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A room temperature luminescent cyclometallated ruthenium(II) complex of 6-phenyl-2,2′-bipyridine

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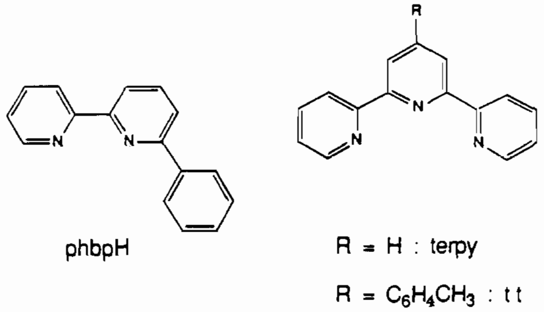
Abstract

The cyclometallated complex Ru(tt)(phbp)$^+$ (tt = 4′-tolyl-2,2′:6′2″-terpyridine, phbp = 6-phenyl-2,2′-bipyridine) with a (N,N,N)(C,N,N) coordination, has been synthesized and characterized by ^{1}H NMR, UV, FAB-MS spectral techniques and by elemental analysis. We have compared its electrochemical and photophysical properties with those of the non-orthometallated analogues Ru(tt)$_2^{2+}$ and Ru(terpy)$_2^{2+}$ (terpy = 2,2′:6′,2″-terpyridine). The most remarkable feature of Ru(tt)(phbp)$^+$ is its ability to luminesce at room temperature in alcoholic and nitrile solvents. The lifetime of its ^{3}MLCT excited state is 60 ns in CH_3CN.

Introduction

Ru(terpy)$_2^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) is nonluminescent at room temperature, its metal-to-ligand charge transfer (MLCT) excited state being very short lived [1–3]. In order to circumvent this weakness, a promising approach is to increase the ligand field (LF) or to diminish the MLCT energy level so that the MLCT and the LF states become well separated [4, 5]. Cyclometallating ligands represent an interesting possibility in order to increase ligand field effects [6]. 2-Phenylpyridine has been used as an orthometallating analogue of bpy (bpy = 2,2′-bipyridine) [7]. Recently, 6-phenyl-2,2′-bipyridine (phbpH) has been proposed as a C–N–N coordinating molecule with geometrical properties very similar to those of terpy [8, 9] when associated to Rh(III), Pd(II), Pt(II), Au(III) or Hg(II).

We now report the synthesis of a ruthenium(II) cyclometallated complex of phbp$^-$ and we compare its electrochemical and photophysical properties with those of the non-orthometallated analogues Ru(tt)$_2^{2+}$ or Ru(terpy)$_2^{2+}$. The most remarkable feature of Ru(tt)(phbp)$^+$ is its ability to luminesce at room temperature in alcoholic and nitrile solvents. The ligands used are represented in Scheme 1.



Scheme 1.

Experimental

Preparation of Ru(tt)(phbp)(PF$_6$)

A solution of Ru(tt)Cl_3 in acetone was heated to reflux, under argon, for 30 min with 3 equivalents of $AgBF_4$. After filtration and evaporation of the solvent, the residue was treated with a stoichiometric amount of 6-phenyl-2,2′ bipyridine in n-butanol. The mixture was heated to reflux, under argon for 6 h, after which the solvent was evaporated. The solid was dissolved in CH_3CN and treated with an excess of NH_4PF_6 in water. The brown precipitate was collected by filtration and subjected to chromatography on silica (acetone–aqueous KNO_3 as eluent). The purple band led to [Ru(tt)(phbp)$^+$][PF$_6^-$] after anion exchange (17% yield).

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^{1}H NMR (CD_3CN): δ (ppm) versus TMS: 8.86 (2H, s), 8.55 (2H, d, 7.3 Hz), 8.42 (2H, m), 8.25 (2H, d, 8 Hz), 8.07 (3H, m), 7.80 (4H, m), 7.50 (5H, m), 7.05 (3H, m), 6.74 (1H, t, 7.5 Hz), 6.52 (1H, t, 7.5 Hz), 5.79 (1H, d, 7.5 Hz), 2.5 (3H, s). FAB-MS: *m/z* 656 [Ru(tt)(phbp)]$^+$. *Anal.* Calc. for Ru(tt)(phbp)(PF_6): C, 56.99; H, 3.52; N, 8.74. Found: C, 56.80; H, 3.69; N, 8.43%.

Physical measurements

Absorption spectra were recorded with a Perkin-Elmer Lamda 5 spectrophotometer. Corrected emission spectra were obtained with a Spex Fuorolog-2 fluorimeter by using software supplied by the firm. The luminescence lifetimes were measured by using an Applied Photophysics single photon counting instrument employing a nitrogen or deuterium excitation lamp and equipped with an Epson PC. Analyses of the decay profiles were performed with programs based on least-squares iterative non-linear procedures [10].

Results and discussion

phbpH was obtained as a by-product in the course of the synthesis of 6,6′-diphenyl-2,2′-bipyridine [11].

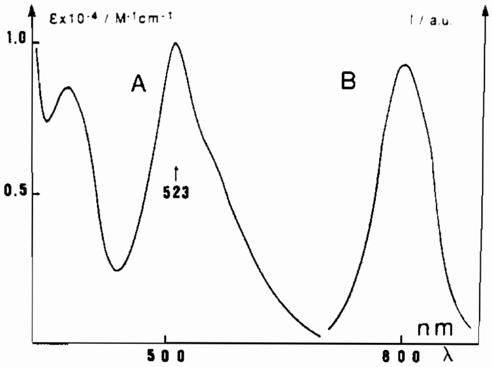

Fig. 1. Absorption (A) and emission spectra ($\lambda_{exc}=500$ nm) (B) of Ru(tt)(phbp)$^+$ in ethanol–methanol (4:1 vol./vol.) at room temperature.

It was reacted with Ru(tt)Cl_3 [12] to afford [Ru(tt)(phbp)$^+$][PF_6^-] in 17% yield.

The redox potential of the Ru(tt)(phbp)$^+$ couple (Ru$^{III/II}$: $E^0=0.54$ V versus SCE in CH_3CN) is drastically less positive than that of Ru(tt)$_2^{2+}$ (Ru$^{III/II}$: $E^0=1.24$ V versus SCE in DMSO) [13]. This is clear evidence for the strong σ-donating character of the anionic ligand phbp$^-$ as compared to a terpy type molecule.

The absorption and emission spectra of Ru(tt)(phbp)$^+$ are shown in Fig. 1.

The intense low energy absorption band ($\lambda_{max}=523$ nm, $\epsilon=9960$ M^{-1} cm^{-1} in ethanol–methanol (4:1 vol./vol.)) corresponds to a MLCT transition. Its bathochromic shift as compared to Ru(terpy)$_2^{2+}$ ($\lambda_{max}=473$ nm) or Ru(tt)$_2^{2+}$ ($\lambda_{max}=490$ nm) is in agreement with the higher electron density of the metal centre. A weak emission band can also be observed, whose excitation spectrum (400–700 nm) in ethanol–methanol (4:1 vol./vol.) or propionitrile–butyronitrile (4:5 vol./vol.) is similar to the absorption spectrum. The emission data are collected in Table 1 together with the corresponding data for Ru(tt)$_2^{2+}$ and Ru(terpy)$_2^{2+}$. The emission properties are consistent with the following picture. With respect to Ru(tt)$_2^{2+}$ or Ru(terpy)$_2^{2+}$, ortho-metallation results in stronger σ-donation by phbp$^-$ so that in Ru(tt)(phbp)$^+$ the luminescent ^{3}MLCT levels move to low energy and the ^{3}MC levels move to high energy, as qualitatively depicted in Fig. 2.

As a consequence, the distorted ^{3}MC excited state (doorway to photochemistry and radiationless paths [15]) becomes thermally less accessible from the ^{3}MLCT excited states and the complex Ru(tt)(phbp)$^+$ is luminescent at room temperature. However, the ^{3}MLCT levels move to very low energy (see Table 1) and according to the 'energy gap law' [16], this causes a dramatic increase of non-radiative processes directly from the luminescent level. Emission is thus weak compared to that of the complexes of the Ru–polypyridine family [15].

TABLE 1. Emission properties[a]

	298 K[b]			77 K[c]		
	λ (nm)	τ (μs)	Φ_{em}[d]	λ (nm)	τ (μs)	Φ_{em}[d]
Ru(tt)(phbp)$^+$	808	0.06	5×10^{-6}	792	0.9	2×10^{-4}
Ru(terpy)$_2^{2+e}$				598	11.0	0.48
Ru(tt)$_2^{2+f}$				609	9.1	

[a] The errors on the various experimental data are as follows: ±30% on Φ_{em} and ±25% on τ. [b] CH_3CN as solvent [c] Propionitrile–butyronitrile (4:5 vol./vol.) solvent unless otherwise stated. [d] Relative to Ru(bpy)$_3^{2+}$ as a standard, deaerated CH_3CN: $\Phi_{em}=0.062$; ref. 14. [e] MeOH/EtOH (4:1 vol./vol.) solvent, from ref. 3. [f] At 90 K; $\lambda_{em}=628$ nm.

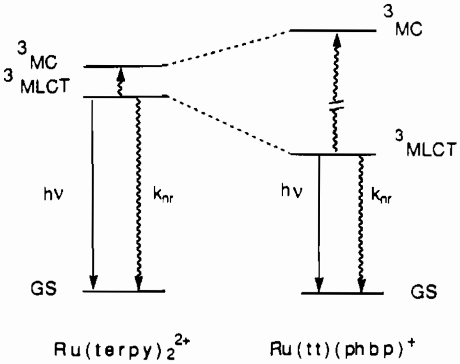

Fig. 2. Qualitative energy level diagram for Ru(terpy)$_2^{2+}$ and Ru(tt)(phbp)$^+$.

In conclusion, replacing one neutral terpy-type ligand with an anionic C–N–N coordinating structure leads to a luminescent complex analogous to Ru(terpy)$_2^{2+}$. Although relatively short lived and of little energy content, the ^{3}MLCT state of Ru(tt)(phbp)$^+$ should turn to be of photochemical use.

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