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Tuning of the reorganization energies by 'innocent' co-ligands in novel mixed-valent dinuclear ruthenium complexes

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Abstract

Two novel mixed-valent ruthenium complexes, of formulae $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(edta)]^+$ and $[(CN)_4Ru^{II}(bpz)Ru^{III}(edta)]^{3-}$ (where tpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine, pz = pyrazine, bpz = 2,2′-bipyrazine, edta = ethylenediaminetetraacetate), were prepared and spectroscopically characterized in aqueous solutions and as solid salts with suitable counterions. For comparison purposes, two new ruthenium complexes: a dinuclear species, of formula $[(CN)_4Ru^{II}(bpz)Ru^{II}(NH_3)_5]$, and a trinuclear species, of formula $\{(CN)_4Ru^{II}(bpz)[Ru^{II}(NH_3)_5]_2\}^{2+}$, were also prepared and characterized in aqueous solutions. From spectral data of metal-to-metal charge transfer (MMCT) absorption bands, a Hush analysis was made, and the reorganization energies for the intramolecular electron transfers were calculated. A dramatic change in these values was disclosed when comparing both mixed-valent species, which can be explained on the basis of the influence exerted by the 'innocent' co-ligands (polypyridines or cyanides) bonded to the ruthenium centers. This tuning is an important factor in devising molecular devices for energy conversion.

Keywords: Mixed-valence; Ruthenium complexes; Intramolecular electron transfer; Inverted region; Reorganization energies; Energy conversion

1. Introduction

Mixed-valence chemistry is an extremely active field of research [1], in part due to its relevance in the design of photochemical molecular devices [2]. The control of intramolecular electron transfer rates in these systems is an important aim to achieve so that high efficiencies in energy conversion can be obtained [3]. We report in this work the dramatic influence on the reorganization energies of inner electron transfers exerted by 'innocent' co-ligands coordinated to one of the metallic centers in novel mixed-valent dinuclear ruthenium complexes.

2. Experimental

2.1. Materials and techniques

All chemicals used were p.a. CH_3CN was distilled over P_4O_{10}. Water was bidistilled. All other solvents were used as supplied. Chemical analyses (C, H, and N) were carried out at INQUIMAE, University of Buenos Aires, Argentina. IR spectra of KBr pellets were recorded on a Perkin–Elmer 983G IR-spectrophotometer. UV–vis spectra were recorded on a Shimadzu UV-160A spectrophotometer, provided with thermostatted cells. Electrochemical data have been measured before by us in previous works using the cyclic voltammetry technique [4], or were inferred from literature data for very similar species. All values of

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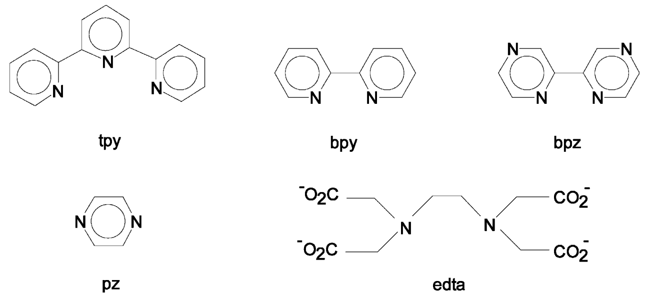

Scheme 1.

redox potentials, $E_{1/2}$, were referred to Ag/AgCl and obtained by using the well-known formula: $E_{1/2} = (E_c + E_a)/2$.

2.2. Syntheses of complexes

The precursor complexes: $[(tpy)(bpy)Ru(pz)](PF_6)_2$ (**I**), (tpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine, pz = pyrazine) was prepared as in ref. [4]; $Na_2[Ru(CN)_4(bpz)]\cdot 4H_2O$ (**II**), (bpz = 2,2′-bipyrazine) as in reference [5]; $K[Ru(edta)(H_2O)]$ (**III**) (edta = ethylenediaminetetraacetate) as in ref. [6]; and $[Ru(NH_3)_5(H_2O](PF_6)_2$ (**IV**), as in ref. [7].

The structure of the ligands is shown in Scheme 1.

By mixing stoichiometric amounts (1:1 M relation) of complexes **I** or **II** with **III** in aqueous solutions at 25 °C and pH 4.0 (HAc/AcO^- buffer, $C = 0.05$ M), the novel mixed-valent dinuclear complexes: $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(edta)]^+$ (**V**), or $[(CN)_4Ru^{II}(bpz)Ru^{III}(edta)]^{3-}$ (**VI**), were obtained respectively.

The PF_6^- salt of complex **V** was obtained as a dihydrate by the following technique: 7 mg of $[Ru(tpy)(bpy)(pz)]Br_2$ (prepared by metastasis of the corresponding PF_6^- salt) dissolved in 8 ml of H_2O were mixed under Ar for 2 h with an excess of K[Ru(edta)Cl] (6 mg in 4 ml of H_2O). One g of NH_4PF_6 dissolved in 2 ml of H_2O were then added to the mixture; the precipitate was filtered, washed with H_2O and dried under vacuum over P_4O_{10}. Yield: 6 mg, 55%. *Anal.* Found: C, 41.12; H, 3.96; N, 10.82. Calc. for $Ru_2C_{39}H_{35}N_9O_8PF_6$: C, 41.06; H, 3.45; N, 11.05%.

The mixed Na^+ and K^+ salt of complex **VI** was obtained as a dihydrate by the following technique: 48 mg of $Na_2[Ru(CN)_4(bpz)]\cdot 4H_2O$ dissolved in 5 ml of H_2O were mixed under Ar for 2 h with a stoichiometric

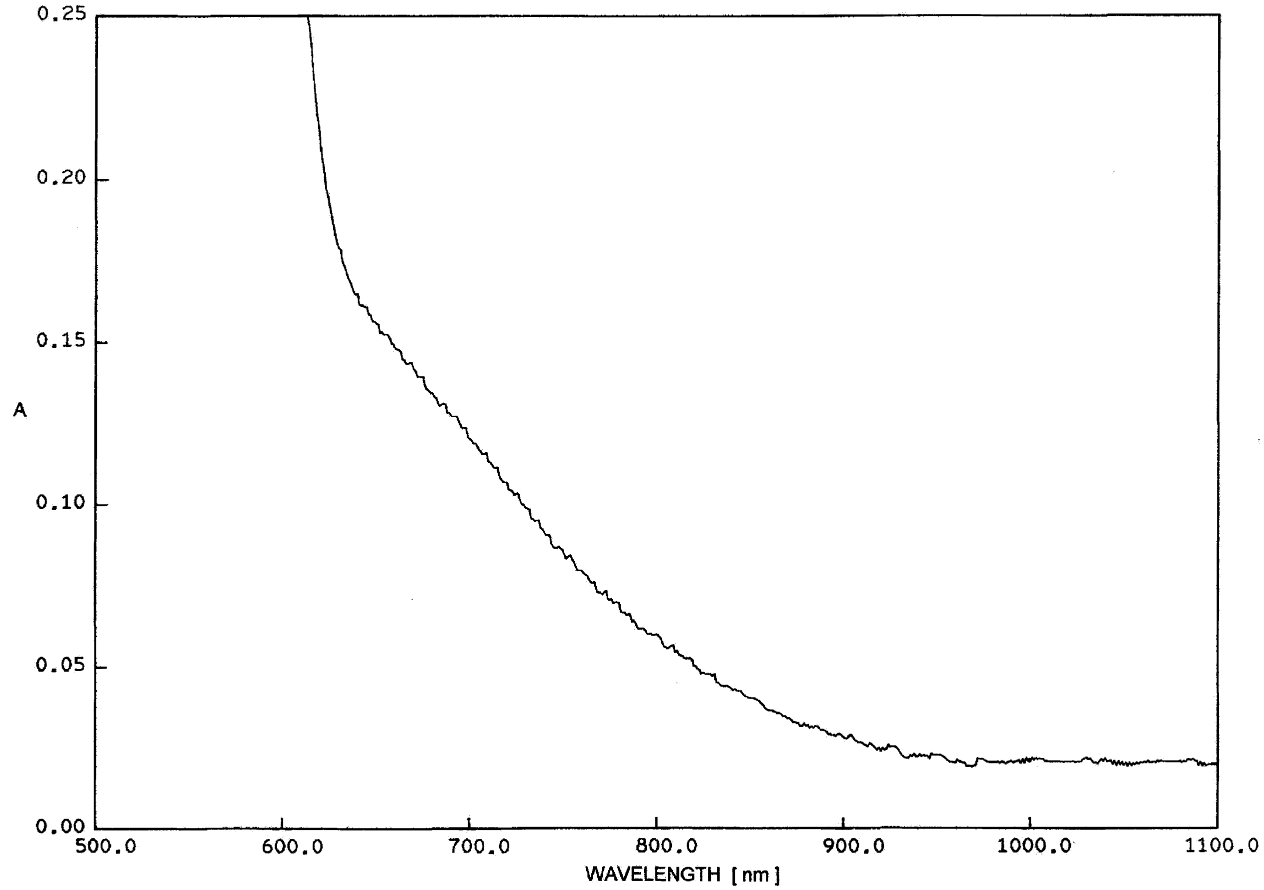

Fig. 1. Visible spectra of **V**, $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(edta)]^+$, in aqueous solution (pH 4.0, $C = 1.4 \times 10^{-3}$ mol dm^{-3}).

$$[(tpy)(bpy)Ru^{III}(pz)Ru^{II}(NH_3)_5]^{5+} \rightarrow [(tpy)(bpy)Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+} \qquad \Delta E_{1/2} = 0.8\ \text{V}$$

$$[(NH_3)_5Ru^{III}(pz)Ru^{II}(edta)]^{+} \rightarrow [(NH_3)_5Ru^{II}(pz)Ru^{III}(edta)]^{+} \qquad \Delta E_{1/2} = 0.3\ \text{V}$$

$$[(tpy)(bpy)Ru_b^{III}(pz)Ru_a^{II}(edta)]^{+} \rightarrow [(tpy)(bpy)Ru_b^{II}(pz)Ru_a^{III}(edta)]^{+} \qquad \Delta E_{1/2} = 1.1\ \text{V}$$

Scheme 2.

amount of K[Ru(edta)Cl] (50 mg in 5 ml of H_2O). The mixture was loaded onto a Sephadex G-25 column and eluted with water. The second fraction was rotoevaporated and dried in a vacuum desiccator over P_4O_{10}. *Anal.* Found: C, 30.21. Calc. for $Ru_2C_{22}H_{35}N_{26}O_{12}Na_2K$: C, 30.24%.

Finally, the novel dinuclear complex $[(CN)_4Ru^{II}(bpz)Ru^{II}(NH_3)_5]$ (**VII**), and the novel trinuclear species $\{(CN)_4Ru^{II}(bpz)[Ru^{II}(NH_3)_5]_2\}^{2+}$ (**VIII**), were obtained by mixing under Ar, in acetone/water (1:1, v/v) for 2 h, stoichiometric amounts of complexes **III** and **IV**; the molar relation being 1:1 for complex **VII** and 1:2 for complex **VIII**. After precipitating with ether, all the solids were chromatographied on a column of Sephadex C-25 and eluted in aqueous solutions with 0.1 M NaCl for obtaining complex **VII** and with 0.6 M NaCl for obtaining complex **VIII**.

All new complexes prepared in situ were characterized in aqueous solutions by UV–vis spectroscopy, while solid salts were also characterized by IR spectra, as discussed below.

3. Results and discussion

The solid salt $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(edta)](PF_6)$ was characterized by its IR spectrum, which displayed bands assigned to coordinated COO^- groups of edta at 1655 cm^{-1}. Fig. 1 shows the visible spectrum in aqueous solution of the mixed-valent complex **V**, $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(edta)]^+$. A new band, undetected in both precursor complexes—**I**, $[(tpy)(bpy)Ru(pz)]^{2+}$ and **III**, $[Ru(edta)(H_2O)]^-$—is observed at $\lambda_{max} \approx 690$ nm ($\varepsilon_{max} \approx 90$ dm^3 mol^{-1} cm^{-1}) in **V** (values obtained by a Gaussian deconvolution using a standard GRAMS program). This can be ascribed to the metal-to-metal charge transfer (MMCT) transition $Ru_b^{II} \rightarrow Ru_a^{III}$, where Ru_b = Ru bonded to bpy and tpy, and Ru_a = Ru bonded to edta; the

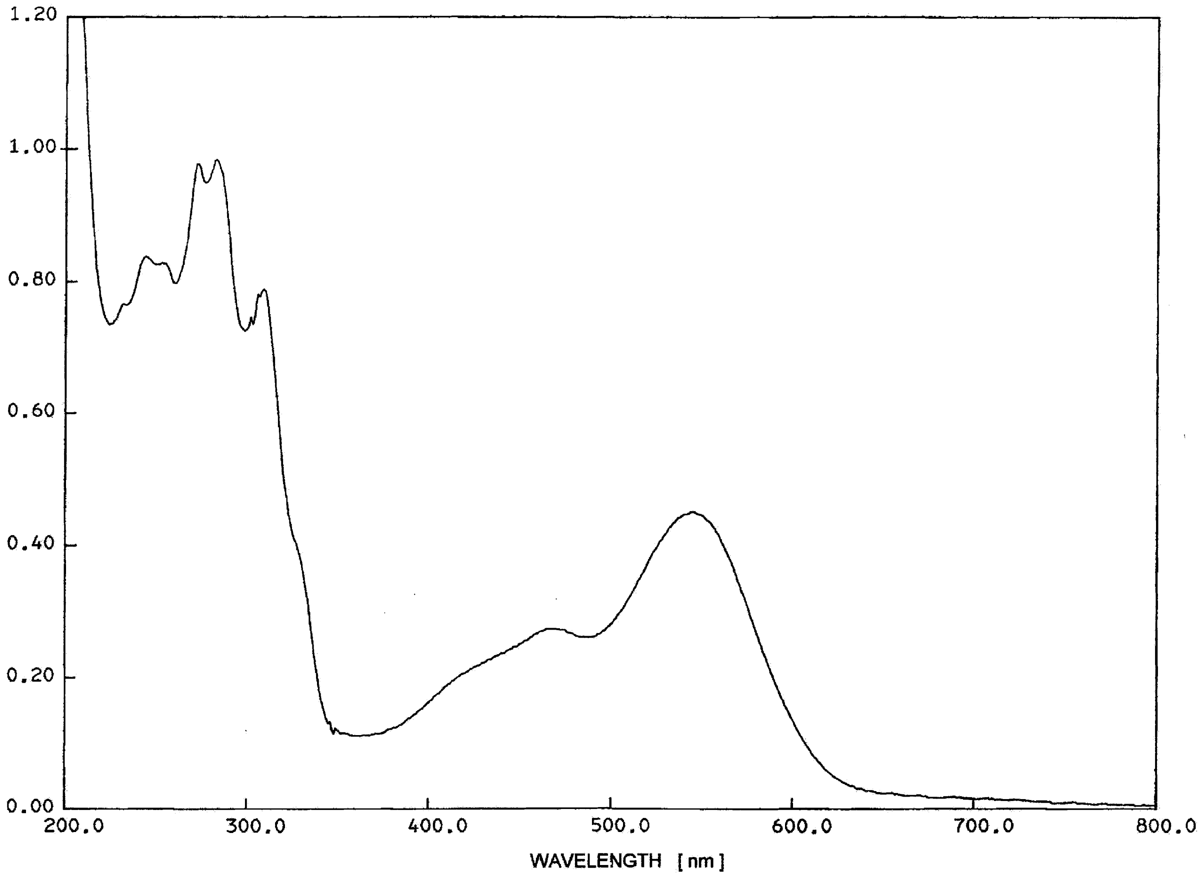

Fig. 2. UV–vis spectrum of complex $[(tpy)(bpy)Ru^{II}(pz)Ru^{II}(edta)]$, obtained by reduction of **V** with ascorbic acid ($C = 2.5 \times 10^{-5}$ mol dm^{-3}).

corresponding band in the analogous species $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+}$ (**IX**), appears at $\lambda_{max} = 794$ nm ($\varepsilon_{max} = 656$ dm^3 mol^{-1} cm^{-1}), in water [4].

Assuming the similarities in inner-sphere reorganization energies for both mixed-valent complexes **V** and **IX**, the difference in λ_{max} for the MMCT bands can be accounted for by the difference in redox potentials between both metallic centers. Since this difference amounts to 0.82 V in $[(tpy)(bpy)Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+}$ [4] and 0.3 eV in $[(NH_3)_5Ru^{II}(pz)Ru^{III}(edta)]^{+}$ [8], a value of $\Delta E_{1/2} = 1.1$ V can be inferred for **V**, $[(tpy)(bpy)Ru_b^{II}(pz)Ru_a^{III}(edta)]^{+}$, where $\Delta E_{1/2} = E_{1/2}[Ru_b^{III}/Ru_b^{II}] - E_{1/2}[Ru_a^{III}/Ru_a^{II}]$, as shown in Scheme 2.

On the other hand, since $\Delta E_{1/2} = 0.8$ V for **IX** [4,9], the energy of the MMCT band for **V** is predicted to be shifted 2.4×10^3 cm^{-1} to higher energies compared with that of complex **IX**; the observed shift is 2.8×10^3 cm^{-1}.

Besides, by reduction of **V** with ascorbic acid (added as a solid), the completely reduced complex, $[(tpy)(bpy)Ru^{II}(pz)Ru^{II}(edta)]$, is obtained in aqueous solution; its visible spectrum is shown in Fig. 2. The new and intense band detected at $\lambda_{max} = 545$ nm ($\varepsilon_{max} = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}) can be assigned to the metal-to-ligand charge transfer (MLCT) transition $d_\pi(Ru)_a \rightarrow \pi^*(pz)$, which compares very well to the corresponding band in the similar complex $[(tpy)(bpy)Ru^{II}(pz)Ru^{II}(NH_3)_5]^{4+}$ ($\lambda_{max} = 543$ nm; $\varepsilon_{max} = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}; in CH_3CN [4]). The lack of absorption of this reduced species near 700 nm confirms the assignment of the band at 690 nm in **V** to an intervalence transfer.

The IR spectrum of the solid salt $Na_2K[(CN)_4Ru^{II}(bpz)Ru^{III}(edta)]\cdot 4H_2O$ showed characteristic bands of coordinated COO^- groups of edta at 1644 cm^{-1}, while the stretching cyanide frequency ν_{CN} appeared at 2084 cm^{-1}, increased to higher energy with respect to the corresponding value of the precursor complex $Na_2[Ru(CN)_4(bpz)]\cdot 4H_2O$ ($\nu_{CN} = 2066$ cm^{-1}, [5]). This shift can be accounted for by the higher π-accepting properties of a ‘ruthenated’ bpz in the dinuclear complex **VI** compared with bpz with free pyrazine nitrogens in the mononuclear species **II** which decreases the extent of π-backbonding from Ru to the cyanide groups.

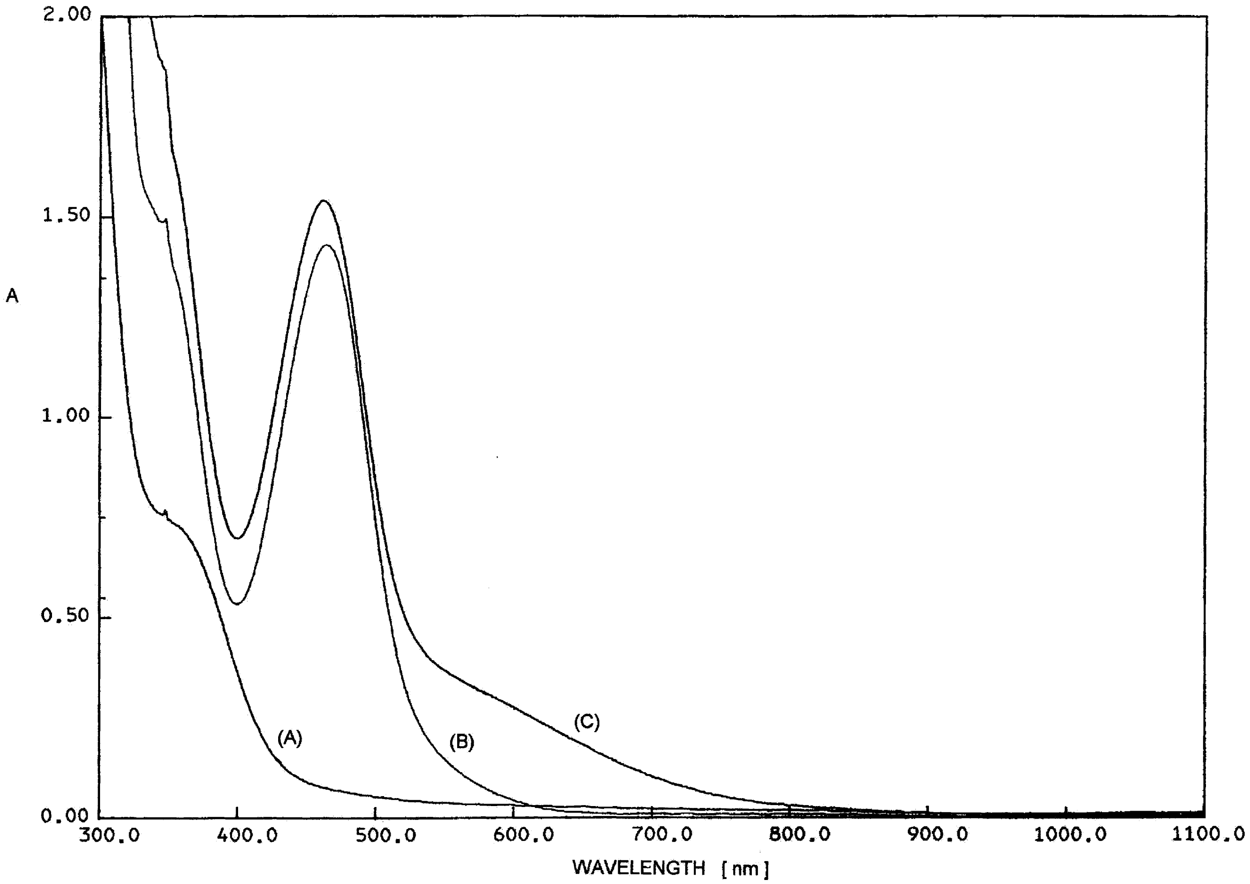

Fig. 3. UV–vis spectra of complexes $[Ru(edta)(H_2O)]^-$, (A); $[Ru(CN)_4(bpz)]^{2-}$, (B); and $[(CN)_4Ru^{II}(bpz)Ru^{III}(edta)]^{3-}$, (C), in water (pH 4.0, $C = 3.3 \times 10^{-4}$ mol dm^{-3}).

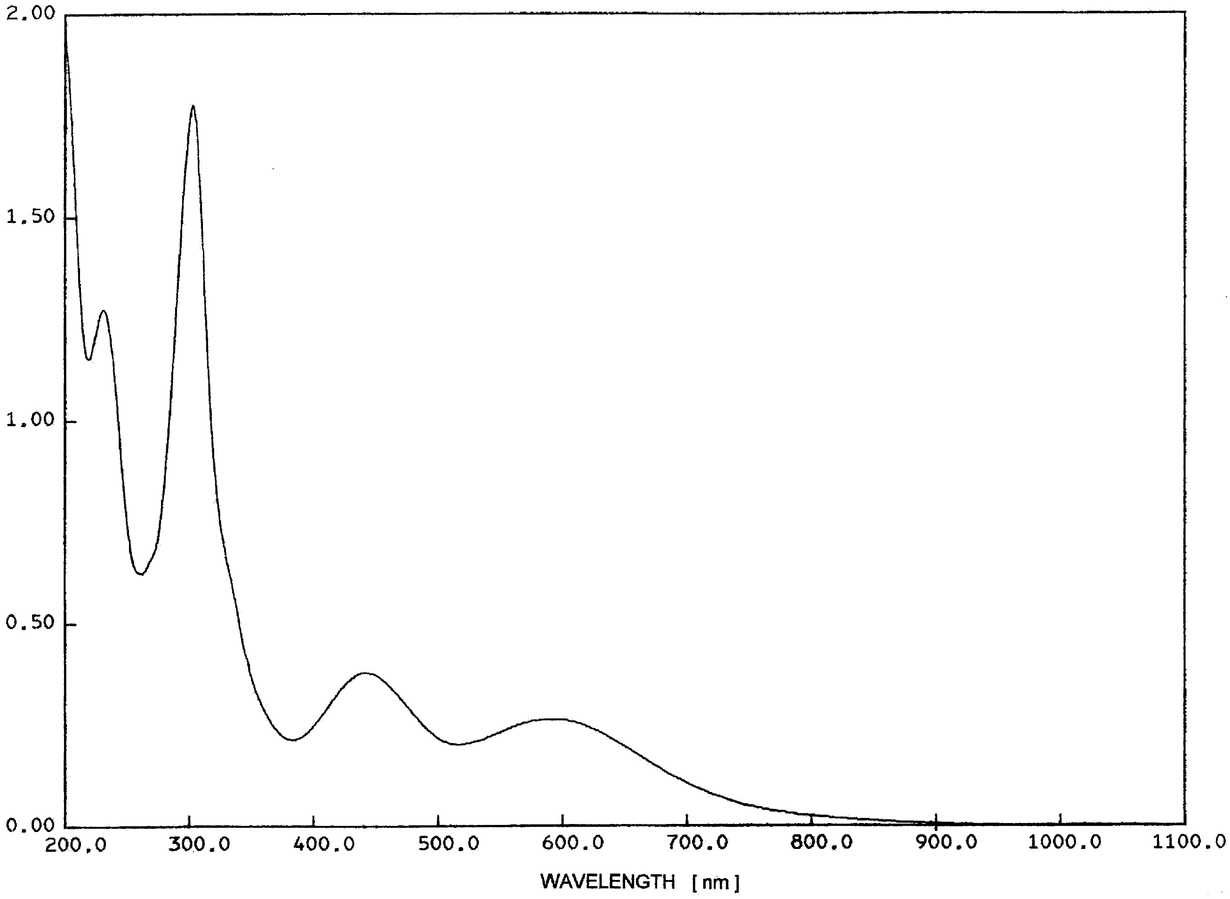

Fig. 4. UV–vis spectrum, in water, of $[(CN)_4Ru^{II}(bpz)Ru^{II}(NH_3)_5]$.

Fig. 3 shows the UV–vis bands recorded in aqueous solutions for the complexes $[Ru(edta)(H_2O)]^-$ [**III**, spectrum A], $[Ru(CN)_4(bpz)]^{2-}$ [**II**, spectrum B], and $[(CN)_4Ru^{II}(bpz)Ru^{III}(edta)]^{3-}$ [**VI**, spectrum C]. In the latter species, the new band observed at $\lambda_{max} = 583$ nm ($\varepsilon_{max} = 871$ dm^3 mol^{-1} cm^{-1}) is due to the MMCT transition $Ru_c{}^{II} \rightarrow Ru_a{}^{III}$ (where $Ru_c = Ru$ bonded to cyanides). By reducing **VI** with ascorbic acid, the species $[(CN)_4Ru^{II}(bpz)Ru^{II}(edta)]^{4-}$ is formed. The new band detected at $\lambda_{max} = 569$ nm ($\varepsilon_{max} = 5.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}) can be attributed to the MLCT transition $d_\pi(Ru)_a \rightarrow \pi^*(bpz)$; this value is similar to that informed previously for $[(tpy)(bpy)Ru^{II}(pz)Ru^{II}(edta)]$ ($\lambda_{max} = 545$ nm).

The last assignment is also confirmed when analyzing the corresponding bands in the related complexes **VII**, $[(CN)_4Ru^{II}(bpz)Ru^{II}(NH_3)_5]$, and **VIII**, $\{(CN)_4Ru^{II}(bpz)[Ru^{II}(NH_3)_5]_2\}^{2+}$, whose spectra in aqueous solutions are shown in Figs. 4 and 5, respectively. In effect, the lowest-energy bands, corresponding to MLCT transitions from the capping amine ruthenium to bpz, appear at $\lambda_{max} = 592$ nm in complex **VII** and at $\lambda_{max} = 593$ nm in complex **VIII**; in the latter case, the intensity of this MLCT band is doubled, when compared with the lowest-energy MLCT transition $d_\pi(Ru)_c \rightarrow \pi^*(bpz)$ ($\lambda_{max} \approx 430$ nm, cf. [5]), as expected for a trinuclear complex. The almost unchanged values of λ_{max} when going from **VII** to **VIII** put into evidence the very weak interaction between both capping ruthenium centers, and compare well to the above reported values of $d_\pi(Ru)_a \rightarrow \pi^*(bpz)$ MLCT bands.

Parameters related to the intramolecular electron transfer in the mixed-valent species **V** and **VI** can be calculated using the Hush formalism [10]. Thus, the electronic coupling element H_{AB} (A, donor; B, acceptor) between the donors, $Ru^{II}(tpy)(bpy)$ or $Ru^{II}(CN)_4$, and the acceptor, $Ru^{III}(edta)$, can be calculated by the formula:

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

where ε_{max} is the absorption coefficient of the MMCT band (in dm^3 mol^{-1} s^{-1}), $\tilde{\nu}_{max}$ is the energy maximum of the same band (in cm^{-1}), $\Delta\tilde{\nu}_{1/2}$ is the bandwidth at half-height (taken as twice the value obtained on the

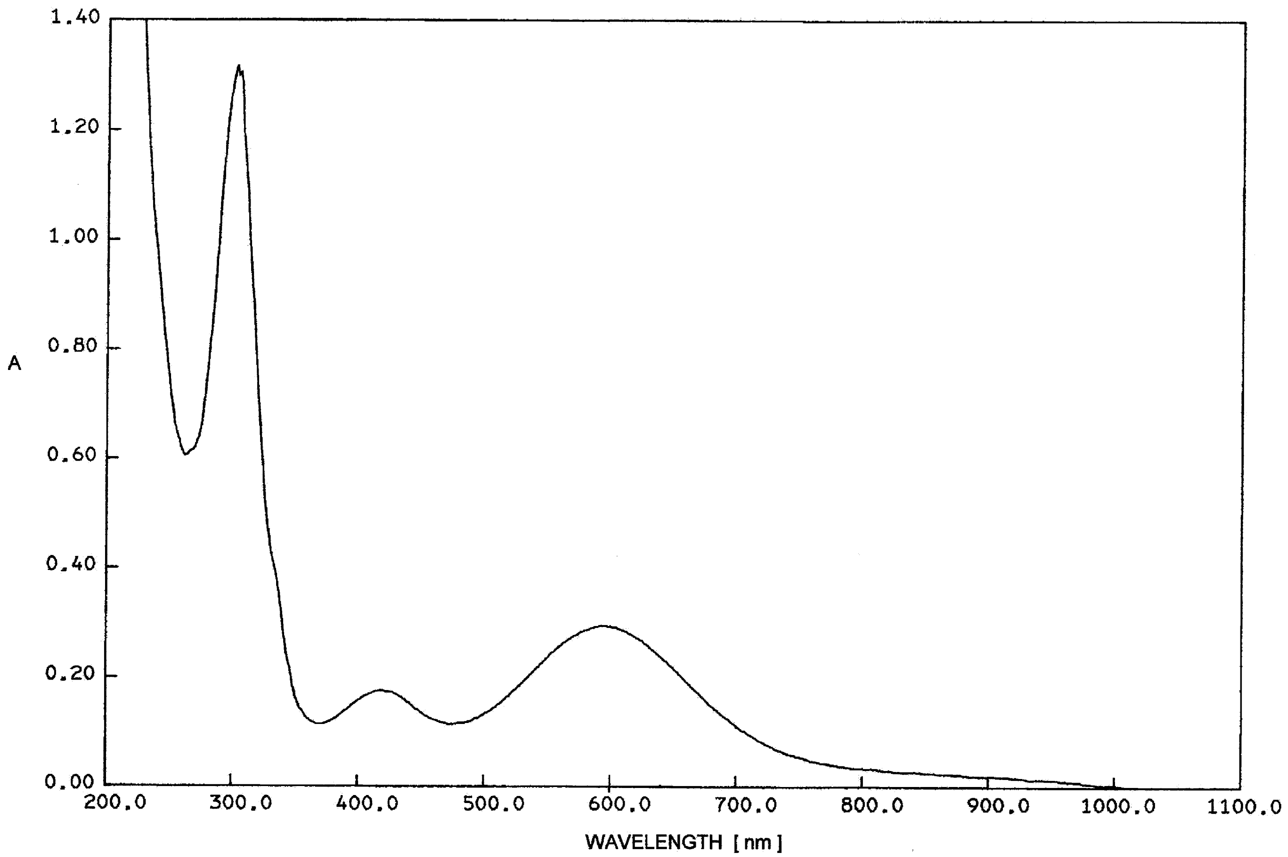

Fig. 5. UV–vis spectrum, in water, of $\{(CN)_4Ru^{II}(bpz)[Ru^{II}(NH_3)_5]_2\}^{2+}$.

low-energy side or by Gaussian deconvolution), and r is the metal-to-metal distance (in Å). Considering the ε_{max}, $\tilde{\nu}_{max}$ and $\Delta\tilde{\nu}_{1/2}$ values for the bands shown in Figs. 1 and 3(c), and literature values for r [11], we obtain $H_{AB} =$ 225 and 733 cm^{-1} (or 0.028 and 0.091 eV) for complexes **V** and **VI**, respectively. On the other hand, the reorganization energy for intramolecular electron transfer can be determined [11] by the following equation:

$$\lambda = E_{op} - \Delta G^{\circ} - \Delta E_{ex} \qquad (2)$$

where E_{op} is the energy of the absorption maximum (in eV), ΔG° is the free energy difference between both redox sites (obtained approximately as the difference in the redox potentials $\Delta E_{1/2}$, defined earlier) and ΔE_{ex} is an excited-state energy difference, estimated as 0.25 eV for various ruthenium complexes [11].

For complex **V**, $E_{op} = 1.8$ eV and $\Delta G^{\circ} = 1.1$ eV; while for complex **VI**, $E_{op} = 2.2$ eV and $\Delta G^{\circ} = 0.7$ eV (by considering that the redox potential of the Ru(III)–Ru(II) couple in the $Ru(CN)_4$ moiety is approximately 0.4 eV lower than that of the Ru(tpy)(bpy) group [5]); therefore, we calculate—from equation (2)—values of $\lambda = 0.5$ and 1.3 eV for complexes **V** and **VI**, respectively.

For both mixed-valent species **V** and **VI** the values of $H_{AB} \ll \lambda$; therefore, these complexes can be classified as Class II (slightly delocalized) of Robin and Day nomenclature [12], with the electronic coupling somewhat higher—by a factor of 3—for complex **VI**. Comparing now the values of λ for both complexes, an increment by a factor of 2 is disclosed when going from **V** to **VI**; i.e. when substituting polypyridines by cyanides in the coordination sphere of the ruthenium(II) site. Although pz and bpz are not strictly the same ligands, we assume that the ligand reorganization energies are slightly changed, considering that the peripheral nitrogen coordinating centers of both ligands have similar electronic densities [13]. What is more impressive, while the reverse intramolecular electron transfer $Ru_a^{II} \rightarrow Ru_c^{III}$ falls in the normal region for complex **VI** [λ ($=1.3$ eV) $> -\Delta G^{\circ}$ ($=0.7$ eV)], the analogous charge recombination transfer $Ru_a^{II} \rightarrow Ru_b^{III}$ is predicted to be in the Marcus inverted region for complex **V** [λ ($=0.5$ eV) $< -\Delta G^{\circ}$ ($=1.1$ eV)]. This tuning of the reorganization energies and the driving forces by ‘innocent’ co-ligands is an important factor in devising efficient photoconverters.

4. Conclusions

The reorganization parameters and driving forces for intramolecular electron transfers in the mixed-valent asymmetric complexes of ruthenium studied in this work can be dramatically altered when changing polypyridines with cyanides as co-ligands in the coordination sphere of the donor ruthenium site. Thus, the charge recombination that follows light excitation in **VI** falls in the normal region, while the same reaction in the related complex **V** is predicted to lie in the Marcus inverted region.

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