Preparation and Spectroscopic, Electrochemical and Photophysical Properties of Mono-, Di-nuclear and Mixed-valence Species derived from the Photosensitizing Group (2,2'-Bipyridine)(2,2':6',2"-terpyridine)ruthenium(II) †

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New mono-, di-nuclear, and mixed-valence complexes derived from the photosensitizing moiety Ru(terpy)(bipy)$^{2+}$ (bipy = 2,2'-bipyridine, terpy = 2,2':6',2"-terpyridine) have been prepared and characterized by spectroscopic, electrochemical and luminescence techniques. The mononuclear species [Ru(terpy)(bipy)(4,4'-bipy)]$^{2+}$ (4,4'-bipy = 4,4'-bipyridine) exhibits λ_{max} at 466 and 420 nm in MeCN, $E_{\frac{1}{2}}$ (Ru^{III}-Ru^{II}) = 1.23 V (vs. saturated calomel electrode, SCE) in MeCN and λ_{em} = 625 nm in an EtOH–MeOH (4:1 v/v) glass at 77 K. The dinuclear complex [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{II}(NH$_3$)$_5$]$^{4+}$ has a new absorption maximum at 538 nm and a new voltammetric wave at $E_{\frac{1}{2}}$ = 0.39 V in MeCN ascribable to a metal-to-ligand charge transfer and a Ru^{III}-Ru^{II} redox process respectively involving the capping ammineruthenium group. On oxidation of this species with bromine vapour the mixed-valence complex [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{III}(NH$_3$)$_5$]$^{5+}$ is obtained, which seems to exhibit a metal-to-metal charge-transfer band, at λ_{max} $\approx$640 nm. Both dinuclear species emit at λ_{em} $\approx$620 nm at 77 K, but with reduced intensity with respect to the parent mononuclear complex, thus pointing to the operation of reductive and oxidative quenching processes for the II,II and the II,III complexes, respectively. The weak metal–metal interaction detected in the mixed-valence ion implies the possibility of using these systems as 'molecular switches' and/or models for the obtention of charge-separated states.

Polypyridine ruthenium(II) complexes have been extensively studied in view of their applications in photocatalysis and energy conversion.[1] We have been interested in the [Ru(terpy)(bipy)]$^{2+}$ moiety (bipy = 2,2'-bipyridine, terpy = 2,2':6',2"-terpyridine) as a photosensitizer and have recently described some properties of mono- and di-nuclear complexes using 4-cyanopyridine (4CN-py) and CN$^-$ as bridging ligands.[2,3] In this work we report the preparation and characterization by spectroscopic, electrochemical and luminescence techniques of new complexes with 4,4'-bipy (4,4'-bipyridine) as a connecting group between [Ru(terpy)(bipy)]$^{2+}$ and a Ru(NH$_3$)$_5$$^{n+}$ capping group which can act as an electron donor ($n = 2$) or acceptor ($n = 3$). A recent report[4] describes the excited-state properties of the [Ru(terpy)(bipy)(4,4'-bipy)]$^{2+}$ ion. We have extended these studies to low-temperature measurements. The dinuclear systems [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru$^{II/III}$(NH$_3$)$_5$]$^{4+/5+}$ are reported for the first time and can be considered as 'supramolecular' entities which may prove useful as models for the obtention of photoinduced charge separation, a process of considerable interest in the field of supramolecular photochemistry.[5]

Experimental

Syntheses.—The complex [Ru(terpy)(bipy)(4,4'-bipy)][PF$_6$]$_2$·H$_2$O **1** was synthesised by refluxing for 6 h [Ru(terpy)(bipy)Cl]Cl·2.5H$_2$O (0.13 g, 0.2 mmol), prepared as in ref. 6, and excess of 4,4'-bipy (0.65 g, 3.3 mmol) in EtOH–water (1:1 v/v, 20 cm^3). The solution was evaporated to remove EtOH, cooled and filtered to separate unreacted 4,4'-bipy. The filtrate was sorbed on to a column of SP-Sephadex C-25 (3 × 10 cm). The unreacted chloro complex was eluted with 0.2 mol dm^{-3} LiCl, while the desired complex was obtained by elution with 0.3 mol dm^{-3} LiCl. This last fraction was rotoevaporated at 40 °C to 5 cm^3, cooled and NH$_4$PF$_6$ (1.5 g in 2 cm^3 of water) added. The orange precipitate was filtered off, washed with cold water and dried under vacuum over P$_4$O$_{10}$. Yield: 0.16 g (80%). It can be further purified by dissolving in acetone and reprecipitating with diethyl ether (Found: C, 45.4; H, 3.1; N, 10.7; Ru, 10.6. Calc.: C, 44.0, H, 3.1; N, 10.3; Ru, 10.6%).

The complex [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{II}(NH$_3$)$_5$]-[PF$_6$]$_4$·2Me$_2$CO **2** was prepared by stirring complex **1** (56 mg, 0.06 mmol) in acetone (5 cm^3) for 1 h under Ar and then adding [Ru(NH$_3$)$_5$(H$_2$O)]$^{2+}$ (34 mg, 0.07 mmol), prepared as in ref. 7. The mixture was stirred for 6 h under Ar in the dark. The desired complex was precipitated with ether, filtered off, washed with cold ether, and air-dried. It was then dissolved in MeCN (2 cm^3) and sorbed on to a neutral alumina column (3 × 10 cm) previously equilibrated with acetonitrile–toluene (1:2 v/v). Acetonitrile was used as an eluent. The last main fraction was collected and the solvent was removed by evaporation. The residue was dissolved in acetone (5 cm^3) and precipitated with ether (90 cm^3), washed with ether and dried under vacuum over P$_4$O$_{10}$. It can be recrystallized from MeCN–toluene. Yield: 20 mg (22%) (Found: C, 32.0; H, 4.1; N, 12.5; Ru, 13.0. Calc.: C, 32.2; H, 3.6; N, 11.0; Ru, 13.2%).

The mixed-valence species [(terpy)(bipy)Ru^{II}(4,4'-bipy)-Ru^{III}(NH$_3$)$_5$]$^{5+}$ **3** was generated in acetonitrile solution by adding an excess of Br$_2$ to **2** as described by Meyer and co-workers.[8]

Materials, Instrumentation and Techniques.—Acetonitrile was heated under reflux with KMnO$_4$, distilled and dried over molecular sieves. Tetrabutylammonium hexafluorophosphate was recrystallized four times from EtOH and dried at 100 °C for
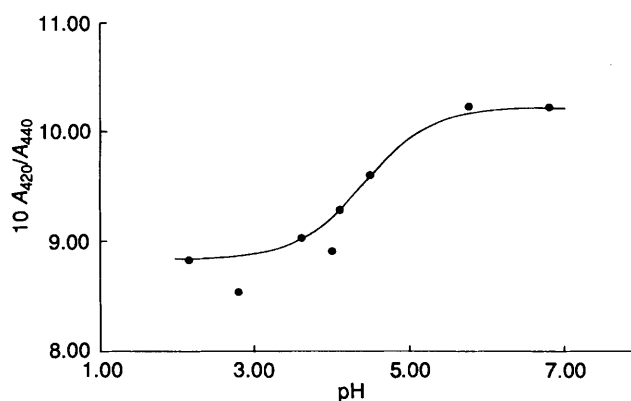
Fig. 1 Plot of the absorbances of $[Ru(terpy)(bipy)(4,4'-bipy)]^{2+}$ in aqueous solution vs. pH, at 22 °C and $I = 0.5$ mol dm^{-3} (KCl). The solid curve is calculated for $pK_a = 4.3$

Fig. 2 Infrared spectra (as KBr pellets) of (a) [Ru(terpy)(bipy)(4,4'-bipy)][PF$_6$]$_2$·H$_2$O and (b) [(terpy)(bipy)Ru(4,4'-bipy)Ru(NH$_3$)$_5$]-[PF$_6$]$_4$·2Me$_2$CO

48 h. All other chemicals were reagent grade and used without further purification.

A Perkin Elmer 983G spectrophotometer was used to obtain IR spectra as KBr pellets; UV/VIS spectra were recorded on a Shimadzu UV-160A spectrophotometer.

An H-type conventional cell with Pt as working and auxiliary electrodes and a saturated calomel electrode (SCE) as a reference were employed in cyclic voltammetry experiments. A glassy carbon working electrode was used for measuring the reductions of complex 2 since it showed greater reversibility than Pt. The equipment used was previously described.[2] Pure Ar was bubbled through the solutions before measurements.

A Perkin Elmer LS5 spectrofluorimeter was used to carry out luminescence measurements of samples 1–3 as EtOH–MeOH (4:1 v/v) glasses at 77 K.

For the pK_a determination of complex 1 a Luftman Reliance II pH-meter was employed. The ionic strength was controlled by adding KCl to solutions of 1 in adequate buffers (NaOH + KH$_2$PO$_4$ and citric acid + Na$_2$HPO$_4$).

A spectrophotometric redox titration of complex 2 was done in deareated MeCN solutions, by adding aliquots of a bromine solution in MeCN, a value of $\varepsilon = 183$ dm^3 mol^{-1} cm^{-1} at $\lambda = 392$ nm being taken for its standardization.[8]

Chemical analyses of C, H and N were performed at Unidad de Microanálisis y Métodos Físicos en Química Orgánica, Universidad de Buenos Aires, Argentina; ruthenium was analysed by following the previously described methods.[9]

Results and Discussion

pK_a Determination for Complex 1.—The basicity of 4,4'-bipy in $[Ru(terpy)(bipy)(4,4'-bipy)]^{2+}$ was determined in water at 22 °C and $I = 0.5$ mol dm^{-3} (KCl) by plotting the ratio of the absorbances at 420 (maximum for the non-protonated species) and 440 nm {maximum for the monoprotonated species $[Ru(terpy)(bipy)(4,4'-Hbipy)]^{3+}$} vs. pH, as shown in Fig. 1. The value obtained, $pK_a = 4.3 \pm 0.2$, is nearly identical to that determined[10] for $[Ru(4,4'-bipy)(NH_3)_5]^{2+}$ ($pK_a = 4.4 \pm 0.1$) and to the free-ligand value ($pK_{a2} = 4.9 \pm 0.1$)[10], as expected from the small perturbation introduced by 4,4'-bipy on the ruthenium orbitals.

IR Spectra.—Fig. 2 shows the IR spectra of complexes 1 and 2. Characteristic ligand (terpy, bipy, 4,4'-bipy) vibrations appear between 1600 and 600 cm^{-1} and are shifted slightly with respect to the free-ligand values. For 2 the value observed for $\delta_{sym}(NH_3)$ (=1286 cm^{-1}) is consistent with a localized oxidation state (II) for the capping ammineruthenium.[2] For the corresponding mixed-valence species 3 (a solid PF$_6^-$ salt obtained by a method similar to that described[8]) this band
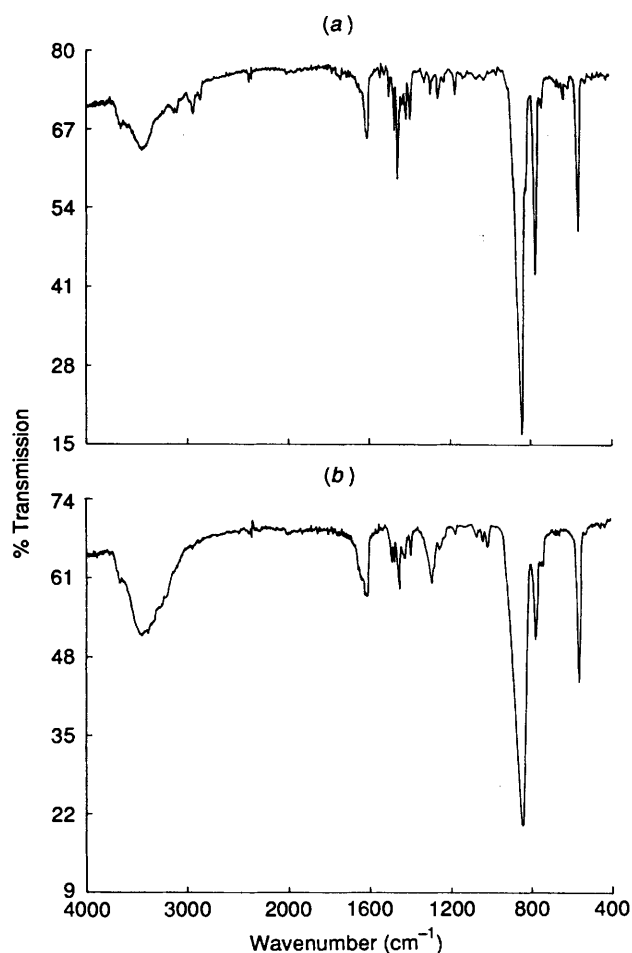
appears at 1314 cm^{-1}, as expected for a capping ammine-ruthenium(III) group.[11]

UV/VIS Spectra.—The UV/VIS spectra of complexes 1 and 2 in MeCN at 22 °C are shown in Fig. 3. The UV absorptions between 200 and 300 nm can be assigned to characteristic $\pi \rightarrow \pi^*$ (terpy, bipy, 4,4'-bipy) transitions.[2] For complex 1 the absorptions at 466 and 420 nm can be assigned to m.l.c.t. (metal-to-ligand charge-transfer) transitions $d_\pi(Ru) \rightarrow \pi^*$ (terpy) and d_π (Ru)$\rightarrow \pi^*$ (bipy) respectively, as revealed by comparison with $[Ru(terpy)(bipy)(4CN-py)]^{2+}$ and analogous systems.[2] For complex 2 the additional band with a maximum at 538 nm can be attributed to a m.l.c.t. d_π (ammineruthenium)$\rightarrow \pi^*$ (4,4'-bipy), since it disappears upon addition of Br$_2$. According to the corresponding redox potentials (see below), Br$_2$ can oxidize the Ru atom of the Ru(NH$_3$)$_5^{2+}$ group but not the Ru of the Ru(terpy)(bipy)$^{2+}$ group. This band shows a solvent dependence similar to those of other pentaammine complexes of Ru^{II}.[12] In effect, as shown in Fig. 4, there is a linear correlation between the absorption maximum E_{op} for this lowest m.l.c.t. and the donor number of the solvent; this is due to specific solvent donor–solvent acceptor interactions. Moreover, the calculated slope (-0.26 mol kcal^{-1} cm^{-1}) is similar to that obtained[12] for [Ru(NH$_3$)$_5$(py)][PF$_6$]$_2$ (py = pyridine) (-0.27 mol kcal^{-1} cm^{-1}), while the correlation coefficient is 0.91. When compared to the $[Ru^{II}(4,4'-bipy)(NH_3)_5]^{2+}$ complex ($\lambda_{max} = 470$ nm),[11] this band is red shifted, indicating the presence of a metal–metal π interaction through the 4,4'-bipy bridge.

A spectrophotometric titration of complex 2 with Br$_2$ in dearated MeCN solutions gave 0.52:1 as the ratio of moles of
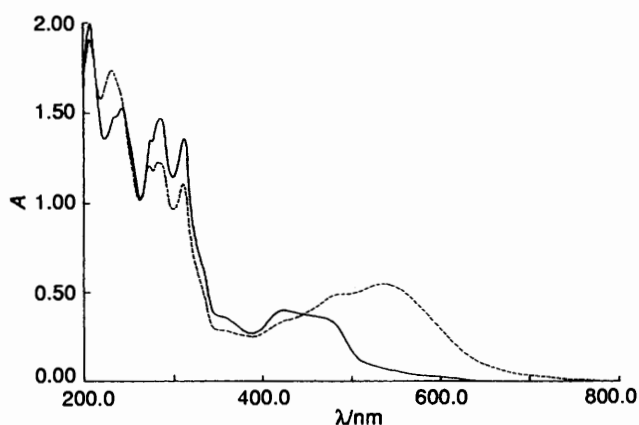
Fig. 3 The UV/VIS spectra at 22 °C in MeCN of [Ru(terpy)(bipy)(4,4'-bipy)]$^{2+}$ (4.2×10^{-5} mol dm^{-3}, ——) and [(terpy)(bipy)Ru(4,4'-bipy)Ru(NH$_3$)$_5$]$^{4+}$ (5.1×10^{-5} mol dm^{-3}, ----)

Fig. 4 Plot of the energy of the maximum absorption for the m.l.c.t. d$_\pi$(Ru$_a$)→π* (4,4'-bipy) of [(terpy)(bipy)Ru$_b^{II}$(4,4'-bipy)Ru$_a^{II}$(NH$_3$)$_5$]$^{4+}$ in various solvents *vs.* solvent donor number. Solvents: **1**, nitrobenzene; **2**, acetonitrile; **3**, acetone; **4**, dimethylformamide. cal = 4.184 J
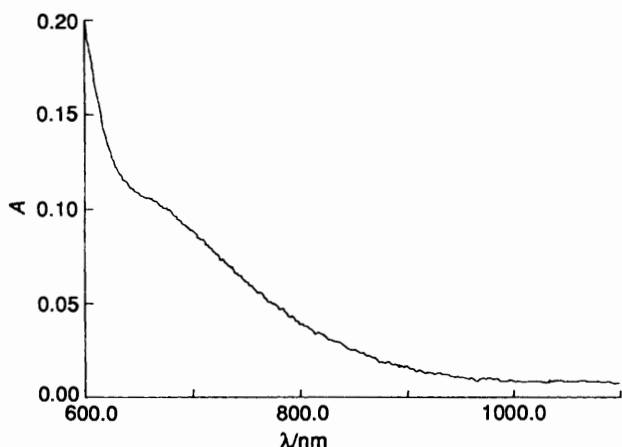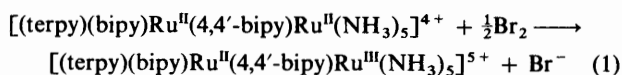

Fig. 5 The m.m.c.t. band of the mixed-valence complex [(terpy)(bipy)-Ru^{II}(4,4'-bipy)Ru^{III}(NH$_3$)$_5$]$^{5+}$ (3.1×10^{-4} mol dm^{-3}) in MeCN

Br$_2$ consumed to moles of dimer consumed, pointing to the stoichiometry (1). The mixed-valence species **3** can also be

[(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{II}(NH$_3$)$_5$]$^{4+}$ + $\frac{1}{2}$Br$_2$ ⟶

    [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{III}(NH$_3$)$_5$]$^{5+}$ + Br$^-$ (1)

obtained by adding bromine vapour. The m.l.c.t. transitions appear at values similar to those of **1** [460 (sh) and 435 nm], while a shoulder at $\lambda_{max} \approx 640$ nm (with ε = 350 dm^3 mol^{-1} cm^{-1} and $\Delta v_{\frac{1}{2}} \approx 5500$ dm^3 mol^{-1} cm^{-1}), shown in Fig. 5, can be

Table 1 Electronic absorption spectral data^a

Complex	λ_{max}/nm (10^{-3} ε$_{max}$/dm^3 mol^{-1} cm^{-1})^b
1 [Ru(terpy)(bipy)(4,4'-bipy)]$^{2+}$	235 (sh), 242 (37.2), 274 (34.8), 286 (38.2), 312 (36.0), 335 (sh), 360 (sh), 420 (10.5), 466 (9.61), 550 (sh), 600 (sh)
2 [(terpy)(bipy)Ru^{II}(4,4'-bipy)-Ru^{II}(NH$_3$)$_5$]$^{4+}$	232 (35.6), 273 (24.8), 286 (25.1), 312 (22.6), 335 (sh), 360 (sh), 425 (7.0), 484 (9.90), 538 (11.2)
3 [(terpy)(bipy)Ru^{II}(4,4-bipy)-Ru^{III}(NH$_3$)$_5$]$^{5+}$	232 (34.1), 240 (sh), 275 (25.7), 287 (28.0), 312 (25.8), 370 (sh), 435 (9.4), 460 (sh), 550 (sh), 583 (sh), 640 (sh)

^{a} In MeCN, at 22 °C. ^{b} Errors: ± 2 nm in λ_{max}, $\pm 5\%$ in ε$_{max}$.

Table 2 Electrochemical potentials (*vs.* SCE) at 22 °C^a

Complex	$E_{\frac{1}{2}}$/V (ΔE_p/mV)
1	+1.23 (60), −1.23 (65), −1.57 (80), −1.77^b
2	+1.25 (60), +0.39 (70), −1.21 (60), −1.55 (65), −1.85 (95)

^{a} In MeCN, 0.1 mol dm^{-3} NBu$_4$PF$_6$, sweep rate 0.1 V s^{-1}. ^{b} Irreversible.

attributed to a m.m.c.t. (metal-to-metal charge-transfer) transition Ru$_b^{II}$→Ru$_a^{III}$ (where Ru$_b$ is polypyridine-bound and Ru$_a$ is ammine-bound), since it disappears upon addition of Ce^{IV}. This assignment is, however, tentative. For the analogous pyrazine (pz) dinuclear complex, studies in progress indicate a well defined m.m.c.t. band at $\lambda \approx 820$ nm in MeCN, as expected on the basis of the decrease in reorganization parameter λ with decreasing metal-to-metal separation.[13]

The UV/VIS data for complexes **1–3** are shown in Table 1.

Electrochemistry.—Table 2 presents the results of cyclic voltammetry studies of complexes **1** and **2** in MeCN, 0.1 mol dm^{-3} NBu$_4$PF$_6$, 22 °C and sweep rate = 0.1 V s/1. All redox potentials, determined from $E_{\frac{1}{2}} = (E_a + E_b)/2$, are reported *vs.* SCE. The ΔE values indicate reversibility for most of the redox processes under consideration. For **1** only one oxidation wave was detected, corresponding to the Ru$_b^{III}$–Ru$_b^{II}$ couple. The measured value of $E_{\frac{1}{2}} = 1.23$ V compares reasonably well to those of other [Ru(terpy)(bipy)L]$^{2+}$ complexes.[2] For **2**, this potential is shifted to 1.25 V, as expected for the higher charge of the dinuclear species, while an additional wave, with $E_{\frac{1}{2}} = 0.39$ V, can be assigned to the Ru$_a^{III}$–Ru$_a^{II}$ couple, in view of its similarity to the value for the mononuclear complex [Ru(4,4'-bipy)(NH$_3$)$_5$]$^{2+}$ (0.43 V, see ref. 11). The $E_{\frac{1}{2}}$ values for ligand reductions are −1.23, −1.57 and −1.77 V for **1** and can be assigned to terpy, bipy and 4,4'-bipy reductions respectively.[2] The corresponding values for **2** are −1.21, −1.55 and −1.85 V. For [Ru(terpy)(bipy)(py)]$^{2+}$ spectroelectrochemical experiments indicate that the terpy ligand is reduced first.[14]

Emission Spectra.—Complexes **1–3** did not exhibit luminescence in MeCN at room temperature with our equipment. However, recent work[4] showed that **1** emits under those conditions (probably the equipment used had higher sensitivity), with $\lambda_{em} = 618$ nm ($\lambda_{ex} = 462$ nm). We have measured the luminescence in EtOH–MeOH (4:1 v/v) glasses at 77 K. Fig. 6 shows the emission spectra of the three species under those conditions, at $\lambda_{ex} = 430$ nm. All samples emit at $\lambda_{em} = 621 \pm 4$ nm, the excitation spectra being very similar to the absorption spectrum of the Ru(terpy)(bipy)$^{2+}$ chromophore, thus confirming that emission occurs from the lowest[3] m.l.c.t. (Ru→terpy) excited state. By measuring the area of the emission spectra between 580 and 750 nm of the three glasses at the same absorbance, we infer that the luminescence of **1** is quenched by a factor of 6 in **2** but only by a factor of 2 in **3**. By following
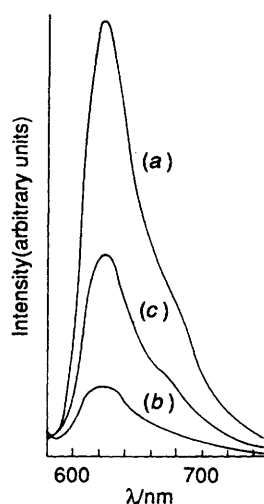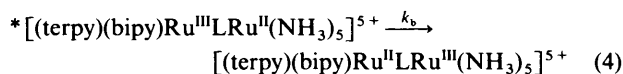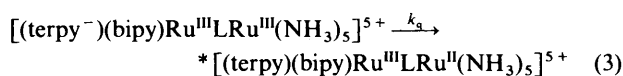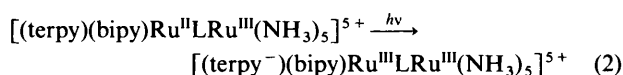
Fig. 6 Emission spectra of (a) [Ru(terpy)(bipy)(4,4'-bipy)]$^{2+}$, (b) [(terpy)(bipy)Ru(4,4'-bipy)Ru(NH$_3$)$_5$]$^{4+}$, and (c) [(terpy)(bipy)Ru-(4,4'-bipy)Ru(NH$_3$)$_5$]$^{5+}$ in EtOH–MeOH (4:1 v/v) glasses at 77 K. λ_{ex} = 430 nm

arguments[15] which explain the lack of emission in metal adducts of [Ru(bipy)$_2$(CN)$_2$], we propose that, in complex 2, a reductive quenching is operative, owing to the presence of low-lying m.l.c.t. states involving the ammineruthenium(II) moiety. In complex 3 an oxidative quenching pathway can be envisaged, owing to the presence of metal-to-metal (or 'intervalence') charge-transfer states of low energy, equations (2)–(4) (L =

[(terpy)(bipy)Ru^{II}LRu^{III}(NH$_3$)$_5$]$^{5+}$ $\xrightarrow{hv}$

[(terpy$^-$)(bipy)Ru^{III}LRu^{III}(NH$_3$)$_5$]$^{5+}$ (2)

[(terpy$^-$)(bipy)Ru^{III}LRu^{III}(NH$_3$)$_5$]$^{5+}$ $\xrightarrow{k_q}$

*[(terpy)(bipy)Ru^{III}LRu^{II}(NH$_3$)$_5$]$^{5+}$ (3)

*[(terpy)(bipy)Ru^{III}LRu^{II}(NH$_3$)$_5$]$^{5+}$ $\xrightarrow{k_b}$

[(terpy)(bipy)Ru^{II}LRu^{III}(NH$_3$)$_5$]$^{5+}$ (4)

4,4'-bipy). If the m.m.c.t. state (the 'unstable' isomer of 2) accumulates its spectrum and the values of the quenching rate constant k_q and the back electron-transfer rate constant k_b could be determined by flash-photolysis techniques; d–d quenching pathways cannot, however, be ruled out at room temperature (see below).

Stability.—Complex 1 is very stable in the absence of light in MeCN. In the solid state 2 decomposes after 2 months, while in MeCN solution the absorbance at λ_{max} = 538 nm decreases by 20% in 2 d. Complex 3 tends to give a small proportion of 2 after 1 d. Under room light, all complexes undergo slow ligand photosubstitution reactions (cf. ref. 16), which imply the presence of low-lying d–d states.

Thermal Intramolecular Electron Transfer.—If we consider that the shoulder at $\lambda \approx$ 640 nm in complex 3 is due to a m.m.c.t. transition, a value of $H_{AB} \approx$ 0.03 eV is obtained by using Hush's formalism,[17] which allows us to classify this mixed-valence system as valence-localized, with a weak metal–metal interaction, in agreement with the spectroscopic results. From equation (5), where E_{op} is the absorption maximum for the

$$E_{op} = \lambda + \Delta G^\circ + \Delta E_{ex} \tag{5}$$

m.m.c.t., λ the reorganization parameter, ΔG° the equilibrium free-energy difference between the two metal sites, and ΔE_{ex} the

excited-state electronic energy difference, and taking ΔG° as ΔE_i = 0.84 eV and ΔE_{ex} = 0.25 eV,[13] a value of λ = 0.84 eV is computed. When considering the reverse electron-transfer reaction, Ru$_b^{III}$ $\xrightarrow{k_b}$ Ru$_a^{II}$ for which ΔG° = −0.84 eV, we conclude that λ = −ΔG°, and this process should be in the rapid barrierless regime at room temperature. Current studies on the analogous mixed-valence pz-bridged complex show that a noticeable decrease in k_b occurs, similar to that observed for the CN$^-$-bridged species.[3] This may indicate the onset of the 'inverted' regime. If this is the case, then a non-adiabatic treatment is compulsory.[18] The contrasting result for the 4,4'-bipy-bridged complex could be due not only to the weaker metal–metal interaction, but also to some configuration changes on oxidizing Ru$_a^{II}$ to Ru$_a^{III}$, such as a twisting of the bipy rings through the C(4)–C(4') bond of the 4,4'-bipy. This suggests the possibility of using this and/or similar systems as 'molecular switches'.[19]

Conclusion

New asymmetric dinuclear complexes can be prepared using Ru(terpy)(bipy)$^{2+}$ as a photosensitizing group, 4,4'-bipy as a bridging ligand and Ru(NH$_3$)$_5^{n+}$ as electron donor (n = 2) or acceptor (n = 3) group. The spectroscopic, electrochemical and photophysical properties of these species point to a weak metal–metal interaction through the 4,4'-bipy bridge. The quenching of the ^{3}m.l.c.t. excited state of the polypyridine ruthenium moiety which occurs at 77 K in the mixed-valence complex [(terpy)(bipy)Ru^{II}(4,4'-bipy)Ru^{III}(NH$_3$)$_5$]$^{5+}$ could be due to an oxidative process that leads to the 'unstable' isomer *[(terpy)-(bipy)Ru^{III}(4,4'-bipy)Ru^{II}(NH$_3$)$_5$]$^{5+}$ which probably decays to the ground state in the barrierless regime at room temperature. The twisting of the bipy rings which may occur on going from the II,II to the II,III species points to the application of this and similar systems as 'molecular switches'.

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