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Observation of ^{3}MC Emission in a Mixed 1,10-Phenanthroline Complex of Ruthenium(II) Having a $Ru^{II}N_6$ Core at Room Temperature in Solution

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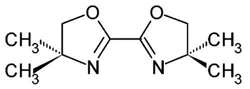
[Ru(1,10-phenanthroline)$_2$(4,4,4′,4′-tetramethyl-2,2′-bisoxazoline)]-$(PF_6)_2 \cdot H_2O$ (**1**) shows a ^{3}MC emission in CH_3CN and CH_3OH at room temperature around 590 nm with radiative lifetimes of 1.22×10^{-4} and 1.40×10^{-4} s, respectively. The X-ray crystal structure of **1** has been determined.

The radiative lifetimes (τ_r) for some polypyridine complexes of Ru(II) at room temperature lie between 10^{-3} and 10^{-4} s.[1,2] In these cases the emission is believed to originate from a triplet state arising from a metal centered (MC) transition. The values of τ_r for a ^{3}MLCT (metal to ligand charge transfer) emission in Ru(II)−polypyridines at room temperature are typically of the order of 10^{-5} s.[1,2] But, to our knowledge, observation of a ^{3}MC emission from a mixed 1,10-phenanthroline (phen) complex of Ru(II) has not yet been reported. Herein we describe such a complex which has been synthesized deliberately.

The lowest excited state in most of the known polypyridine complexes of ruthenium(II) is a ^{3}MLCT one. However, it has been found that the orbital nature of the lowest excited state can be manipulated by appropriate choice of the ligand(s). Emission from a ^{3}MC state, which usually lies higher than the ^{3}MLCT state in energy, can be achieved by decreasing the ligand field strength, e.g., replacing one or two polypyridine ligands by Cl^- ions.[3] Guided by this fact, we have been motivated to synthesize a mixed phen complex of ruthenium(II) which can give rise to a ^{3}MC emission. For $[Ru(phen)_3]^{2+}$, the τ_r values[1] in water and ethanol are 1.6×10^{-5} and 1.5×10^{-5} s, respectively. The 10 *Dq* of phen[4] with respect to Ni(II) is 12745 cm^{-1}. As a weak field ligand, we have chosen 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline (L), which is a nonaromatic 1,4-diimine.[4] Its 10 *Dq* value[5] with respect to Ni(II) is ∼10100 cm^{-1}. Another reason for its choice is that since L binds a metal through the N ends,[6,7] we can maintain a RuN_6^{2+} chromophore.



L

We have synthesized $[Ru(phen)_2L](PF_6)_2 \cdot H_2O$ (**1**) by refluxing *cis*-$Ru(phen)_2Cl_2 \cdot 2H_2O$ with a slight excess of L in a 1:1 water−methanol mixture followed by addition of excess NH_4PF_6.[8−10] The X-ray crystal structure[11,12] of the cation in **1** is shown in Figure 1. The Ru−N(phen) bond distances lie within the narrow range of 2.050−2.063 Å. The bonds to the ligand L are somewhat longer: 2.119(7) and 2.128(6) Å. The geometry around the metal is distorted from octahedral by the chelate bite of the three ligands; the bite

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(8) 0.15 g (0.75 mmol) of L, synthesised by a reported procedure,[9] was added to 0.28 g (0.5 mmol) of *cis*-$Ru(phen)_2Cl_2 \cdot 2H_2O$ (synthesized by a reported produre[10]) dissolved in 25 mL of degassed 1:1 methanol−water mixture and refluxed for 6 h under N_2 atmosphere. The resulting red solution was then cooled to room temperature, and 1 g of NH_4PF_6 dissolved in 5 mL of water was added to it dropwise with constant stirring. Immediately a dark red crystalline compound started appearing. The mixture was left in the air for 30 min. Then it was filtered, washed with diethyl ether, and dried in vacuo over $CaCl_2$. Yield: 0.31 g (64%). Dark red single crystals of **1** were grown by direct diffusion of petroleum ether into a dilute acetone solution of the complex. Anal. Found (calcd): C, 42.40 (42.29); H, 3.58 (3.55) N, 8.65 (8.70)%. Λ_M (CH_3CN): 258 Ω^{-1} cm^2 mol^{-1} (1: 2 electrolyte). FTIR ν/cm^{-1} (KBr): 839vs (PF_6). UV/vis λ_{max}/nm (ϵ/M^{-1} cm^{-1}) (CH_3CN): 223 (63000), 263 (81000), 312 (4800), 445 (15 150). UV/vis λ_{max}/nm (ϵ/M^{-1} cm^{-1}) (CH_3OH): 224 (60650), 261 (70100), 313 (6000), 445 (15400). UV/vis λ_{max}/nm (ϵ/M^{-1} cm^{-1}) (CH_2Cl_2): 229 (47800), 263 (79600), 317 (4850), 450 (14700). ESI-MS: 329.1 (**1** − H_2O − $2PF_6^-$; 100%), 803.5 (**1** − PF_6^- − H_2O; 8%). ^{13}C NMR (DMSO-d_6) δ/ppm: 25.66, 25.92 (methyl C’s of L); 69.97 (alkyl quaternary C of L); 83.28 (methylene C’s of L); 126.92−158.56 (aromatic C’s of phens); 218.86 (imino C of L).

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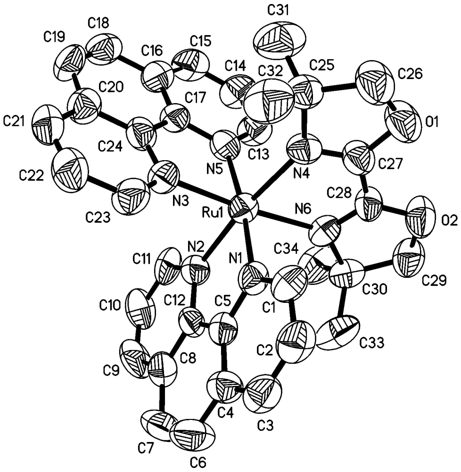

Figure 1. X-ray crystal structure of the cation in **1**. Selected bond distances (Å): Ru1−N1 2.058(6); Ru1−N2 2.057(7); Ru1−N3 2.050(6); Ru1−N5 2.063(7); see text also.

angles are 79.5(4), 78.8(4)° (phen) and 76.3(4)° (L). The two five membered rings of L are practically coplanar with a deviation of 3.3°.

To have an idea of the strength of binding of L to ruthenium(II) in **1**, we take recourse to the bond valence sum (BVS) model[13,14] which relates the bond distances around a metal ion with its oxidation state. Our BVS calculations show that the ideal value of a Ru(II)−N bond in a symmetric RuN_6^{2+} chromophore is 2.08 Å (the relevant "r_o" parameter is 1.671 Å[15]). Thus the binding of L to the metal in **1** seems to be weaker than phen.

In the ^1H NMR spectrum of **1** in DMSO-d_6 (deuterated dimethyl sulfoxide) the four methyl groups of L are found to be magnetically nonequivalent resonating as two singlets at 1.40 and 3.67 ppm. Such magnetic nonequivalence is observed for the methylene protons also; two of the four methylene protons of L appear as a doublet around 4.91 ppm with $J = 9$ Hz and the other two appearing as another doublet around 5.06 ppm with the same J value. In the ^1H NMR spectrum of free L in $CDCl_3$, the methyl protons appear as a singlet at 1.37 ppm and the methylene protons as another singlet at 4.13 ppm.[7] The phen protons in **1** resonate in the region 7.86−9.72 ppm with the expected splitting patterns.

Table 1. Cyclic Voltammetric Data for **1** in Acetonitrile at a Planar Glassy Carbon Electrode[a]

	$E_{1/2}(\Delta E_p)$	
complex	Ru(III/II) couple	ligand based redox
1	1.25(80)	−1.36(90), −1.63(−),[b] −2.18(−)[b]
$[Ru(phen)_3]^{2+}$	1.32(59)[c]	−1.54(−),[b,d] −1.67(−),[b,d] −1.97(−),[b,d]

[a] Half-wave potentials ($E_{1/2}$) are given in V vs SCE, and peak-to-peak separation ΔE_p (at a scan rate of 50 mV s^{-1}) is given in mV. [b] Only the cathodic peak potential is given. The corresponding anodic peak could not be observed. [c] At a Pt electrode.[17] [d] At a Pt electrode.[18]

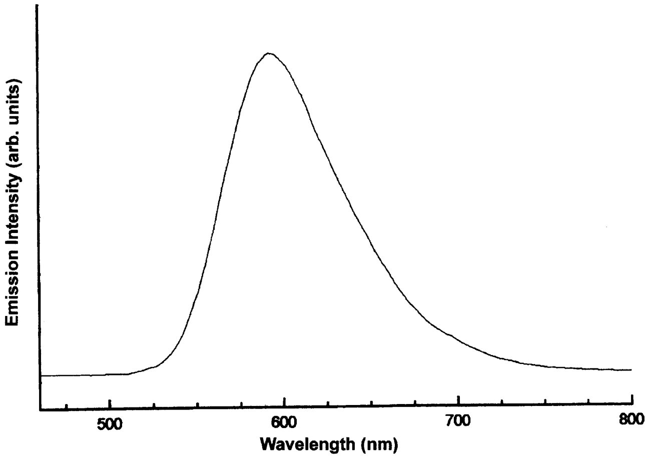

Figure 2. Emission spectrum of **1** in deoxygenated CH_3CN at room temperature. Excitation wavelength: 450 nm. Absorbance of the solution at 450 nm: 0.42.

Complex **1** displays a quasireversible Ru(III/II) couple in cyclic voltammetry in purified CH_3CN at a planar glassy carbon electrode at 1.25 V vs. SCE (saturated calomel electrode) and three of the six possible[16] ligand-based reductions in the range −1.36 V to −2.18 V (Table 1). For comparison, cyclic voltammetric data for $[Ru(phen)_3]^{2+}$ are also given in Table 1.[17,18] The Ru(III/II) potential in **1** is found to be less than that in $[Ru(phen)_3]^{2+}$ by 70 mV. This is in accord with the lower 10 *Dq* of L compared to that of phen; the crystal field splitting between t_2 and e orbitals of the Ru^{2+} ion (a d^6 system) decreases in **1** in comparison with that in $[Ru(phen)_3]^{2+}$ lifting the t_2^6 level in **1** to higher energy which is reflected in the metal oxidation potentials.

The electronic spectra of **1** in CH_3CN, CH_3OH, and CH_2Cl_2 show a charge-transfer band around 447 nm. When excited with 450 nm radiation, complex **1** displays a broad structureless (Gaussian shaped) emission band around 590 nm in deoxygenated CH_3CN (Figure 2), CH_3OH, and CH_2Cl_2 at room temperature (Table 2). The emission is much weaker than that in $[Ru(phen)_3]^{2+}$ (Table 2). The quantum yields Φ lie in the range 0.0015−0.0027. The measured lifetimes (τ_m) are small (Table 1), yielding a radiative lifetime τ_r ($=\tau_m/\Phi$) of 1.22×10^{-4} s in CH_3CN and 1.40×10^{-4} s in CH_3OH.[19−21] The order of the values of τ_r shows that here in **1** the lowest excited state at room temperature has an MC character and not an MLCT one. This has been possible

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(11) Crystal data: $C_{34}H_{34}F_{12}N_6O_3P_2Ru$, $M = 965.7$, orthorhombic, space group *Pnma*, $a = 12.241(2)$ Å, $b = 39.105(8)$ Å, $c = 17.690(4)$ Å, $V = 8468(3)$ Å^3, $\rho = 1.515$ g cm^{-1}, $Z = 8$, $\mu = 0.539$ mm^{-1}. The 7465 independent reflections for **1** were collected at an automatic four-circle Nicolet R3mV diffractometer at 293(2) K using graphite monochromated Mo Kα radiation. Three standard reflections were remeasured every 97 scans; no significant variation in intensity was observed. Data were corrected using routine procedures, and empirical absorption correction was applied (ψ scan method). The structure was solved by direct methods and refined to convergence (SHELXL 93).[12] The asymmetric unit contains one cation, one PF_6^- ion in a general position, and two PF_6^- ions residing on mirror planes. Non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in idealized positions and assigned a fixed thermal parameter ($U_{iso} = 0.08$ Å^2). In the latter stages of refinement a disordered water molecule was observed and was refined over three sites. Final residuals: $R_1 = 0.0730$, $wR_2 = 0.1827$ for the observed data [$I > 2\sigma(I)$]; $R_1 = 0.1441$, $wR_2 = 0.2294$ for all data.

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Table 2. Some Photophysical Properties of **1** in Some Solvents at Room Temperature[a]

complex	solvent	λ_{abs}	λ_{em}	$10^4\Phi$	$10^9\tau_m$	$10^4\tau_r$
1	CH_3CN	444	593	27	332	1.22
	CH_3OH	445	590	20	281	1.44
	CH_2Cl_2	450	580	15	<200	
$[Ru(phen)_3]^{2+}$	CH_3CN	442	604	280	460	0.16
	C_2H_5OH			190	290	0.15

[a] Excitation wavelength, 450 nm; absorbance of the solutions at 450 nm, 0.3−0.5; λ_{abs}, maxima of the absorption around 450 nm (in nm); λ_{em}, emission maxima (in nm); the τ values are given in s. The data for $[Ru(phen)_3]^{2+}$ are taken from ref 1.

because of the lower ligand field strength of L coupled with weak Ru−L bonding. When the lowest excited state is MC in nature, the nonradiative pathways become so much facilitated that usually no emission can be observed in room temperature.[1] This explains why Φ in **1** is so much less than that in $[Ru(phen)_3]^{2+}$. In this context, we note that $[Ru(bisthiazoline)_3]Cl_2$, where the ligand is essentially similar to L and the metal has a N_6 coordination sphere, is not photoluminescent at room temperature in solution.[22]

To gain further insight into the nature of the lowest excited state of our complex **1**, we have investigated the profile of its emission at low temperature. At 77 K in deoxygenated methanol, complex **1** displays an emission with one fine structure (Figure 3); the energy difference between the two peaks is 1492 cm^{-1}. For a pure ^{3}MC emission no fine structures are expected at low temperatures. For $[Ru(phen)_3]^{2+}$, where the emission is undoubtedly ^{3}MLCT in nature, two fine structures are observed at 77 K in 4:1 (v/v) ethanol−methanol medium with the energy difference between two consecutive peaks of 1290−1360 cm^{-1}.[23] The observation of the fine structure in the emission of **1** at 77 K indicates that the ^{3}MLCT and ^{3}MC states are in thermal equilibrium in **1**; while at room temperature the ^{3}MC state is predominantly populated, at low temperature ^{3}MLCT is populated. The presence of thermally equilibrated ^{3}MLCT and ^{3}MC states has been earlier observed[24] in the emission of $[Ru(2,2'\text{-bipyridine})_2(4,5\text{-diaza-fluorene})]^{2+}$; 10 *Dq* of 4,5-diazafluorene with respect to Ni(II) is 10250 cm^{-1} whereas that of 2,2′-bipyridine is 12650 cm^{-1}.

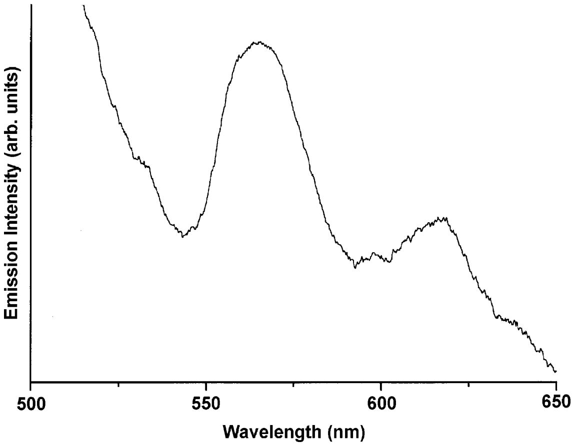

Figure 3. Emission spectrum of **1** in deoxygenated methanol at 77 K. Excitation wavelength: 450 nm. Absorbance of the solution at 450 nm at room temperature: 0.42.

One of our observations in the room-temperature emission behavior of **1** is that the emission maximum shifts from 580 to 593 nm (by 378 cm^{-1}) in going from acetonitrile to dichloromethane. Such a small shift probably corresponds to a predominantly ^{3}MC emission. A pure ^{3}MC emission is thought to be relatively matrix independent in contrast with a pure ^{3}MLCT one.[25] However, this aspect has not been investigated properly in the past possibly because, as pointed out above, Ru(II) complexes that can display ^{3}MC emission are rare.

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Supporting Information Available: X-ray CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The Φ's were determined using $[Ru(bpy)_3](PF_6)_2$ as the standard (Φ = 0.062 in CH_3CN at room temperature[20]). The details of the instrumentations for lifetime measurements are the same as described elsewhere.[21] All the decays were monoexponential and were measured at the emission maximum with 532 nm excitation.

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