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Synthesis, spectroscopic and electrochemical characterization and molecular structure of polypyridyl ruthenium complexes containing 4,4'-azobis(pyridine)

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ABSTRACT

New coordination compounds of formulae: $[Ru(trpy)(bpy)(4,4'-azpy)]^{2^+}$, **1**, $[Ru(tpm)(bpy)(4,4'-azpy)]^{2^+}$, **2**, $[(trpy)(bpy)Ru(4,4'-azpy)Ru(NH_3)_5]^{4^+}$, **3**, and $[(trpy)(bpy)Ru(4,4'-azpy)Ru(bpy)(trpy)]^{4^+}$, **5**, with trpy = 2,2'.6',2''-terpyridine, tpm = tris(1-pyrazolyl)methane), bpy = 2,2'-bipyridine and 4,4'-azpy = 4,4'-azobis(pyridine), have been synthesized as PF₆⁻ salts and characterized by spectroscopic and electrochemical techniques. The structure of the cation $[Ru(trpy)(bpy)(4,4'-azpy)]^{2^+}$ has been determined by X-ray diffraction analysis, which reveals a *trans*-configuration of coordinated 4,4'-azpy and a packing structure that is based on extensive π -interactions within neighboring molecules. Upon controlled potential electrolysis of the dinuclear $[Ru^{II}, Ru^{II}]$ complex **3**, a stable $[Ru^{II}, Ru^{III}]$ mixed-valent species, **4**, was detected. From spectral data and Gaussian deconvolution analysis of the intervalence transition in **4**, a strong electronic interaction between both ruthenium centers is disclosed ($H_{AB} = 550 \text{ cm}^{-1}$), pointing to possible applications of 4,4'-azpy as a conducting bridge in "molecular wires".

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1. Introduction

The ligand 4,4'-azobis(pyridine), or 4,4'-azpy, can act as an effective bridge connecting two metal centers in ruthenium ammines and ruthenium porphyrins [1,2]. The presence of the azo group makes this ligand a promising conductor through electronic coupling, while the possibility of protonation and/or isomerization, such as those studied in ferrocenylazobenzenes [3], is important in the design of "molecular switches". Moreover, the π - π stacking effects caused by the planar structure of this ligand lead to interesting supramolecular structures with potential applications in host-guest chemistry [4–7]. On the other hand, polypyridyl ruthenium(II) complexes have been extensively studied in association with fundamental energy and electron transfer processes relevant in the design of solar energy conversion schemes used, for example, in dye-sensitized solar cells [8].

In this work, we describe the synthesis and structural, spectroscopic and electrochemical characterization of the following new polypyridyl ruthenium complexes containing 4,4'-azobis(pyridine): the PF₆⁻ salts of the mononuclear complexes [Ru(trpy)(bpy)(4,4'-azpy)]²⁺, **1**, and [Ru(tpm)(bpy)(4,4'-azpy)]²⁺, **2**, with trpy = 2,2':6',2"-terpyridine, tpm = tris(1-pyrazolyl)methane, and bpy = 2,2'-bipyridine, as well as the PF_6^- salts of the dinuclear complexes [(trpy)(bpy)Ru(4,4'-azpy)Ru(NH₃)₅]⁴⁺, **3**, and [(trpy)(bpy)Ru(4,4'-azpy)Ru(bpy)(trpy)]⁴⁺, **5**. The mixed-valent species [(trpy)(bpy)Ru(4,4'-azpy)Ru(NH₃)₅]⁵⁺, **4**, has been obtained by controlled potential electrolysis of **3** in solution. We intended to elucidate the transmission properties of 4,4'-azpy as a bridge by comparing it to other nitrogen heterocycles without azo groups that were used before as bridging ligands in ruthenium polypyridyl complexes [9–12]. Scheme 1 shows the structures of the ligands used in this work.

2. Experimental

2.1. Techniques and equipment

All chemicals used in this work were analytical-reagent grade. CH_3CN was freshly distilled over P_4O_{10} and dried over molecular sieves for electrochemical measurements. UV–Vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer, using 1-cm quartz cells. Infrared spectra were obtained as KBr pellets, with a Perkin–Elmer Spectrum RX-1 FTIR spectrometer. Electrochemistry experiments were carried out using a BAS Epsilon EC equipment, with vitreous C as working electrode, Pt wire as auxiliary



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Scheme 1.

electrode, and Ag/AgCl (3 M KCl) as reference electrode. All solutions were prepared in CH₃CN, with 0.1 M TBAH (tetrakis-n-butylammonium hexafluorophosphate) as the supporting electrolyte, and thoroughly degassed with argon, prior to each experiment. Cyclic voltammograms were run at a sweep rate of 100 mV s^{-1} . The reported $E_{1/2}$ values were calculated as the average value between the peak values corresponding to the cathodic (E_c) and anodic (E_a) waves: $E_{1/2} = (E_c + E_a)/2$. Controlled potential electrolysis were performed using an OTTLE cell from BAS at a fixed potential of 800 mV, in CH₃CN (0.1 M TBAH), for 10 min. All NMR spectra were obtained in CD₃CN with a Bruker 500 MHz Avance spectrometer. 2D ¹H-¹H COSY and NOESY (mixing time 500 ms) and 2D ¹H-¹³C HSQC and HMBC experiments were collected in order to unambiguously assign both ¹H and ¹³C spectra. 2D ¹H-¹⁵N HMBC were also recorded to obtain ¹⁵N chemical shifts of all ¹⁵N non-protonated centers. Chemical analyses were carried out at INQUIMAE, University of Buenos Aires, Buenos Aires, Argentina, with an estimated error of ±0.5%.

2.2. X-ray crystallographic study

 $C_{35}H_{27}N_9Ru_1 \cdot 0.85PF_6^- \cdot 0.15CF_3SO_3^- \cdot$ Crystal data for 0.5CH₃CN, 987.37 g mol⁻¹, monoclinic, P2/n, a = 14.5890(12) Å, b = 10.7663(9) Å, c = 24.948(2) Å, $\beta = 94.491(2)^{\circ}$, V = 3906.5(6) Å³, Z = 2, $\rho_{calcd} = 1.679 \text{ Mg/m}^3$, $R_1 = 0.0535$ (0.0794), $wR_2 = 0.1365$ (0.1517), for 14825 reflections with $I > 2\sigma(I)$ (for 19631 reflections $[R_{int}: 0.0513]$ with a total measured of 69467 reflections), goodness-of-fit on F^2 = 1.081, largest diff. peak (hole) = 2.277 (-1.790) e Å⁻³. Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with Mo K α radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (*T* = -173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection APEX2 V. 1.0-22 (Bruker-Nonius 2004), data reduction saint+ Version 6.22 (Bruker-Nonius 2001), absorption correction sadabs V. 2.10 (2003) and SHELXTL Version 6.10 (Sheldrick, 2000).

2.3. Syntheses

The ligand 4,4'-azo(bis)pyridine was synthesized following a procedure reported in the literature [1]. The precursor [Ru(trpy)-(bpy)(H₂O](PF₆)₂ was obtained according to known methods [13].

2.3.1. [Ru(trpy)(bpy)(4,4'-azpy)](PF₆)₂ · H₂O, **1**(PF₆)₂ · H₂O

Seventy two milligrams (0.09 mmol) of the known complex $[Ru(trpy)(bpy)(H_2O](PF_6)_2$ were dissolved in acetone (36 mL), to-

gether with 165 mg (0.9 mmol) of 4,4'-azpy. After heating at reflux and stirring for 2 h, the solution was evaporated to ca. 10 mL, cooled at room temperature and then diethyl ether (100 mL) was added. The dark red precipitate formed after chilling overnight was removed by filtration, washed with diethyl ether and passed over a Sephadex LH-20 column with a CH₃CN/CH₂Cl₂ (1:1 v/v) mixture. The third eluted red band was rotoevaporated to 5 mL and then precipitated with NH_4PF_6 (2 g/20 mL of H_2O). The obtained red solid was removed by filtration, washed with ether, dried and stored under vacuum over P_4O_{10} for 1 day. Yield: 34 mg (38%). Anal. Calc. for C₃₅H₂₉N₉OP₂F₁₂Ru (982.67): C, 42.8; H, 3.0; N, 12.8. Found: C, 42.5; H, 3.0; N, 12.7%. ¹H NMR (CD₃CN, 500.13 MHz): δ = 8.86 (dd, J = 4.6 and 1.5 Hz, 2H, H_D), 8.78 (ddd, *J* = 5.2, 1.4 and 0.7 Hz, 1H, H₁₅), 8.71 (ddd, *J* = 8.0, 1.5 and 0.7 Hz, 1H, H_{12}), 8.57 (d, J = 8.15 Hz, 2H, H_9 and H_{11}), 8.48 (ddd, J = 8.1, 1.3 and 0.7 Hz, 2H, H₄ and H₅), 8.45 (ddd, *J* = 8.0, 1.3 and 0.7 Hz, 1H, H₁₇), 8.36 (dt, *J* = 8.0 and 1.5 Hz, 1H, H₁₃), 8.26 (t, *J* = 8.15, 1H, H_{10}), 8.08 (ddd, I = 8.1, 7.5 and 1.4 Hz, 2H, H_3 and H_6), 7.99 (dd, J = 5.5 and 1.5 Hz, 2H, H_A), 7.87 (ddd, J = 8.0, 5.2 and 1.3 Hz, 1H, H₁₄), 7.86 (ddd, *J* = 8.0, 7.5 and 1.3 Hz, 1H, H₁₈), 7.84 (ddd, *J* = 5.5, 1.4 and 0.7 Hz, 2H, H₁ and H₈), 7.72 (dd, *J* = 4.6 and 1.5 Hz, 2H, H_{c}), 7.58 (dd, J = 5.5 and 1.5 Hz, 2H, H_{B}), 7.46 (ddd, J = 7.5, 5.5 and 1.3 Hz, 2H, H₂ and H₇), 7.31 (ddd, *J* = 5.5, 1.3 and 0.7 Hz, 1H, H_{20}), 7.12 (ddd, I = 7.3, 5.5 and 1.3 Hz, 1H, H_{19}) ppm.

¹³C NMR (CD₃CN, 100.62 MHz) δ = 159.1 (C_{4a} and C_{5a}), 158.5 (C_{9a} and C_{11a}), 158.1 (C_{17a}), 157.8 (C_{B'}), 157.4 (C_{C'}), 157.2 (C_{12a}), 155.4 (C_A), 154.1 (C₁ and C₈), 152.8 (C_D), 152.7 (C₁₅), 152.2 (C₂₀), 139.7 (C₃ and C₆), 138.8 (C₁₃), 138.5 (C₁₈), 137.3 (C₁₀), 129.6 (C₂ and C₇), 128.6 (C₁₄), 127.7 (C₁₉), 126.0 (C₄ and C₅), 125.5 (C₁₂), 124.9 (C₉ and C₁₁), 124.6 (C₁₇), 119.3 (C_B), 117.0 (C_C) ppm.

2.3.2. $[Ru(tpm)(bpy)(4,4'-azpy)](PF_6)_2 \cdot 3H_2O, 2(PF_6)_2 \cdot 3H_2O)$

Fifty five milligrams (0.07 mmol) of the precursor [Ru(tpm)- $(bpy)(H_2O)](PF_6)_2$ were dissolved in acetone (28 mL) together with an excess of 4,4'-azpy (128 mg, 0.7 mmol). After heating under reflux and stirring for 3 h, the solution was evaporated to ca. 10 mL, cooled at room temperature and then diethyl ether (100 mL) was added. After keeping in the refrigerator for 24 h, the dark red precipitate was removed by filtration and washed with diethyl ether $(2 \times 10 \text{ mL})$, dried and stored under vacuum over P₄O₁₀ for 1 day. Yield: 62 mg (89%). Anal. Calc. for C₃₀H₃₂N₁₂O₃P₂F₁₂Ru (999.66): C, 36.0; H, 3.2; N, 16.8. Found: C, 35.7; H, 2.7; N, 16.6%. ¹H NMR $(CD_3CN, 500.13 \text{ MHz})$: $\delta = 9.08$ (s, 1H, H₄), 8.86 (dd, I = 1.6 and 4.6 Hz, 2H, H_D), 8.80 (ddd, I = 8.2, 1.3, and 0.7 Hz, 2H, H₁₂ and H_{17}), 8.65 (ddd, J = 5.7, 1.5 and 0.7 Hz, 2H, H_{15} and H_{20}), 8.57 (dd, J = 2.9 and 0.5 Hz, 2H, H₁ and H₅), 8.39 (dd, J = 2.9 and 0.7 Hz, 1H, H₈), 8.24 (ddd, *J* = 8.2, 7.7, and 1.6 Hz, 2H, H₁₃ and H₁₈), 8.00 (dd, *J* = 2.3 and 0.5 Hz, 2H, H₃ and H₇), 7.73 (dd, *J* = 4.6 and 1.6 Hz, 2H, H_{C}), 7.72 (dd, J = 5.5 and 1.6 Hz, 2H, H_{A}), 7.56 (ddd, J = 7.7, 5.6 and 1.3 Hz, 2H, H₁₄ and H₁₉), 7.51 (dd, J = 5.5 and 1.6 Hz, 2H, H_B), 6.79 (dd, J = 2.9 and 2.3 Hz, 2H, H₂ and H₆), 6.61 (dd, J = 2.3 and 0.7 Hz, 1H, H₁₀), 6.32 (dd, J = 2.9 and 2.3 Hz, 1H, H₉) ppm. ¹³C NMR (CD₃CN, 100.62 MHz): δ = 158.6 (C₁₁ and C₁₆), 157.6 (C_C), 157.5 ($C_{B'}$), 156.1 (C_A), 154.0 (C_{15} and C_{20}), 152.7 (C_D), 148.5 (C_3 and C₅), 144.8 (C₁₀), 139.0 (C₁₃ and C₁₈), 136.7 (C₁ and C₇), 136.6 (C_8), 127.5 (C_{14} and C_{19}), 126.0 (C_{12} and C_{17}), 118.2 (C_B), 117.0 (C_C), 110.9 (C₂ and C₆), 109.6 (C₉), 77.0 (C₄) ppm.

2.3.3. $[(trpy)(bpy)Ru(4,4'-azpy)Ru(NH_3)_5](PF_6)_4 \cdot 10H_2O,$ **3** $(PF_6)_4 \cdot 10H_2O$

A solution of **1** $(PF_6)_2 \cdot H_2O$ (60 mg, 0.062 mmol) in acetone (15 mL) was purged with argon for 30 min. The other precursor $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (30 mg, 0.062 mmol), prepared as described before [14], was added to this solution under argon, and the resulting mixture was stirred in darkness, for 2 h, under argon. Deaerated diethyl ether (100 mL) was added and the cloudy solution

was stored in the refrigerator overnight. The red precipitate that formed was removed by filtration, washed with diethyl ether (2 × 10 mL), sorbed onto a Sephadex LH-20 column and eluted with a CH₃CN/CH₂Cl₂ (1:1 v/v) solution. The second eluted portion (green) was collected, concentrated to *ca*. 5 mL under reduced pressure and precipitated with diethyl ether (50 mL). The dark green solid was removed by filtration, washed with diethyl ether, dried and stored under vacuum over P_4O_{10} for 1 day. Yield: 16 mg (16%). *Anal.* Calc. for $C_{35}H_{62}N_{14}O_{10}P_4F_{24}Ru_2$ (1620.96): C, 25.9; H, 3.9; N, 12.1. Found (mean of several determinations): C, 25.5; H, 3.5; N, 12.8%.

2.3.4. [(trpy)(bpy)Ru(4,4'-azpy)Ru(bpy)(trpy)](PF₆)₄ · 2H₂O, **5**(PF₆)₄ · 2H₂O

211 mg (0.26 mmol) of $[Ru(trpy)(bpy)(H_2O)](PF_6)_2$ were dissolved in acetone (50 mL) together with 4,4'-azpy (24 mg, 0.13 mmol). After heating under reflux and stirring for 15 h, the solution was cooled at room temperature, evaporated to *ca*. 5 mL and precipitated with diethyl ether (50 mL). After keeping in the refrigerator for 24 h, the dark red precipitate was filtered and

H

washed with diethyl ether (2 × 10 mL). Purification was accomplished by chromatography over Sephadex LH-20, using a CH₃CN/CH₂Cl₂ (1:1 v/v) solution as eluent and collecting only the first of the two obtained fractions. After precipitation with diethyl ether and filtration, the red solid was dried and stored under vacuum over P₄O₁₀ for 1 day. Yield: 38 mg (8%). *Anal.* Calc. for C₆₀H₅₀F₂₄N₁₄O₂P₄Ru₂ (1781.14): C, 40.5; H, 2.8; N, 11.0. Found: C, 40.7; H, 2.9; N, 10.7%.

3. Results and discussion

3.1. Syntheses and IR spectra

The synthetic procedures used in this work are slight modifications of techniques previously developed in our laboratories [11,12]. The IR spectra of all synthesized complexes display characteristic vibrational modes of the polypyridyl ligands (trpy, tpm, bpy and 4,4'-azpy). Besides, a typical ammonia symmetric deformation mode $\delta_{\text{sym}}(\text{NH}_3)$ appears in the IR spectrum of the PF₆⁻ salt of complex **3** at 1270 cm⁻¹, which clearly evidenced a localized oxidation







state (II) for the ammine-bonded Ru atom [10], as shown in Supplementary Fig. 1. The presence of water is also disclosed by the

broad band appearing at 1624 cm^{-1} corresponding to H–O–H bending vibrations.









Fig. 2. (A) ORTEP diagram (ellipsoids at 70% probability) for the cationic moiety of **1**, with labelling scheme for N atoms. Hydrogen atoms are omitted in the sake of clarity. (B) View of the crystal packing of **1** showing the cationic and anionic 2D layers. (C) View of the two-dimensional layer formed by the cationic part of the complex showing the intermolecular π interactions marked with colored backgrounds (see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. NMR spectra

Compounds **1** and **2** show well dispersed ¹H NMR spectra in the region between 6 and 9 ppm. As an example, Fig. 1 shows the ¹H–¹H COSY spectra of complex **1** in CD₃CN. Besides, the presence of a symmetry plane simplifies a little bit the NMR spectra: in **1** the plane incorporates the 4,4'-azpy and bpy ligands, whereas in **2** the plane includes the 4,4'-azpy ligand and splits the tmp and bpy ligands in two symmetric moieties. Two-dimensional homonuclear COSY and NOESY spectra, together with ¹³C and ¹⁵N HSQC and HMBC spectra allowed the complete assignment of the signals, as stated in Section 2. The knowledge of the ¹⁵N chemical shifts permitted a precise distinction between linked and non-linked connectivities in multicoordinated N-ligands, as discussed before [15].

3.3. Solid state structure

Crystals suitable for X-ray diffraction of $1(PF_6)_{1.70}(CF_3SO_3)_{0.30} \cdot 0.5CH_3CN$ were obtained by slow diffusion of ether into a concentrated acetone solution of $1(PF_6)_2$ in the presence of NaCF_3SO_3 and a small amount of CH_3CN. An ORTEP diagram of the cation is shown in Fig. 2A. A *trans*-structure of the 4,4'-azpy ligand is disclosed, as already observed in polymeric structures incorporating this ligand [6]. The Ru metal center displays a distorted octahedral coordination with Ru–N bond distances within the range 1.97–2.09 Å (see Table 1), similar to those obtained for related complexes indicating the presence of a strong $d_{\pi}(Ru) \rightarrow \pi^*(L)$ backbonding [16]. The pyridylic groups of the three ligands are significantly away from planarity with relative rotation angles of 12.6° for bpy, 13.2° for 4,4'-azpy and 15.2° for the peripheral pyridyls of trpy.

In the crystal packing it can be observed that the cationic and anionic parts are forming two-dimensional layers which are contacting through weak interactions (CH-groups with fluorine atoms in the case of PF_6^- , see Fig. 2B). The counter anions are disordered in a proportion 0.85:0.15 (PF_6^- : $CF_3SO_3^-$) occupying exactly the same positions. The cationic part of the crystal has a packing structure that is based on extensive π -interactions within neighboring molecules. In the 3D arrangement represented in Fig. 2C, neighboring azpy ligands are showing a π - π stacking (azo double bond-pyridy) ring with a centroid-centroid distance of 3.5 Å, blue background). Furthermore, this dimer type of arrangement interacts with neighboring dimers via bpy-bpy $\pi - \pi$ (shortest distance of 3.6 Å, green background) and bpy-trpy C-H··· π ($d_{\text{H-centroid}}$ = 3.3 Å, violet background) contacts. Besides, trpy ligands are having $\pi - \pi$ interactions with neighboring trpy ligands (shortest distance 3.6 Å, brown background) and C-H $\cdots\pi$ interactions with azpy ligands

Table	e 1	

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Bond distances (Å)	Angles (°)
Ru1 N2 1.9705(14)	N2 Ru1 N4 95.91(6)
Ru1 N4 2.0601(14)	N2 Ru1 N1 79.69(6)
Ru1 N1 2.0751(15)	N4 Ru1 N1 93.18(6)
Ru1 N3 2.0837(14)	N2 Ru1 N3 79.46(6)
Ru1 N5 2.0858(14)	N4 Ru1 N3 85.21(6)
Ru1 N6 2.0910(14)	N1 Ru1 N3 158.81(6)
	N2 Ru1 N5 173.80(6)
	N4 Ru1 N5 78.76(6)
	N1 Ru1 N5 97.34(6)
	N3 Ru1 N5 103.04(6)
	N2 Ru1 N6 90.32(6)
	N4 Ru1 N6 171.95(6)
	N1 Ru1 N6 92.94(5)
	N3 Ru1 N6 90.95(6)
	N5 Ru1 N6 95.28(6)

 $(d_{\text{H-centroid}} = 3.3 \text{ Å}$, yellow background). Finally, the acetonitrile molecules are packing between the metallorganic molecules generating π - π interactions with four pyridyl rings of two trpy and two azpy ligands ($d_{\text{acetonitrile-trpy}} = 3.3 \text{ Å}$ and $d_{\text{acetonitrile-azpy}} = 2.9 \text{ Å}$; red background).

3.4. UV–Vis spectroscopy

The UV-Vis spectra in CH₃CN of all complexes synthesized in this work are shown in Table 2. Fig. 3 shows the UV-Vis spectrum of complex **1** as a representative example. In all cases, the bands between 200 and 300 nm are assigned to intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the polypyridyl ligands (trpy, bpy and 4,4'-azpy). The lowest energy band in complex **1** (λ_{max} = 456 nm) can be assigned to overlapping metal-to-ligand charge transfer (MLCT) transitions $d_{\pi}(Ru) \rightarrow \pi(trpy), d_{\pi}(Ru) \rightarrow \pi(bpy)$ and $d_{\pi}(Ru) \rightarrow \pi(4,4'$ azpy). In related $[Ru(trpy)(bpy)(L)]^{2+}$ complexes, with L = pz, 4,4'bpy and BPE (pz = pyrazine; 4,4'-bpy = 4,4'-bipiridine; BPE = trans-1,2-bis(4-pyridyl)ethylene), the lowest energy MLCT transitions appear at λ_{max} = 464, 466 and 479 nm, respectively [9,10]. The shift to lower wavelengths detected in **1** points to 4,4'-azpy being the acceptor ligand L with the strongest electron withdrawing effect in the series, similar to that of pz. On the other hand, complex **2** showed two lowest energy bands at λ_{max} = 416 nm and 488 nm, as shown in Table 2, which can be assigned to $d_{\pi}(Ru) \rightarrow \pi_1^{*}(bpy)$ and overlapping $d_{\pi}(Ru) \rightarrow \pi_2^{*}(bpy)$ and $d_{\pi}(Ru) \rightarrow \pi^{*}(4,4'$ -azpy) MLCT transitions, respectively, by comparison to related $[Ru(tpm)(bpy)(L)]^{2+}$ complexes, with L = pz, 4,4'-bpy and BPE [11]. In this case, the strongest electron acceptor character of 4,4'-azpy is evidenced by the highest shift recorded for the lowest energy band.

The dinuclear asymmetric complex **3** revealed two lowest energy bands at λ_{max} = 459 nm and 738 nm, which can be readily assigned to MLCT transitions $d_{\pi}(Ru_b) \rightarrow \pi^*(trpy, bpy, 4,4'-azpy)$ and $d_{\pi}(Ru_a) \rightarrow \pi^*(4,4'-azpy)$, with Ru_b = Ru bonded to bpy and Ru_a = Ru

Table 2Electronic absorption data of complexes 1-5, in CH₃CN

Complex	λ_{max} , nm (10 ⁻³ ε_{max} , M ⁻¹ cm ⁻¹)
$[Ru(trpy)(bpy)(4.4'-azpy)]^{2+}$	231 (23.8), 242 (23.0), 286 (42.8), 309 (35.7), 456 (12.5)
$[Ru(tpm)(bpv)(4.4'-azpv)]^{2+}$	235 (12.8), 254 (14.4), 286 (31.5), 416 (5.2), 488 (6.8)
[(trpy)(bpy)Ru(4,4'-	243 (19.9), 286 (36.4), 309 (30.2), 459 (9.5), 738 (12.6)
$azpy)Ru(NH_3)_5]^{4+}$	
[(trpy)(bpy)Ru(4,4'-	242 (28.8), 286 (43.8), 309 (37.0), 456 (12.3), 557 (3.1),
$azpy)Ru(NH_{3})_{5}^{5+}$	670 (1.8)
[(trpy)(bpy)Ru(4,4'-	242 (27.5), 286 (47.0), 310 (38.6), 458 (13.9), 512 sh
azpy)Ru(bpy)(trpy)] ⁴⁺	





bonded to NH₃, respectively. The previously reported mononuclear species $[Ru(NH_3)_5(4,4'-azpy)]^{+2}$ absorbs at $\lambda_{max} = 645$ nm in CH₃CN [1], while the dinuclear species $[(NH_3)_5Ru^{II}(4,4'-azpy)Ru^{II}(NH_3)_5]^{4+}$ has $\lambda_{max} = 710 \text{ nm} [1]$, a value similar to that of complex **3**, thus evidencing a comparable electronic distribution. A spectrophotometric titration of **3** was performed by using Br₂ in CH₃CN. After adding a stoichiometric amount of Br₂, the band at λ_{max} = 738 nm disappeared. The same behavior was observed in a controlled potential electrolysis of 3, as shown in Fig. 4. After applying a potential of 800 mV during 10 min, only the ammine-bonded Ru_{a} undergoes oxidation to give the mixed-valent species 4, of formula: $[(trpy)(bpy)Ru_b^{II}(4, 4'-azpy)Ru_a^{III}(NH_3)_5]^{5+}$. The reversibility of the process confirms the identity of complex 4. Gaussian deconvolution of the UV-Vis spectrum of 4 in the region 400-1000 nm, shown as Supplementary Fig. 2, gives $\lambda_{max} = 670 \text{ nm}$ for the lowest-energy band, which can be assigned to the intervalence or metal-to-metal charge transfer (MMCT) transition: $[Ru_b^{II}, Ru_a^{III}] \rightarrow$ $[Ru_h^{III}, Ru_a^{II}]$, since the same transition appears at $\lambda_{max} \simeq 640$ nm in the corresponding 4,4'-bpy-bridged mixed-valent complex [9].

The dinuclear symmetric complex **5** displays an UV–Vis spectrum very similar to that of the mononuclear species **1**, as shown in Table 2. However, a new shoulder appears at $\lambda_{max} \cong 512$ nm, which can be ascribed to the $d_{\pi}(Ru) \rightarrow \pi^{*}(4,4'$ -azpy) MLCT transition, shifted to lower energies as compared to **1**, because of increased electronic delocalization.

3.5. Electrochemistry

The cyclic voltammograms for **1** and **2** display very similar redox potentials associated with the couple $\text{Ru}_{b}^{\text{III}}/\text{Ru}_{b}^{\text{II}}$, as displayed in Table 3. Fig. 5 shows the CV of complex **1** as a representative example. In both complexes (**1** and **2**), reversible oxidation wave were observed at $E_{1/2} = 1.27$ V and $E_{1/2} = 1.22$ V, respectively (versus SCE). The first one is intermediate between the values obtained for the corresponding Ru couples in the related complexes [Ru(trpy)(bpy)(pz)]²⁺ and [Ru(trpy)(bpy)(4,4'-bpy)]²⁺ ($E_{1/2} = 1.34$ and 1.23 V, respectively, versus SCE) [9,10], while the second one is intermediate between those of [Ru(tpm)(bpy)(pz)]²⁺ and [Ru(tpm)(bpy)(4,4'-bpy)]²⁺ ($E_{1/2} = 1.34$ and 1.21 V, respectively, versus SCE) [11].

The dinuclear complex **3** shows two reversible waves in the oxidative range of potentials. The redox potential of the Ru_b^{II}/Ru_b^{I} couple ($E_{1/2} = 1.27$ V) is the same as that recorded for the mononuclear species **1**, while the redox potential of the Ru_a^{III}/Ru_a^{II} couple ($E_{1/2} = 0.45$ V), lies again intermediate between the values reported for the related dinuclear complexes [(trpy)(bpy) $Ru_b^{II}(pz)Ru_a^{II}$ (NH₃)₅]⁴⁺



Fig. 4. Controlled potential electrolysis of complex **3**, in CH₃CN ($C = 1.1 \times 10^{-5}$ M), at 800 mV. The arrow indicates increasing times from 0 to 10 min. Each spectrum was taken every minute.

Table 3

Electrochemical data for complexes 1-5, in CH₃CN, at v = 100 mV/s

Complex	Process	E_{ν_2} (V) (ΔE , mV) ^a
[Ru(trpy)(bpy)(4,4'-azpy)] ²⁺	Ru ^{3+/2+} 4,4'-azpy ^{0/-} trpy ^{0/-} bpy ^{0/-}	1.27 (89) -0.58 (80); -0.98(i) -1.36 (83) -1.69 (88)
[Ru(tpm)(bpy)(4,4'-azpy)] ²⁺	Ru ^{3+/2+} 4,4'-azpy ^{0/-} bpy ^{0/-}	1.22 (96) -0.64 (70); -0.86 (i) -1.62 (96)
[(trpy)(bpy)Ru _b ^{II} (4,4'-azpy)Ru _a ^{II} (NH ₃) ₅] ⁴⁺	$\begin{array}{l} Ru_b^{3+/2+} \\ Ru_a^{3+/2+} \\ 4,4'\text{-}azpy^{0/-} \\ trpy^{0/-} \\ bpy^{0/-} \end{array}$	1.27 (70) 0.45 (109) -0.55 (127); -0.92(i) -1.34 (76) -1.66 (165)
[(trpy)(bpy)Ru ^{II} (4,4'- azpy)Ru ^{II} (bpy)(trpy)] ⁴⁺	Ru ^{3+/2+} 4,4'-azpy ^{0/-} trpy ^{0/-} bpy ^{0/-}	1.27 (127) -0.39(104); -0.82 (126) -1.37(135) -1.73(88)

^a $E_{1/2}$ values are referred to SCE.



Fig. 5. Cyclic voltammogram of complex **1**, in CH₃CN, 0.1 M TBAH, at v = 100 mV/s. *E* values are referred to Ag/AgCl.

 $(E_{1/2} = 0.66 \text{ V}$ versus SCE) and $[(\text{trpy})(\text{bpy})\text{Ru}_{\text{b}}^{\text{II}}$ (4,4'-bpy) $\text{Ru}_{\text{a}}^{\text{II}}$ (NH₃)₅]⁴⁺ ($E_{1/2} = 0.39 \text{ V}$ versus SCE) [9,10]. The difference of redox potential between both Ru couples is therefore: $\Delta E_{1/2} = E_{1/2}(\text{Ru}_{\text{b}}^{\text{III}}/\text{Ru}_{\text{b}}^{\text{II}}) - E_{1/2}(\text{Ru}_{\text{a}}^{\text{III}}/\text{Ru}_{\text{a}}^{\text{II}}) = 0.82 \text{ V}$. On the reductive side of the voltammograms, the ligands trpy and bpy display their characteristic reversible waves at $E_{1/2}$ *ca*. -1.3 and -1.6 V, as reported in the literature for similar systems [10]. On the other hand, 4,4'-azpy reductions give rise to one reversible peak at $E_{1/2}$ *ca*. -0.5 V and a quasi-reversible peak at -0.9 V, as expected [1].

The cyclic voltammogram of complex **5** is very similar to that of complex **1**, as shown in Table 3. The main distinction is the difference between the cathodic and anodic peaks of the wave corresponding to the redox couple Ru_b^{III}/Ru_b^{II} , which amounts to 127 mV in **5**, pointing to a two-electron process with a comproportionation constant ($K_c \approx 26$) relatively high for weakly coupled mixed-valent complexes [14].

3.6. Intramolecular electron transfer

By using the Marcus–Hush formalism [17], the electronic coupling element can be calculated from the spectral properties of the mixed-valent complex **4**. The parameters $\Delta \tilde{v}_{1/2}$ (bandwidth at half-height), ε_{max} (molar absorptivity at the absorption maximum) and \tilde{v}_{max} (energy of the intervalence absorption maximum) were obtained after gaussian deconvolution of the visible bands of complex 4 (Supplementary Fig. 2) Using these experimental parameters ($\Delta \tilde{v}_{1/2} = 4700 \text{ cm}^{-1}$, $\varepsilon_{\text{max}} = 1800 \text{ M}^{-1} \text{ cm}^{-1}$, $\tilde{v}_{\text{max}} = 15000 \text{ cm}^{-1}$) in Eq. (1), where *r* is the distance (in Å) between both metal centers, estimated as 13.2 Å from the X-ray analysis of complex 1 and the typical Ru_a-N bond length for an aromatic N heterocycle bonded to Ru [16], the electronic coupling was determined to be: $H_{\rm AB}$ = 550 cm⁻¹.

$$H_{\rm AB} \ (\rm cm^{-1}) = 2.06 \times 10^{-2} [(\epsilon_{\rm max})(\tilde{\nu}_{\rm max})(\Delta \tilde{\nu}_{1/2})]^{1/2} (1/r) \tag{1}$$

 H_{AB} is higher by almost a factor of 3 than that determined for the related BPE-bridged mixed-valent species with a similar metal-metal distance (H_{AB} = 189 cm⁻¹), evidencing higher electronic delocalization in the 4,4'-azpy-bridged species. This finding is consistent with previous reports; in effect, Launay et al. have already determined that the comproportionation constant, a measure of the electronic metal-metal interaction, for the mixed-valent species $[(NH_3)_5Ru(4,4'-azpy)Ru(NH_3)_5]^{5+}$ is $K_c = 40$, a value appreciably higher than that of the isoelectronic BPE complex, for which $K_c = 14$ [1]. The intermediate value of $K_c = 26$, determined for the mixed-valent complex [(trpy)(bpy)Ru(4,4'-azpy)Ru(bpy)(trpy)]⁵⁺, is consistent with the competition between trpy, bpy and 4,4'-azpy for the π -electron density of the metals. Finally, when representing H_{AB} versus r, the slope is increased when including the value for complex **4**, which leads to the conclusion that 4,4'-azpy is a promising ligand for designing "molecular wires", systems in which the electronic transmission is slightly attenuated by the donor-acceptor distance [18].

On the other hand, the reorganization energy λ can be calculated as follows:

$$\lambda = E_{\rm op} - \Delta G^0 - \Delta E_{\rm exc} \tag{2}$$

where ΔG^0 is the free energy difference between both redox centers, assumed as approximately $\Delta E_{1/2}$ = 0.82 V, and ΔE_{exc} is the energy difference between the excited and ground states, estimated as 0.25 eV for several ruthenium complexes in the event that the MMCT transition results in the population of an excited state [19]. Eq. (2) gives a value of λ = 0.79 eV, which is close to the value expected from the slope of the plot of λ versus *r* calculated for this type of asymmetric mixed-valent complexes [10].

4. Conclusions

New polypyridyl ruthenium mononuclear complexes containing 4,4'-azpy have been prepared and characterized by spectral, diffraction and electrochemical techniques. In complex 1, extensive π - π interactions within neighboring molecules are disclosed. 4,4'-azpy connects two metal centers in the dinuclear complex **3**, which can be partially oxidized electrochemically to the stable mixed-valent complex 4. The value of H_{AB} for this latter species is almost 3 times higher than that reported for the related dinuclear complex with BPE, indicating a considerable electronic delocalization in 4,4'-azpy, which confers "molecular wire" properties to complexes with this *N*-heterocycle as a bridging ligand.

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Appendix A. Supplementary data

CCDC 669446 contains the supplementary crystallographic data for $[Ru(trpy)(bpy)(4,4'-azpy)](PF_6)_{1,70}(CF_3SO_3)_{0,30} \cdot 0.5CH_3CN.$ These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary Figs. 1 and 2 show the FTIR spectrum of complex 3 and the Gaussian deconvolution of the visible bands of complex 4, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.06.014.

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