogous tpm complexes, in order to establish the degree of influence of ligand electronic properties and geometry when going from a meridional (trpy) to a facial (tpm) coordination. Scheme 1 shows the structures of the ligands used in this work and Scheme 2 shows the structure of complex **2** as a representative example.

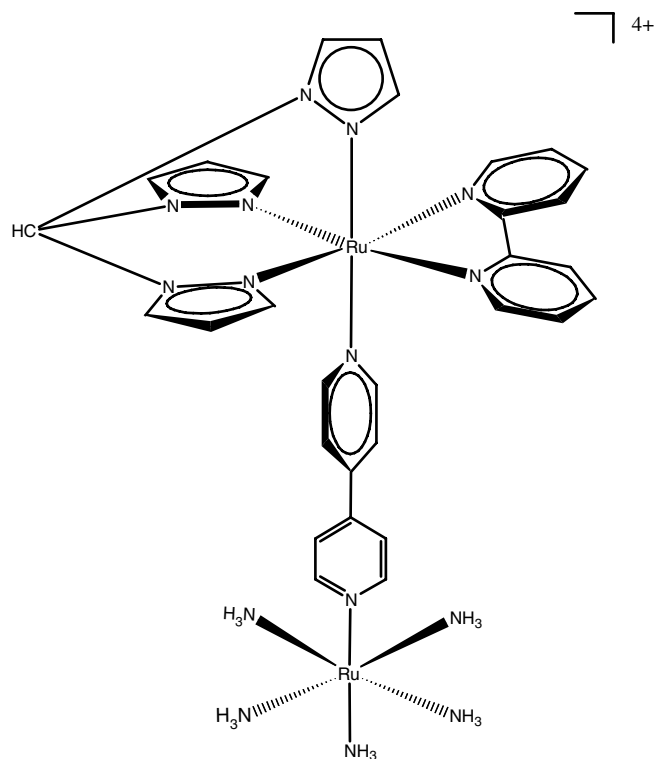
2. Experimental

2.1. Preparations

All synthetic manipulations were routinely performed under a nitrogen atmosphere using Schlenk tubes and vacuum line techniques. Electrochemical experiments were performed in the dark under a N_2 or Ar atmosphere with degassed solvents.

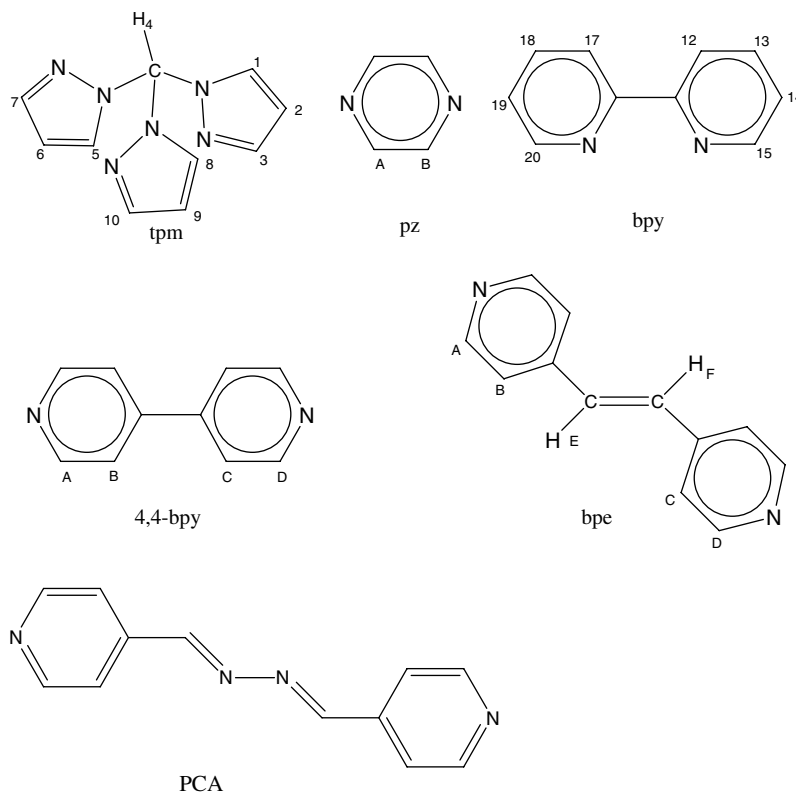
2.2. Syntheses

Complexes of formulae $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{II}}(\text{NH}_3)_5](\text{PF}_6)_4$ (with $\text{L} = \text{pz}$ (**1**), $4,4'\text{-bpy}$ (**2**), BPE (**3**) and PCA (**8**)) have been prepared by the following technique: 0.2 g of $[\text{Ru}(\text{tpm})(\text{bpy})(\text{L})](\text{PF}_6)_2$, prepared as in Ref. [3], or by refluxing for 2 h $[\text{Ru}(\text{tpm})(\text{bpy})(\text{H}_2\text{O})](\text{PF}_6)_2$ with



Scheme 2. Structure of complex **2**.

an excess of L in MeOH , were mixed with an equimolar amount of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$, obtained as in Ref. [5], in 10 mL of acetone, under Ar in the dark and using



Scheme 1. Structure of the ligands.

Schlenk techniques. After stirring the mixture for 4 h at room temperature, the desired complexes were precipitated with 50 mL of ether, filtered, washed with ether and dried under vacuo over P₄O₁₀. Purification was achieved by chromatography in Sephadex LH-20. Yields were between 70% and 80%. Elution of the dinuclear species were performed with CH₃CN. After rotoevaporating to complete dryness, samples were re-precipitated from acetone/ether.

2.2.1. [(tpm)(bpy)Ru(pz)Ru(NH₃)₅](PF₆)₄ · 0.5(CH₃)₂CO (1)

Anal. Calc. for C_{25.5}H₄₀F₂₄N₁₅O_{0.5}P₄Ru₂ (1346.7): C, 22.7; H, 3.0; N, 15.6. Found: C, 22.5; H 2.9; N 15.7%.

2.2.2. [(tpm)(bpy)Ru(4,4'-bpy)Ru(NH₃)₅](PF₆)₄ · (CH₃)₂CO (2)

Anal. Calc. for C₃₃H₄₇F₂₄N₁₅OP₄Ru₂ (1451.8): C, 27.3; H, 3.3; N 14.5. Found: C, 27.3; H 3.1; N 14.9%. ¹H NMR (500 MHz, CD₃CN, 25 °C): δ, 6.31 (dd, 1, J_{9–10} = 3.0 Hz, J_{9–8} = 2.2 Hz, H₉), 6.59 (d, 1, J_{9–10} = 2.2 Hz, H₁₀), 6.78 (dd, 1, J_{2–1} = 2.1 Hz, J_{2–3} = 3.0 Hz H₂), 7.50 (d, 2, J_{C–D} = 6.8 Hz, H_C), 7.54 (o, 2, H_B), 7.55 (o, 2, H_A), 7.57 (dd, 2, J_{13–14} = 8.8 Hz, J_{15–14} = 6.0 Hz, H₁₄), 7.95 (d, 2, J_{3–2} = 2.1 Hz, H₃), 8.23 (dd, 2, J_{12–14} = 8.8 Hz, J_{12–13} = 8.1 Hz, H₁₃), 8.38 (d, 1, J_{8–9} = 3.0 Hz H₈), 8.51 (d, 2, J_{D–C} = 6.8 Hz, H_D), 8.57 (d, 2, J_{1–2} = 3.0 Hz, H₁), 8.67 (d, 2, J_{15–14} = 6.0 Hz, H₁₅), 8.79 (d, 2, J_{12–13} = 8.1 Hz, H₁₂), 9.06 (s, 1, H₄) ppm. ¹³C NMR (500 MHz CD₃CN, 25 °C): δ, 75.9 (C₄), 108.7 (C₉), 110 (C₂), 120.7 (C_B) 121.4 (C_C), 125.1 (C₁₂), 126.5 (C₁₄), 135.6 (C₈), 135.9 (C₁), 137.8 (C₁₃), 144.1 (C₁₀), 147.4 (C₃, C_D), 152.8 (C₁₅), 154.1 (C_A) ppm.

2.2.3. [(tpm)(bpy)Ru(BPE)Ru(NH₃)₅](PF₆)₄ · (CH₃)₂CO (3)

Anal. Calc. for C₃₅H₄₉F₂₄N₁₅OP₄Ru₂ (1477.9): C, 28.5; H, 3.3; N 14.2. Found: C, 28.6; H 3.1; N, 15.0%. ¹H NMR (500 MHz, CD₃CN, 25 °C): δ, 6.30 (dd, 1, J_{9–8} = 2.8 Hz, J_{9–10} = 2.0 Hz H₉), 6.58 (dd, 1, J_{9–10} = 2.0 Hz, J_{10–8} = 2.8 Hz H₁₀), 6.77 (dd, 2, J_{2–3} = 2.0 Hz J_{2–1} = 2.6 Hz H₂), 7.27 (d, 2, J_{B–A} = 6.75 Hz H_B), 7.35(d overlapped, 1, H_E), 7.39 (d overlapped, 1, H_F), 7.43 (d, 2, J_{B–A} = 6.75 Hz H_A), 7.47 (d, 2, J_{C–D} = 6.0 Hz, H_C), 7.54 (dd, 2, J_{14–15} = 5.7 Hz, J_{14–13} = 7.8 Hz, H₁₄), 7.96 (d, 2, J_{2–3} = 2.0 Hz H₃), 8.21 (dd, 2, J_{14–13} = 7.8 Hz, J_{12–13} = 8.2 Hz, H₁₃), 8.37 (t, 1, J_{9–8} = 2.8 Hz, H₈), 8.55 (d 2.6 Hz, 2, H₁), 8.59 (d, 2, J_{C–D} = 6.0 Hz, H_D), 8.65 (d, 2, J_{14–15} = 5.7 Hz, H₁₅), 8.76 (d, 2, J_{12–13} = 8.2 Hz H₁₂), 9.02 (s, 1, H₄) ppm. ¹³C NMR (500 MHz, CD₃CN, 25 °C): δ, 76.0 (C₄), 108.7 (C₉), 110.0 (C₂), 122.1 (C_B), 125 (C₁₂), 126.4 (C₁₄), 128.0 (C₁₂), 128.7 (C_{E,F}), 135.7 (C₈), 135.8 (C₁), 138 (C₁₃), 143.8 (C₁₀), 147.3 (C₃), 150.7 (C_D), 152.9 (C₁₅), 153.3 (C_A) ppm.

The mixed-valent species [(tpm)(bpy)Ru^{II}(L)Ru^{III}-(NH₃)₅]⁵⁺ (L = pz (4), 4,4'-bpy (5), and BPE (6)) were generated *in situ* by adding Br₂ vapour to an acetonitrile solution of (1), (2) and (3), respectively, or by bulk electrolysis at 0.5–0.8 V in CH₃CN, 0.1 M TBAH.

2.2.4. [(tpm)(bpy)Ru(PCA)](PF₆)₂ · 4H₂O (7)

Anal. Calc. for C₃₂H₃₆F₁₂N₁₂O₄P₂Ru (1043.7): C, 36.8; H, 3.5; N 16.1. Found: C, 36.9; H, 3.0; N 15.4%.

The corresponding dinuclear complexes [(tpm)(bpy)-Ru^{II}(PCA)Ru^{II}(NH₃)₅]⁴⁺ (8) and [(tpm)(bpy)Ru^{II}(PCA)-Ru^{III}(NH₃)₅]⁵⁺ (9) were obtained and characterized in solution by procedures similar to those already described for the other complexes.

2.3. Equipments and techniques

All used chemicals were reagent grade. CH₃CN was freshly distilled for electrochemical measurements. UV–Vis spectra were recorded with Shimadzu UV-160A and Cary 50 spectrophotometers. IR spectra were performed on a Perkin–Elmer 983G spectrophotometer. Cyclic voltammetry experiments were carried out in CH₃CN, using a BAS Epsilon EC equipment, with Ag/AgCl (3 M KCl) as reference electrode, vitreous C as working electrode, Pt wire as auxiliary electrode and 0.1 M TBAH [tetrakis-(*n*-butyl)ammonium hexafluorophosphate] as supporting electrolyte. A special OTTLE cell designed by BAS was used for the spectroelectrochemical measurements. All NMR data were recorded in CD₃CN with a Bruker 500 MHz spectrometer. 2D COSY, 2D HSQC and 2D NOESY (mixing time 500 ms) experiments were collected in routine conditions. Chemical Analyses were carried out at INQUIMAE, UBA, Argentina, with an estimated error of ±0.5%.

3. Results and discussion

3.1. Synthesis and IR spectra

All dinuclear complexes of the type [(tpm)(bpy)Ru(L)-Ru(NH₃)₅](PF₆)₄ (with L = pz, 4,4'-bpy, BPE and PCA) were prepared by mixing stoichiometric amounts of [Ru(tpm)(L)(bpy)](PF₆)₂ and [Ru(NH₃)₅(H₂O)](PF₆)₂ in acetone under Ar for 2 h, with subsequent purification by standard chromatographic techniques, as described in the experimental section. The mixed-valent species were synthesized *in situ* by adding excess of bromine to CH₃CN solutions of the reduced complexes, since the redox potential of the Br₂/Br₂[−] couple is higher than that of the Ru^{III}_b/Ru^{II}_a couple but lower than that of the Ru^{III}_a/Ru^{II}_b couple (*vide infra*) [6].

IR spectra (as KBr pelletes) of 1, 2, and 3 show characteristic ligand vibrations between 1600 and 600 cm^{−1}. The typical ammonia symmetric deformation frequencies δ_{sym}(NH₃) appear in these complexes at 1287, 1286 and 1286 cm^{−1}, respectively, indicating oxidation

states (II) for all ruthenium atoms bonded to amines (= Ru_a) [5].

3.2. NMR spectra

Fig. 1 shows the ¹H NMR spectrum of [(tpm)(bpy)Ru^{II}-(BPE)Ru^{II}(NH₃)₅]⁴⁺ in CD₃CN at 500 MHz, as a representative example. NMR chemical shifts are closely related to those reported [3] for the mononuclear species of the type [Ru(tpm)(L)(bpy)]²⁺, confirming the molecular symmetry of the complexes and the relative position of each coordinating position of all N-containing ligands around the first Ru center. The effect of the additional Ru(NH₃)₅ moiety has minor effects on chemical shift values. All NMR data have been confirmed and fully assigned by using 2D COSY, HSQC and NOESY experiments.

3.3. Redox properties

The electrochemical measurements in CH₃CN (0.1 M TBAH) for complexes **1**, **2** and **3** show in the oxidative range of potentials two reversible redox waves that can be assigned to the couples Ru_b^{III}/Ru_b^{II} ($E_{1/2}$ = 1.30, 1.21 and 1.19 V, versus SCE, for the species bridged by pz, 4,4'-bpy and BPE, respectively) and Ru_a^{III}/Ru_a^{II} ($E_{1/2}$ = 0.46, 0.35 and 0.35 V, versus SCE, for the same species, respectively). The redox potentials for the Ru_b^{III}/Ru_b^{II} couples decrease in the order pz > 4,4'-bpy > BPE, evidencing the decreasing order of π -backbonding effects from Ru_b to the L ligands, as demonstrated before for the corresponding mononuclear precursors [Ru(tpm)(L)(bpy)]²⁺ ($E_{1/2}$ = 1.20, 1.15 and 1.10 V, versus SCE, for L = pz, 4,4'-bpy and BPE, respectively) [3]. The higher values obtained here for the dinuclear species can be attributed to their higher charges. On the other hand, the values of the redox potentials for the Ru_a^{III}/Ru_a^{II} couples are consistent with those already obtained in the analogous [(trpy)(bpy)Ru^{II}(L)-Ru^{II/III}(NH₃)₅]^{4+/5+} series ($E_{1/2}$ = 0.66, 0.39 and 0.31 V, versus SCE, for L = pz, 4,4'-bpy and BPE, respectively) [5]. When comparing these values to those of the mono-

nuclear complexes [Ru(NH₃)₅(L)]²⁺, a small increase in $E_{1/2}$ is observed when pz is the bridging ligand, but almost no changes are detected when BPE is the bridging ligand [5]. Complex **8** (with PCA as a bridging ligand) exhibits values of $E_{1/2}$ at 1.21 and 0.41 V, versus SCE, for the Ru_b^{III}/Ru_b^{II} and Ru_a^{III}/Ru_a^{II} couples, respectively, indicating electronic π -backbonding effects intermediate between those of pz and 4,4'-bpy. Fig. 2 shows the CV of complex **8**, as a representative example of this series.

3.4. UV-Vis spectra

Fig. 3 shows the UV-Vis spectrum of complex **3** in CH₃CN, as a representative example.

Table 1 shows the UV-Vis absorption spectral data of complexes **1**, **2**, **3** and **8** in CH₃CN. The bands observed between 200 and 300 nm can be assigned to intraligand $\pi \rightarrow \pi^*$ absorptions [3,5]. The bands at λ_{\max} = 397, 416, 420 and 444 nm (corresponding to L = pz, 4,4'-bpy, BPE and PCA, respectively) are readily assigned to MLCT (metal-to-ligand charge transfer) transitions $d_{\pi}(\text{Ru}_b) \rightarrow \pi^*(\text{bpy})$ of lowest energy, since these values are similar to those obtained for the mononuclear species [Ru(tpm)(L)(bpy)]²⁺ (λ_{\max} = 392, 395, 410 and 430 nm, corresponding to L = pz, 4,4'-bpy, BPE and PCA, respectively) [3]. The bands at λ_{\max} = 510, 514, 523 and 545 nm (for L = pz, 4,4'-bpy, BPE and PCA, respectively), which disappear upon addition of Br₂ vapour, can be assigned to MLCT transitions $d_{\pi}(\text{Ru}_a) \rightarrow \pi^*(\text{L})$. These latter bands, as the former ones, are shifted to lower energies than the corresponding ones in [Ru(NH₃)₅L]²⁺ complexes (λ_{\max} = 455, 470, 500 and 536 nm for pz, 4,4'-bpy, BPE and PCA, respectively) [4,7], indicating a considerable decrease in the energies of the $d-\pi^*$ excited states when connecting a second metallic center to the free N of the bridging ligand.

In the mixed-valent species **4**, **5**, **6** and **9**, the lowest energy bands of **1**, **2**, **3** and **8** disappear completely and new bands appear at 790, 680, 674 and 630 nm (values determined by gaussian deconvolution) for L = pz, 4,4'-bpy, BPE and PCA, respectively, due to MMCT

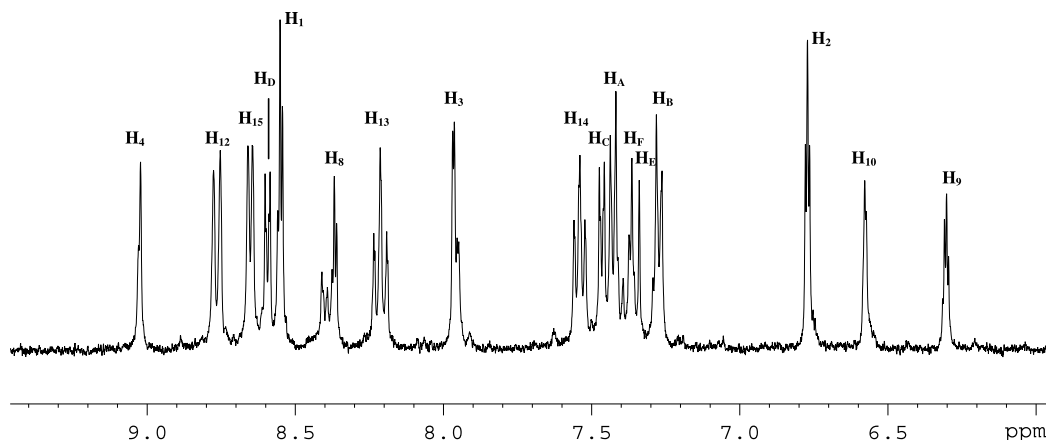


Fig. 1. ¹H NMR spectrum of [(tpm)(bpy)Ru^{II}(BPE)Ru^{II}(NH₃)₅]⁴⁺, in CD₃CN, at 500 MHz.

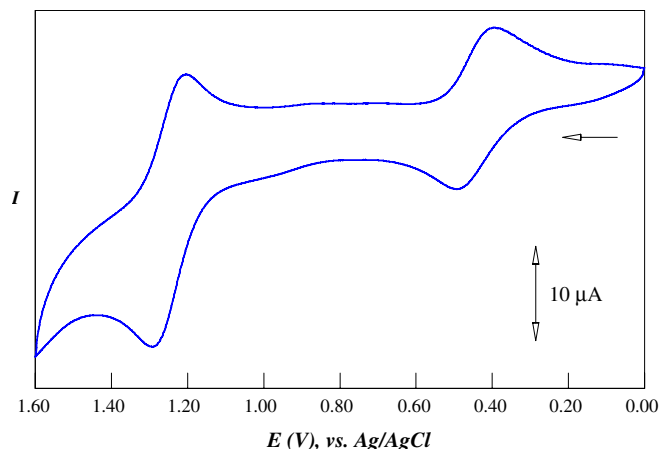


Fig. 2. Cyclic voltammogram of $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{PCA})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, in CH_3CN , 0.1 M TBAH, $v = 100 \text{ mV s}^{-1}$.

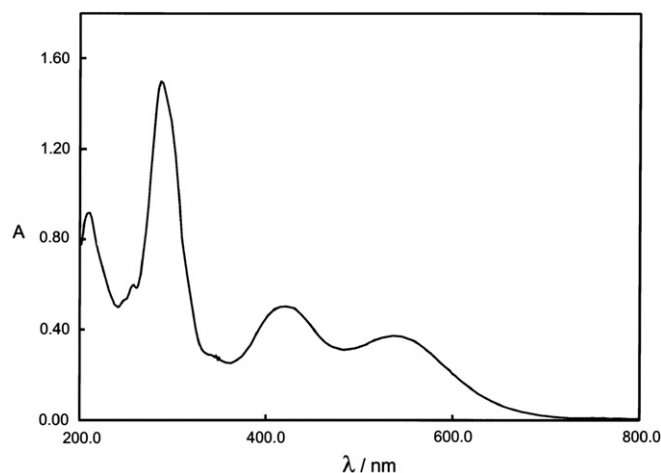


Fig. 3. UV-Vis spectra of $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{BPE})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, in CH_3CN , at room temperature ($C = 2.8 \times 10^{-5} \text{ M}$).

Table 1

Electronic spectral data in CH_3CN at 22°C of complexes of the type: $[(\text{tpm})(\text{bpy})\text{Ru}(\text{L})\text{Ru}(\text{NH}_3)_5]^{4+}$

L	Complex	λ_{max} (nm)	$(\epsilon_{\text{max}} \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1})$
pz	1	510 (14.0), 397 (10.6), 338 (sh), 284 (31.1), 224 (18.9)	
4,4'-bpy	2	508 (17.8), 416 (15.0), 337 (sh), 286 (33.6), 245 (30.4)	
BPE	3	534 (13.3), 420 (17.9), 343 (sh), 288 (53.2), 209 (32.5)	
PCA ^a	8	545 (10.1), 444 (10.4), 330 (sh), 285 (36.0), 256 (23.0)	

^a Values of ϵ_{max} are estimated by comparison with the UV bands of the mononuclear species **7**.

(metal-to-metal charge transfer) transitions $[\text{Ru}_b^{\text{II}} \rightarrow \text{Ru}_a^{\text{III}}]$. As a representative example, Fig. 4 shows the spectrum of **6** obtained after adding Br_2 vapour to a concentrated solution of **3** in CH_3CN . This assignment is confirmed by the detection of MMCT bands in similar ranges of the related complexes $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ and $\{(\text{bpy})_2\text{Ru}^{\text{II}}[(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]_2\}^{8+}$, with $\text{L} = \text{CN}^-$, pz, 4-CNpy, 4,4'-bpy and BPE [5,8]. Controlled potential electrolyses at 0.5–0.8 V for the three complexes showed identical

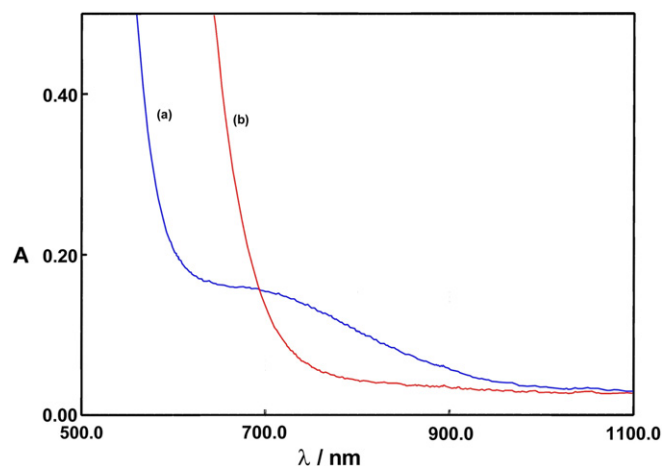


Fig. 4. UV-Vis spectra of: (a), $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{BPE})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ and (b), $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{BPE})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, in CH_3CN , at room temperature ($C = 2.8 \times 10^{-4} \text{ M}$). (a) was obtained from (b) by oxidation with bromine vapour.

results, as shown in Fig. 5, where the spectra of complexes **2** and **5** (the latter one obtained by electrolysis of **2**) are compared. These oxidation processes are reversible in a longer time-scale (*ca.* 1 h).

3.5. Intramolecular electron transfer parameters

Using the Marcus–Hush formalism [9,10] and the experimental spectral data of the MMCT bands in the mixed-valent species, the reorganization energy (λ) for the intramolecular electron transfer through the bridging ligand L and the electronic coupling element between both metal centers (H_{AB}) can be calculated as follows:

$$\lambda = E_{\text{op}} - \Delta G^0 - \Delta E_{\text{ex}} \quad (1)$$

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

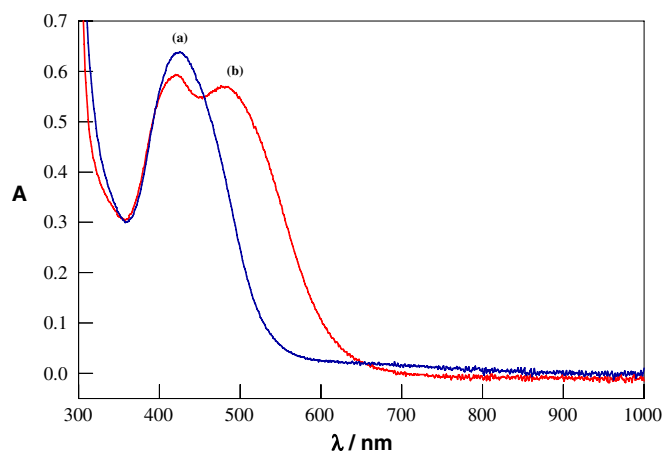


Fig. 5. UV-Vis spectra of: (a), $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ and (b), $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, in CH_3CN , 0.1 M TBAH, at room temperature ($C = 3.8 \times 10^{-5} \text{ M}$). (a) was obtained from (b) by electrolysis at $V = 0.5 \text{ V}$.

where E_{op} is the energy of the absorption maximum (in eV), ΔG° is the free energy difference between both redox sites (approximated as the difference in the redox potentials $\Delta E_{1/2}$) and ΔE_{exc} is an excited-state energy difference, estimated as 0.25 eV [8]. ε_{max} is the absorption coefficient of the MMCT band, $\tilde{\nu}_{\text{max}}$ is the energy maximum of the same band (in cm^{-1}), $\Delta\tilde{\nu}_{1/2}$ is the bandwidth at half-height, and r is the metal–metal distance in Å [10].

Table 2 shows the obtained values for these parameters in the series of mixed-valent complexes **4**, **5**, **6** and **9**.

For all these mixed-valent species, the values of $H_{\text{AB}} \ll \lambda$; therefore, they can be classified as belonging to Class II according to Robin and Day nomenclature [10]. The reorganization energy λ increases with r in going from pz to PCA, as predicted by Marcus theory [11]. Moreover, this increment is reflected in the increasing values of E_{op} with r , as recently reported in unsymmetric mixed-valent $\text{Co}^{\text{III}}\text{--Fe}^{\text{II}}$ complexes [12]. For $L = \text{pz}$ and 4,4'-bpy, the reverse intramolecular electron transfers $\text{Ru}_{\text{a}}^{\text{II}} \rightarrow \text{Ru}_{\text{b}}^{\text{III}}$ are predicted to be in the Marcus inverted region, since $\lambda < -\Delta G^\circ$, while for $L = \text{BPE}$, the analogous charge recombination falls almost in the barrierless region ($\lambda \cong -\Delta G^\circ$). This trend is similar to that found for the corresponding species with trpy [5]. In the case of $L = \text{PCA}$, this charge recombination falls in the normal region, since $\lambda > -\Delta G^\circ$.

The electronic coupling H_{AB} decreases with increasing metal-to-metal distance, as expected from Marcus theory [11], but the obtained values are higher than those found in the trpy complexes by an average factor of *ca.* 1.3 [5]; for example, the value of H_{AB} is 750 cm^{-1} for $[(\text{tpm})\text{-(bpy)}\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ and 614 cm^{-1} for $[(\text{trpy})(\text{bpy})\text{-Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$, pointing to a stronger electronic communication in the tpm series. Moreover, as shown in Fig. 6, the distance dependence is less steeper: a value of $\beta = 0.3 \text{ \AA}^{-1}$ is obtained (where β is the slope of $2\ln H_{\text{AB}}$ versus r), when considering the four ligands, which is 25% lower than the value determined for the series of the trpy complexes ($\beta = 0.4 \text{ \AA}^{-1}$) [5].

As stated before [13], the value of β determines the attenuation with distance of the electronic overlap between both metallic centers with the bridging ligand. Pure σ -connectors, such as polyprolines acting as bridges in ruthenium amines [14], have a slope $\beta = 0.6 \text{ \AA}^{-1}$. Pure π -connectors, such as polyenes acting as bridges in ruthenium amines [15], have a slope $\beta = 0.2 \text{ \AA}^{-1}$. Since the value of β obtained in this work is much closer to that of the pure π -connectors, we deduce that the facial geom-

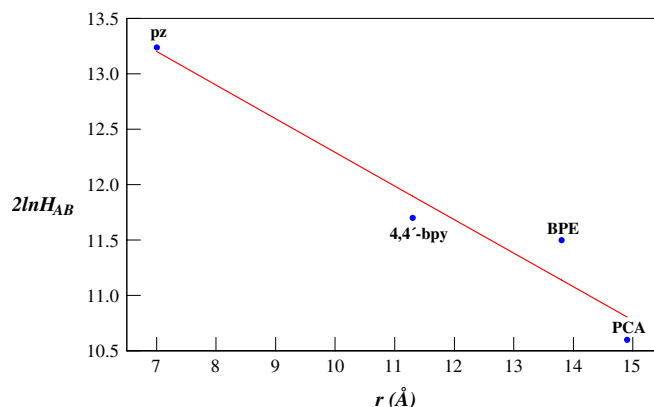


Fig. 6. Plot of $2\ln H_{\text{AB}}$ vs. r for the four mixed-valent species $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$, in CH_3CN ($L = \text{pz}$, 4,4'-bpy, BPE and PCA).

etry and poor π -acceptor character of tpm induce a better transmission of the metal-to-metal electronic interaction in these complexes. Connecting at least three metal centers may eventually lead to a molecular-wire behaviour [16].

4. Conclusions

We conclude that the distance dependence of the reorganization energies and the electronic coupling elements in the new mixed-valent unsymmetric complexes prepared and characterized in this work point to a stronger electronic communication between both metallic centers than in the analogous complexes with trpy. Moreover, an increased transmission of the electronic interaction is induced in these complexes by using tpm instead of trpy as a spectator ligand.

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Table 2

Intramolecular electron transfer parameters in the series of mixed-valent complexes of the type $[(\text{tpm})(\text{bpy})\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$

L	Complex	r (Å)	E_{op} (eV)	ΔG° (eV)	λ (eV)	H_{AB} (cm^{-1})
pz	4	7.0	1.62	0.84	0.53	750
4,4'-bpy	5	11.3	1.82	0.86	0.71	350
BPE	6	13.8	1.84	0.84	0.75	320
PCA	9	14.9	1.97	0.80	0.92	200

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