Fine Tuning of MLCT States in New Mononuclear Complexes of Ruthenium(II) Containing Tris(1-pyrazolyl)methane, 2,2′-Bipyridine and Aromatic Nitrogen Heterocycles

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The syntheses of new mononuclear ruthenium(II) complexes of the type: [Ru(bpy)(L)(tpm)](PF6)2 {tpm = tris(1-pyrazolyl)methane; bpy = 2,2′-bipyridine; L = pz (pyrazine; 1), 4,4′-bpy (4,4′-bipyridine; 2), and bpe [trans-1,2-bis(4-pyridyl)ethylene; 3]} are described, together with their spectroscopic, electrochemical, and photophysical properties. A complete assignment of the NMR resonances of the three species could be made in CD3CN by bidimensional techniques. A fine tuning of the energies of MLCT (metal-to-ligand charge transfer) states in these complexes is disclosed when comparing, in CH3CN, the values of their maximum absorption wavelengths for the most intense visible bands (λmax) and their redox potentials for the RuII/RuIII couples; this effect, relevant to the design of efficient photocatalysts, can be attributed to a decreasing order of dπ(Ru) → π*(2,2′-bpy) backbonding when decreasing the distance between both N atoms in the aromatic nitrogen heterocycle L that acts in a monodentate manner. Only the species with L = bpe emits at room temperature, pointing to the conclusion that MLCT excited states in this series become higher in energy than dd excited states when the value of λmax is lower than 400 nm. These species are also useful building blocks for new dinuclear mixed-valent complexes.

Introduction

Polypyridylruthenium(II) complexes represent a keystone in the development of photochemistry and electron- and energy-transfer disciplines,[1] and, among other applications, have led to the design of molecular electronic devices[2] including wires and switches.[3] Furthermore, polypyridylruthenium(II) complexes are often used as building blocks for the development of macromolecular assemblies of interest in biochemistry and clinical diagnosis,[4] as well as for the design of molecular machines.[5] In most of these areas, the synthetic strategy followed to obtain the desired compounds is by RuII substitution chemistry.[6] Unfortunately, full mechanistic studies on these reactions are scarce and, in many cases, incomplete.[7] As a result of these two factors, it is of primary importance to understand and control the electronic and steric factors exerted by different types of ligands in order to properly monitor their substitution processes.

Ruthenium(II) complexes of the type [Ru(bpy)(L)(tpm)]+2 with the tripodal ligand tpm [tris(1-pyrazolyl)methane], the bidentate ligand bpy (2,2′-bipyridine), and monodentate ligands L (Cl−, H2O, O2− or py) are well known.[8,9] A coarse control of MLCT (metal-to-ligand charge transfer) excited states can be achieved by changing substituents in the 4,4′-positions of bpy.[9–11] In this work, we report on the fine tuning of the energies of dπ(Ru) → π*(bpy) MLCT states introduced by changing the nature of the ligand L in [Ru(bpy)(L)(tpm)]+2 complexes with L = pz (pyrazine), 4,4′-bpy (4,4′-bipyridine), and bpe [trans-1,2-bis(4-pyridyl)ethylene]. These changes can be compared to the variations observed in the analogous series [Ru(bpy)(L)(trpy)]+2 (trpy = 2,2′:6′,2′″-terpyridine),[12–16] and can be related to the electronic and structural variations induced when going from a meridional (trpy) to a facial (tpm) coordination.[17] The control of MLCT excited states is relevant in photocatalysis, as demonstrated by the extensive literature concerning artificial photosynthesis based on transition-metal complexes.[18–22]

On the other hand, scorpionate ligands, like tpm, can be

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Fine Tuning of MLCT States in Mononuclear Complexes of Ruthenium(II)

Results and Discussion

Synthesis and Solid-State Structures

The synthetic procedures followed to obtain complexes 1–3 are straightforward and involve the substitution of the anionic \( \text{Cl}^- \) ligand in the complex \([\text{Ru}^\text{III} \text{Cl}(\text{bpy})(\text{tpm})]\) \(^{2+}\) by the desired monodentate ligand \( \text{L} \) (pz, 4,4'-bpy or bpe), as shown below.

\[
[\text{Ru}^\text{III} \text{Cl}(\text{tpm})(\text{bpy})]^{2+} + \text{L} \xrightarrow{\text{MeOH/H}_2\text{O},\text{reflux}} [\text{Ru}^\text{III}((\text{L})(\text{tpm})(\text{bpy}))]^{2+} + \text{Cl}^- 
\]

The crystal structure of complex 1 was solved by means of a single-crystal X-ray diffraction analysis. Figure 1 shows the ORTEP diagram of the molecule along with the corresponding labeling scheme. The Ru center adopts a pseudo-octahedral type of geometry with three N atoms (N1, N3, N5) from the tpm ligand coordinated in a facial fashion. Two other positions are occupied by the 2,2'-bpy ligand (N7, N8), which acts in chelate manner, while the sixth one is occupied by the nitrogen atom, N9, of the monodentate pz ligand. The Ru–N bond lengths are within the range found for similar complexes previously described in the literature\(^{[24,25]}\). The bonding angles are also within the ranges found in the literature\(^{[24,25]}\) and reflect the nature of the different ligands.

Complex 1 has a local pseudo-\( C_m \) symmetry with the mirror plane located in the plane formed by the pyrazine ring and the pyrazolyl group of tpm \( \text{trans} \) to the pyrazine. This symmetry is slightly disturbed by a 4.3° rotation of the bpy out of the mirror plane. The local \( C_m \) symmetry of the molecule is broken by the location of the anions in the crystal packing. These are arranged around the complex and together they form a one-dimensional \( 2_1 \) screw axis which gives the chirality to the crystal.

Spectroscopic and Redox Properties

Complexes of the type \([\text{Ru}(\text{bpy})(\text{L})(\text{tpm})]\)^{2+} are well known in relation to catalysis.\(^{[8]}\) However, the influence of slight variations in the structure of the ligands \( \text{L} \) on the spectral, electrochemical, and photophysical properties of these species has not been much studied; besides, there are no examples so far of mixed-valent species that incorporate tpm in their coordination sphere. As noted before\(^{[9]}\), the simplification introduced by having a poor \( \pi \)-backbonding ligand such as tpm would, in principle, disclose the role of the chromophoric ligands in controlling the spectroscopic, electrochemical, and photophysical properties of MLCT excited states.

NMR Spectroscopy

Figure 2 shows the aromatic region of the \(^1\text{H} \) NMR spectrum of complex 1 in [D\(_8\)]-acetoniitrile, as a representative example; the COSY, NOESY and HSQC spectra together with all the NMR spectra for complexes 2 and 3 are provided as Supporting Information. The spectra can be unambiguously assigned thanks to molecular symmetry, the smaller coupling constants of five-membered pyrazolyl rings with regard to six-membered pyridyl and pyrazinyl...
rings, and with the aid of 2D NMR spectra. The symmetry lost in the solid state is recovered in solution and thus the two pyrazolyl rings cis to the pyrazine ligand become magnetically equivalent, as do the pyridyl moieties of bpy. Two intraligand NOE effects are observed for tpm between H4 and H1 and H8, together with a third interligand NOE between H3 of tpm and H20 of bpy (d_{H3-H20} = 2.46 Å); the latter is a key feature that allows us to assign the NMR resonances with total confidence. The pyrazine and the other ligands acting in a monodentate fashion — 4,4’-bpy and bpe — lose their symmetry upon coordination, a fact that is clearly manifested in their NMR spectra.

Figure 2. 1H NMR spectrum showing the aromatic region of [Ru(bpy)(pz)(tpm)]2+ in CD3CN

Photophysical Properties

Table 1 includes the values for the redox potentials of the RuII/RuIII and the bpy6−/bpy5− couples present in the three complexes; the cyclic voltammogram for 1 is shown in the Supporting Information. The order disclosed by the MLCT bands is also shown in the decreasing values of $E_{1/2}$ (RuII/RuIII) redox potentials in the series: pz > 4,4’-bpy > bpy. The RuII state is stabilized when the total $\pi$-backbonding effects are maximized. The reduction potentials, $E_{1/2}$ (bpy6−/5−), of the ligand bpy are almost unchanged in this series.

Conclusions

The spectroscopic and electrochemical properties of the new complexes described in this work disclose the following order of decreasing energies of RuII → bpy MLCT states: [Ru(bpy)(pz)(tpm)]2+ > [Ru(4,4′-bpy)(bpy)(tpm)]2+ > [Ru(bpe)(bpy)(tpm)]2+. This can be accounted for by the decreasing $\pi$-backbonding effects along the series. While a coarse control of the energies of the MLCT states in com-
Table 1. Electrochemical and absorption spectroscopic data of complexes of the type [Ru(bpy)(L)(tpm)]2+ in CH3CN at room temperature

| Complex[a]                  | $E_{1/2}$(RuIII/RuII)[b] | $E_{1/2}$(bpy0/H11002)[b] | $\lambda_{max}$ (10$^{-3}$ ε)[c] | Assignment                  |
|-----------------------------|--------------------------|--------------------------|----------------------------------|-----------------------------|
| [Ru(bpy)(pz)(tpm)]2+        | 1.26                     | -1.41                    | 457 sh (2.0)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 418 sh (2.0)                     | $d_{\pi}\rightarrow\pi^*$ (pz) |
|                             |                          |                          | 392 (8.4)                        | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 327 (6.8)                        | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 294(19)                          | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 286(22)                          | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 254(15)                          | $\pi\rightarrow\pi^*$       |
| [Ru(4,4'-bpy)(bpy)(tpm)]2+  | 1.21                     | -1.41                    | 464 sh (2.3)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 424 sh (5.7)                     | $d_{\pi}\rightarrow\pi^*$ (4,4'-bpy) |
|                             |                          |                          | 395 (11)                         | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 339 (6.8)                        | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 290 sh(17)                       | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 286 (22)                         | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 254 sh (19)                      | $\pi\rightarrow\pi^*$       |
| [Ru(bpe)(bpy)(tpm)]2+       | 1.15                     | -1.39                    | 466 sh (4.6)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 426 sh (4.6)                     | $d_{\pi}\rightarrow\pi^*$ (bpe) |
|                             |                          |                          | 410 (13)                         | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 343 sh (6.7)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 294 sh (32)                      | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 285 (35)                         | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 254 (27)                         | $\pi\rightarrow\pi^*$       |
| [Ru(bpy)(py)(tpm)]2+ [d]    | 1.15                     | -1.39                    | 466 sh (1.8)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 416 sh (4.2)                     | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 343 sh (12.5)                    | $d_{\pi}\rightarrow\pi^*$ (bpy) |
|                             |                          |                          | 287 (26)                         | $\pi\rightarrow\pi^*$       |
|                             |                          |                          | 244 (15)                         | $\pi\rightarrow\pi^*$       |

[a] As their PF$_6^-$ salts. [b] V vs. SCCE, with 0.1 M TBAH as supporting electrolyte. [c] $\lambda_{max}$ in nm, $\epsilon$ values in M$^{-1}$cm$^{-1}$. [d] From ref.[2]

plexes of the type [Ru(bpy)(tpm)(X 2bpy)]2+ has been reported[9] by changing the nature of the substituents X on the 2,2'-bipyridine unit, a much finer control can be exerted by changing the $\pi$-backbonding abilities of the ligand L. Therefore, a whole range of Ru-bpy excited states can be finally obtained, which is relevant for the development of efficient photocatalysts.[18] Furthermore, these mononuclear species are useful building blocks for new mixed-valent photocatalysts.

**Figure 3.** UV/Vis spectrum of [Ru(bpy)(pz)(tpm)]2+ in CH3CN at room temperature ($C = 9.5 \times 10^{-3} \text{ M}$)

**Figure 4.** Emission spectrum, at room temperature, of [Ru(bpy)(bpe)(tpm)]2+ in CH3CN ($\lambda_{exc} = 400 \text{ nm}$)
species that incorporate tpm in their coordination spheres.[27]

Experimental Section

Materials: All reagents were obtained from Aldrich Chemical Co. and used without further purification. CH3CN was freshly distilled for electrochemical measurements.

Preparations: All synthetic manipulations were routinely performed under nitrogen using Schlenk tubes and vacuum-line techniques. Electrochemical experiments were performed in the dark under N2 or Ar with degassed solvents. IR spectra were recorded with an FT Nicolet 205 spectrophotometer with a reflectance accessory. UV/Vis spectra were recorded with a Cary 50 Scan (Varian) spectrophotometer, with 1-cm quartz cells. Cyclic voltammetry (CV) measurements were carried out with an IJ-Cambria III-660 equipment with a three-electrode cell. A glassy carbon disk electrode (3 mm diameter) from BAS was used as working electrode, platinum wire as auxiliary electrode, and SSCE as reference electrode. All CV experiments were recorded at a 200 mVs⁻¹ scan rate under nitrogen purge, in pure CH3CN containing 0.1 M tetraethylammonium hexafluorophosphate (TBAH). The values for the redox potentials, \( E_{1/2} \), were estimated from cyclic voltammetry as the average of oxidative and reductive peak potentials (\( E_{pa} + E_{pc} \)/2).

Synthesis of \([\text{Ru}(\text{tpm})(\text{bpy})(\text{pz})] \text{(PF}_6\text{)}_2\) (1): A sample of \([\text{RuCl}(\text{bpy})(\text{tpm})] \text{Cl}_2 \cdot 2\text{H}_2\text{O}\) (80 mg, 0.14 mmol), prepared as described before,[8] was added to a solution of pz (0.6 g, 7 mmol) in ethanol/water (1:1, 25 mL) and the mixture heated at reflux for 6 h. After cooling, the ethanol was evaporated and the remaining aqueous solution was loaded onto a Sephadex C-25 column. The unchanged chloro complex was eluted with 0.2 M LiCl, while the pz complex was eluted with 0.3 M LiCl. This last eluate was concentrated to 5 mL and then a concentrated solution of NH4PF6 (1 g in 2 mL of water) was added. After cooling, the precipitate was filtered, washed thoroughly with cold water, dried in vacuo over KOH, and recrystallized from acetone/diethyl ether. Yield: 37 mg (33%). \( \text{C}_{34} \text{H}_{22} \text{F}_{12} \text{N}_{10} \text{P}_{2} \text{Ru} \) (841.07): calcd. C 34.30, H 2.63, N 42.0, H 3.4, N 14.0; found C 38.1, H 2.7, N 14.1. 1H NMR (500 MHz, CD3CN, 25 °C): δ = 6.30 (dd, 1 H, H9), 6.60 (d, 1 H, H10 - g = 2.3 Hz, H10), 7.88 (dd, 1 H, H2), 8.40 (d, J = 2.9 Hz, 1 H, H8), 8.57 (d, J = 3.0 Hz, 2 H, H11), 8.60 (br. d, J = 5.4 Hz, 2 H, H11), 8.78 (br. d, J = 8.1 Hz, 2 H, H12), 9.18 (s, 1 H, H4), ppm. 13C NMR (500 MHz, CD3CN, 25 °C): δ = 76.0 (C4), 108.8 (C9), 110.3 (C2), 125.6 (C12), 126.5 (C14), 135.8 (C8), 135.9 (C1), 138.6 (C13), 144.3 (C10), 145.5 (C2), 147.4 (C3), 148.5 (C4), 153 (C15) ppm. NOEs: H4 with H1 and H8; H3 with H15 and HA.

Synthesis of \([\text{Ru}(4,4'-\text{bpy})(\text{ppy})(\text{tm})] \text{(PF}_6\text{)}_2\cdot 2\text{H}_2\text{O}\) (2): A sample of \([\text{RuCl}(\text{bpy})(\text{tm})] \text{Cl}_2 \cdot 2\text{H}_2\text{O}\) (70 mg, 0.12 mmol) was added to a solution of 4,4'-bpy (1 g, 6.4 mmol) in ethanol/water (1:1, 25 mL) and the mixture heated at reflux for 6 h. After cooling, the ethanol was evaporated and the remaining aqueous solution was filtered to eliminate excess 4,4'-bpy. The filtrate was loaded onto a Sephadex C-25 column. The unchanged chloro complex was eluted with 0.2 M LiCl, while the 4,4'-bpy complex was eluted with 0.3 M LiCl. This last eluate was concentrated to 5 mL and then a concentrated solution of NH4PF6 (1 g in 2 mL of water) was added. After cooling, the precipitate was filtered, washed thoroughly with cold water, dried in vacuo over KOH, and recrystallized from acetone/diethyl ether. Yield: 37 mg (33%). \( \text{C}_{34} \text{H}_{22} \text{F}_{12} \text{N}_{10} \text{P}_{2} \text{Ru} \) (841.07): calcd. C 34.30, H 2.63, N 42.0, H 3.4, N 14.0; found C 38.1, H 2.7, N 14.1. 1H NMR (500 MHz, CD3CN, 25 °C): δ = 6.30 (dd, 1 H, H9), 6.60 (d, 1 H, H10 - g = 2.3 Hz, H10), 7.88 (dd, 1 H, H2), 8.40 (d, J = 2.9 Hz, 1 H, H8), 8.57 (d, J = 3.0 Hz, 2 H, H11), 8.60 (br. d, J = 5.4 Hz, 2 H, H11), 8.78 (br. d, J = 8.1 Hz, 2 H, H12), 9.18 (s, 1 H, H4), ppm. 13C NMR (500 MHz, CD3CN, 25 °C): δ = 76.0 (C4), 108.8 (C9), 110.3 (C2), 125.6 (C12), 126.5 (C14), 135.8 (C8), 135.9 (C1), 138.6 (C13), 144.3 (C10), 145.5 (C2), 147.4 (C3), 148.5 (C4), 153 (C15) ppm. NOEs: H4 with H1 and H8; H3 with H15 and HA.

X-ray Structure Determination for 1: Yellow, needle-shaped crystals of 1 were grown by slow diffusion of diethyl ether into a concentrated acetone solution of the complex at room temperature. The crystal to be measured (700 × 40 × 20 μm) was isolated under inert conditions and immersed in perfluoropolyether as protection. Empirical formula \( \text{C}_{34} \text{H}_{22} \text{F}_{12} \text{N}_{10} \text{P}_{2} \text{Ru} \). \( M = 841.53 \), monoclinic, space group \( P2_1 \), \( a = 10.310(1) \text{Å}, b = 14.5022(10) \text{Å}, c = 11.1954(7) \text{Å}, \beta = 117.021(2) \text{°} \), \( V = 1491.20(17) \text{Å}^3 \), \( Z = 2, \mu = 0.746 \text{ mm}^{-1} \), \( d_{calc} = 1.874 \text{ g/cm}^3 \). The measurement was carried out with a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co. rotating anode with Mo-Kα radiation, a graphite monochromator and a Siemens low-temperature device LT2 (\( T = 120 {\text{°C}} \)). The measurement range was 2.04–31.52°; 23212 reflections were collected of which 9439 were unique (\( R_{int} = 0.0574 \)) and 8449 observed (\( |F_o| > 4\sigma (F_o) \)). Full-
sphere data collection ω and φ scans. Programs used: Data collection Smart V. 5.060 (Bruker AXS, 1999), data reduction Saint + Version 6.02 (Bruker AXS, 1999) and absorption correction SAD-ABS (max/min transmission: 1.000000/0.490397, Bruker AXS, 1999). Structure solution and refinement were performed using SHELX TL Version 5.10 (Sheldrick, Universität Göttingen, Göttingen, Germany, 1998). The structure was solved by direct methods and refined by full-matrix least-squares against F^2. All calculated hydrogen positions were refined as constrained. Final R1 [I > 2σ(I)] = 0.0449 and wR2(I) [I > 2σ(I)] = 0.1045. The number of refined parameters was 564. Absolute structure parameter −0.03(2). CCDC-230222 contains the supplementary crystallographic data for this paper. These can be obtained free of charge at 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; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available: Additional spectroscopic and electrochemical data (see also footnote on the first page of this article).

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