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Syntheses and characterization of new mononuclear and dinuclear complexes derived from ruthenium polypyridines*

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Abstract

New complexes containing the Ru(bpy)(trpy)$^{2+}$ moiety (bpy = 2,2′-bipyridine; trpy = 2,2′:6′,2″-terpyridine) as a photosensitizer, 4-CNpy (=4-cyanopyridine) as a bridging ligand and Ru(NH$_3$)$_5{}^{n+}$ as an electron donor (n=2) or acceptor (n=3) capping group were synthesized and characterized by spectroscopic and electrochemical techniques. In the mononuclear complex [Ru^{II}(bpy)(trpy)(4-CNpy)]$^{2+}$ (I) IR, UV–Vis and cyclic voltammetry data (νCN(nitrile) = 2237 cm^{-1}; λ_{max} = 432 and 464 nm, in CH$_3$CN; E$_{1/2}$(Ru^{III}/Ru^{II}) = 1.23 V, in CH$_3$CN versus SCE) point to a pyridine-bonded isomer of 4-CNpy. In the bridged complex [Ru^{II}(bpy)(trpy)(4-CNpy)Ru^{II}(NH$_3$)$_5$]$^{4+}$ (II) the nitrile end of 4-CNpy coordinates to a capping Ru^{II}(NH$_3$)$_5$ group, as disclosed by the shifts in spectral absorptions (νCN(nitrile) = 2174 cm^{-1}; λ_{max} = 490 nm, in CH$_3$CN) and the occurrence of a new voltammetric wave ($E_{1/2}$ = 0.74 V, in CH$_3$CN versus SCE). A related bridged species, [Ru^{II}(bpy)(trpy)(4-CNpy)Fe^{II}(CN)$_5$]$^-$ (III) was obtained and characterized in aqueous solution (λ_{max} = 460 nm, in water). The mixed-valence complex [Ru^{II}(bpy)(trpy)(4-CNpy)Ru^{III}(NH$_3$)$_5$]$^{5+}$ (IV) can be prepared in CH$_3$CN solution (λ_{max} = 438 nm) by oxidation of **II** with Ce(IV); it presents a comproportionation constant $K_c = 2\times10^8$, thus indicating a high stability arising from the asymmetric nature of this species. The 'supramolecular' systems described in this work can be used as models for systematic studies of intramolecular electron transfers.

Introduction

Polynuclear complexes derived from ruthenium bipyridines and terpyridines are important in connection with the study of intramolecular electron (or energy) transfer processes, which may find application in energy conversion devices [1]. We report in this work the preparation and structural and electrochemical properties of new mononuclear and dinuclear complexes composed of the Ru(bpy)(trpy)$^{2+}$ moiety (bpy = 2,2′-bipyridine; trpy = 2,2′:6′,2″-terpyridine) as a photosensitizer group [2], 4-CNpy (= 4-cyanopyridine) as a bridging ligand and Ru(NH$_3$)$_5{}^{n+}$ as a capping group that can operate as a 'relay', i.e. as an electron donor (n = 2) or acceptor (n = 3). This is a part of continuing studies on supramolecular systems with 4-CNpy as an effective electronic conductor [3, 4]. Our aim is to develop a systematic way of determining the barriers to electron transfer in mixed-valence compounds by varying the structure of the bridged/bridging groups.

Experimental

Syntheses

Ru(trpy)Cl$_3$, prepared as in ref. 5, was used to obtain the precursor complex [Ru(bpy)(trpy)-Cl]Cl·3H$_2$O [6]. The new complex [Ru(bpy)(trpy)-(4-CNpy)]$^{2+}$ (I) was synthesized as a PF$_6{}^-$ salt by refluxing for 8 h [Ru(bpy)(trpy)Cl]Cl·3H$_2$O (0.3 g, 0.5 mmol) and excess 4-CNpy (0.5 g, 4.8 mmol) in 50 ml of a 1:1 ethanol–water mixture. The solution was cooled, evaporated, filtrated and then excess NH$_4$PF$_6$ (6 g in 40 ml of water) was added. The resulting precipitate was dissolved in acetone and sorbed onto a 3×6 cm column of SP-Sepadex C-25. The unreacted chloro complex was eluted with 0.1 M NaCl in acetone–water (1:1) solution. The desired complex was eluted with 0.3 M NaCl in a 1:1 acetone–water solution. It was further purified by dissolving in acetone and precipitating with ether. The salt was filtered, washed with ether and dried

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in a vacuum dessicator over P_4O_{10}. *Anal.* Found: C, 43, H, 3.1. Calc.: C, 42; H, 2.6%. Yield 0.25 g (60%).

The dinuclear complex $[Ru(bpy)(trpy)(4\text{-}CNpy)Ru(NH_3)_5]^{4+}$ (**II**) was obtained as a PF_6^- salt by mixing **I** (90 mg, 0.1 mmol) with a stoichiometric amount of $[Ru(NH_3)_5(H_2O)](PF_6)_2$, prepared as in ref. 7, at room temperature, in 30 ml of deaerated acetone for 4 h. Pure Ar was bubbled continuously through the solution. 75 ml of ether were added to precipitate the complex. Purification was achieved by dissolving in acetone and reprecipitating with ether.

The dinuclear ion $[Ru(bpy)(trpy)(4\text{-}CNpy)Fe(CN)_5]^-$ (**III**) was prepared in aqueous solution by mixing stoichiometric amounts of **I** and $[Fe(CN)_5(NH_3)]^{3-}$ (prepared as in ref. 8).

The mixed-valence ion $[Ru(bpy)(trpy)(4\text{-}CNpy)Ru(NH_3)_5]^{5+}$ (**IV**) was obtained in acetonitrile solution by adding stoichiometric amounts of Ce(IV) to **II** [9].

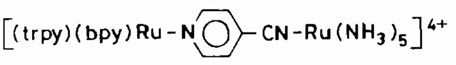
Instrumentation and techniques

All chemicals were reagent grade and used without further purification. CH_3CN was dried over molecular sieves for electrochemical measurements. Tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized three times from ethanol. IR spectra were obtained as KBr pellets in a Perkin-Elmer model 983G spectrophotometer. UV–Vis spectra were recorded on a Perkin-Elmer model Coleman 124 spectrophotometer. Conventional cyclic voltagramms were obtained with a L.Y.P. model M5 potentiostat/galvanostat, a L.Y.P. signal generator and a Hewlett-Packard X-Y recorder. A three-electrode conventional cell (with Pt as working and auxiliary electrodes and saturated potassium chloride calomel (SCE) as reference electrode) was used. CH_3CN was chosen as a solvent, 0.1 M TBAH as a supporting electrolyte and pure N_2 was bubbled prior to measurements. Chemical analyses were carried out at UMYMFOR, Universidad de Buenos Aires.

Results and discussion

IR spectra

Figure 1 shows the IR spectra of **I** and **II** as PF_6^- salts. The nitrile stretching frequency νCN of 4-CNpy appears at 2237 cm^{-1} for **I** and at 2174 cm^{-1} for **II**, which can be compared to the free ligand value of 2241 cm^{-1} [10]. Since the $Ru(NH_3)_5^{2+}$ moiety has an increased π-backbonding ability to a sixth ligand with respect to the $Ru(bpy)(trpy)^{2+}$ group (similar in properties to $Ru(bpy)_2^{2+}$, see ref. 4), coordination to L = nitrile should shift νCN(nitrile) to lower values. This fact points to coordination through the pyridine N of 4-CNpy in **I** and the following structure for **II**.



Because of sterical constraints, trpy usually adopts a meridional geometry [11], thus affording an explanation for the lack of steric hindrance in the pyridine-bonded isomer, in contrast to the case of 4-CNpy complexes of $Ru(bpy)_2^{2+}$ [4] and $Ru(NH_3)_5^{2+}$ [10], where the nitrile bound isomers are kinetically favored.

Bands characteristic of ligand (bpy, trpy, 4-CNpy) vibrations appear at 1468, 1450, 1391, 1288, 1246, 1165, 1127, 740, 732 and 558 cm^{-1} in the spectrum of **I** [4]. For complex **II**, the ammonia symmetric deformation mode $\delta_s(NH_3)$ appears at 1287 cm^{-1}, which is typical of a $Ru^{II}(NH_3)_5$ group [4, 12a].

UV–Vis spectra

Table 1 shows the UV–Vis absorption data of **I**, **II** and **IV** in CH_3CN solution and of **III** in aqueous solution. No spectral shifts were observed when 1 M HCl was added to a dilute aqueous solution of **I**, thus indicating no titratable protons, i.e. a pyridine bound structure for 4-CNpy, in agreement with IR data. The lowest MLCT (metal-to-ligand charge transfer) transition at 464 nm in **I** can be assigned to d_π (Ru) → π^* (trpy), as deduced from previous observations that trpy, with a more extended π system than bpy, should present more stable π^* orbitals and thus a lower excited energy state [13]. Besides, there is a correspondence with the first electrochemical reduction, as shown below. The broad band at 432 nm in **I** can be assigned to MLCT transitions from d_π orbitals of Ru(II) to π^* orbitals of bpy and 4-CNpy [4]. As already pointed out by Keene and co-workers [14], the position of the MLCT band of lowest energy in $[Ru(bpy)(trpy)L]^{n+}$ ions is rather insensitive to the nature of L, unless it is capable of substantial π-backbonding. Thus, for substituted pyridines, λ_{max} for this transition falls between pyridine (py) and benzonitrile (PhCN) and corresponds with the position of $E_{1/2}$ for the Ru(II) → Ru(III) oxidation, as shown in Table 2. The close similitude for the spectra for L = 4-CNpy and L = isonicotinamide [17] again indicates a pyridine bound isomer for **I**.

For complex **II**, the new band at 490 nm (Table 1) can be attributed to a MLCT transition from the capping Ru atom of a pentaammineruthenium(II) unit to a π^* orbital of 4-CNpy. A blue shift occurs with respect to the monomer species $[Ru(NH_3)_5(4\text{-}CNpy)]^{2+}$ (nitrile bound isomer; $\lambda_{max} = 425$ nm [4]), as expected from the inductive effect of the

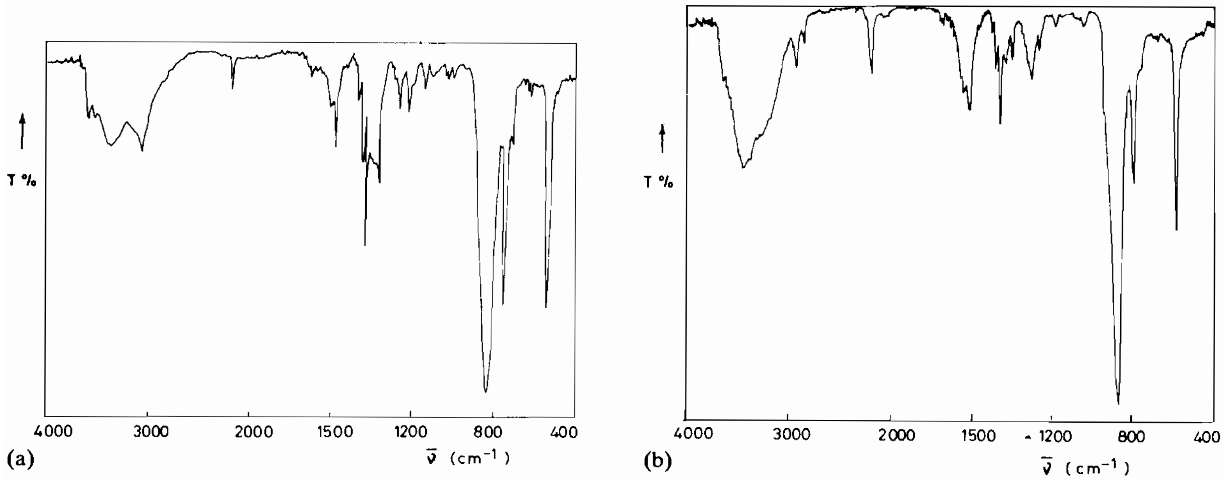


Fig. 1. IR spectra (as KBr pellets) of PF_6^- salts of (a) $[Ru(bpy)(trpy)(4\text{-}CNpy)]^{2+}$ and (b) $[Ru(bpy)(trpy)(4\text{-}CNpy)Ru(NH_3)_5]^{4+}$.

TABLE 1. Electronic absorption spectra of 4-CNpy complexes[a]

Complex	λ_{max} (nm)[b] ($10^{-3}\times\epsilon_{max}$ (M^{-1} cm^{-1}))[c]
$[Ru(bpy)(trpy)(4\text{-}CNpy)]^{2+}$ (**I**)	464sh (6.3), 432 (7.5), 380sh (4.0), 310 (20), 285 (21)
$[Ru(bpy)(trpy)(4\text{-}CNpy)Ru(NH_3)_5]^{4+}$ (**II**)	490 (8.0), 312 (15), 282 (17)
$[Ru(bpy)(trpy)(4\text{-}CNpy)Fe(CN)_5]^-$ (**III**)[d]	460 (10)
$[Ru(bpy)(trpy)(4\text{-}CNpy)Ru(NH_3)_5]^{5+}$ (**IV**)[e]	438 (5.0)

[a] In CH_3CN at 22 °C, unless otherwise stated. [b] Error: ±2 nm. [c] Error: ±5%. [d] In aqueous solution. [e] Generated by oxidation of **II** by Ce(IV).

TABLE 2. MLCT absorptions of lowest energy and $E_{1/2}$ values for the Ru^{III}/Ru^{II} couple in $[Ru(bpy)(trpy)L]^{n+}$ complexes

L	λ_{max} (nm)	$E_{1/2}$ (V, vs, SCE)[a]	Reference
NH_3	482	1.02	14
Cl^-	479	1.09	14
H_2O	476	1.08	14
$NH{=}CMe_2$	474	1.10	14
py	468	1.22	15
4-CNpy	464	1.23	this work
$S(CH_3)_2$	454	1.32	16
PhCN	449	1.34	14

[a] In CH_3CN, at 22 °C.

$Ru(bpy)(trpy)^{2+}$ moiety [4, 10]. For complex **III**, an analogous band appears at 460 nm, corresponding to a d_π (Fe) → π^* (4-CNpy) transition, also displaced to the blue with respect to the monomer species (λ_{max} = 405 nm [12b]).

Oxidation of **II** with Ce(IV) gives complex **IV**, which presents a spectrum similar to that of **I**. The occurrence of a capping Ru(III) causes the disappearance of the MLCT band of 490 nm (which can be restored by adding Sn(II)). No MMCT (metal-to-metal charge transfer) absorptions were detected in the visible region for **IV**. Further investigation in the near IR might be necessary to find these transitions. For $L = CN^-$, however, a band at ≈690 nm (in H_2O) was found; studies are in progress in order to confirm its assignment to a MMCT transition.

For all complexes, UV bands can be assigned to $\pi \rightarrow \pi^*$ (bpy, trpy, 4-CNpy) intraligand transitions [4, 18].

Complex **I** is not luminiscent at room temperature. This reduced quantum yield can be explained by rapid deactivation to low-lying available d–d states [18].

Electrochemistry

Figure 2 shows the voltammogram of **I** in CH_3CN, 0.1 M TBAH, 25 °C, sweep rate = 200 mV/s. The $E_{1/2}$ values were obtained from the formula $E_{1/2} = (E_a + E_c)/2$. The ΔE_p values ($\geqslant$80 mV) were higher than the theoretical ones for reversible processes; this could be due to solution resistance [19]. There is only one oxidation wave, with $E_{1/2} = 1.23$ V, attributable to the process Ru(II) → Ru(III). This value corresponds well with absorption data of a pyridine bound isomer, as disclosed in Table 2. The $E_{1/2}$ values

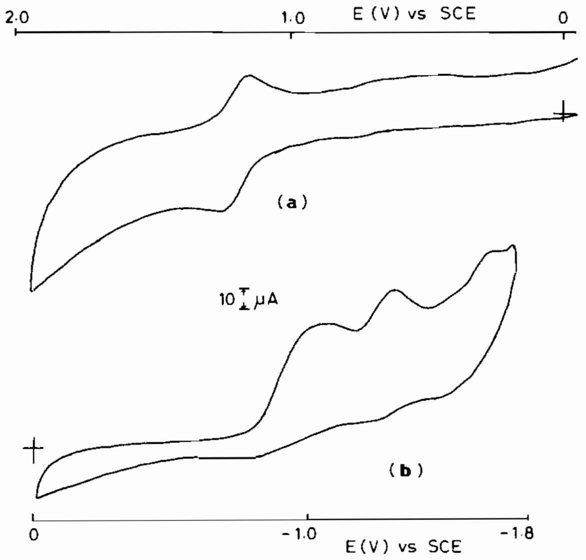


Fig. 2. Oxidative (a) and reductive (b) cyclic voltammograms of $[Ru(bpy)(trpy)(4\text{-}CNpy)]^{2+}$ in CH_3CN, at 22 °C, $v = 200$ mV s^{-1}. The wave at *c.* −0.89 V may be due to dissolved oxygen.

for ligand reduction appear at −1.29 and −1.59 V, which can be assigned to bpy and trpy reductions, respectively [4, 13], according to a decreasing π-backbonding ability.

For complex **II**, a value of 1.25 V was obtained for $E_{1/2}$ of the Ru^{II}/Ru^{III} polypyridine couple, very similar to that of the parent complex **I**. An additional oxidation wave was observed, with $E_{1/2} = 0.74$ V, attributed to the Ru^{II}/Ru^{III} ammine couple. The corresponding value for the mononuclear complex $[Ru(NH_3)_5(4\text{-}CNpy)]^{2+}$ (nitrile bonded) is 0.56 V [4]. The shift of ≈ 0.2 V is due to increased charge in the dinuclear complex. From the equation

$$K_c = \exp(\Delta E°/25.69)$$

at 25 °C with $\Delta E°$ in mV [20] a high comproportionation constant results: $K_c = 2 \times 10^8$, indicating high stability for the mixed-valence species. This extra stability arises not through valence delocalization but from the asymmetric nature of the system.

Conclusions

New stable complexes with Ru(II) polypyridines can be obtained with 4-CNpy as a conducting bridge and $Ru(NH_3)_5^{n+}$ (or $Fe(CN)_5^{3-}$) as either an electron acceptor ($n = 3$) or donor ($n = 2$) group. They can be characterized in the solid state and in solution by spectroscopic and electrochemical techniques. The mixed-valence systems can be used as models for studies on intramolecular electron transfers.

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