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Heteroleptic Dipyrrin/Bipyridine Complexes of Ruthenium(II)

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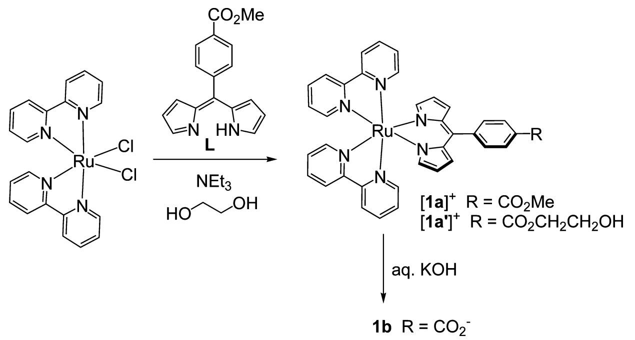
The synthesis and characterization of a series of heteroleptic dipyrrinato/2,2′-bipyridine complexes of ruthenium(II) are reported. Spectroscopic analysis, including resonance Raman, indicates that the complexes are only weakly emissive and that the dipyrrin and Ru → bipyridine (metal-to-ligand charge transfer) chromophores are uncoupled.

The coordination chemistry of dipyrromethene (dipyrrin) ligands, first studied several decades ago, is undergoing a rapid resurgence.[1,2] Meso-substituted dipyrrins are easily accessible from arylaldehydes via condensation with pyrrole followed by oxidation.[3] They typically coordinate as monoanionic dipyrrinato chelates. Various functional groups may be incorporated on the periphery of complexes of dipyrrinato ligands by substitution on the aryl or pyrrole rings. On kinetically inert complexes, these functional groups can be interconverted using standard synthetic methodologies.[4] Dipyrrin ligands possess a conjugated π system, analogous to porphyrins, which can endow their complexes with useful optical properties including intense absorption bands in the visible region of the spectrum and photoluminescence (particularly BF_2 complexes or BODIPYs).[5] As such, dipyrrin complexes hold promise as functional components of light-harvesting and energy transfer systems.

Although dipyrrinato complexes of many transition metal ions have been reported,[1] ruthenium does not feature on this list. Ruthenium(II) complexes are generally stable, diamagnetic, and kinetically inert and have justifiably received great attention for their unparalled photophysical properties. As ruthenium−dipyrrin complexes could conceivably combine these properties with those of dipyrrins, they represent a very attractive synthetic target. We herein report the first dipyrrin complexes of ruthenium(II), namely, heteroleleptic dipyrrin/2,2′-bipyridine (bipy) complexes.

Scheme 1. Synthetic Route to Complexes $[\mathbf{1a}]^+$ and **1b**



Ligand **L** was synthesized from methyl 4-formylbenzoate via a slightly modified literature procedure.[6] Complex $[\mathbf{1a}]PF_6$ was obtained as a green solid in good yield by reacting equal equivalents of **L** and $[Ru(bipy)_2Cl_2]$ in ethylene glycol under microwave irradiation in the presence of a base (Scheme 1). Subsequent hydrolysis of the ester moiety in aqueous base provided complex **1b**. When the carboxyl group is deprotonated, complex **1b** is neutral and conveniently precipitates from the aqueous solution. It was found necessary to employ microwave irradiation in the synthesis of $[\mathbf{1a}]^+$, as conventional heating methods failed to provide the desired product. The use of ethylene glycol as a solvent resulted in a significant degree of trans-esterification (giving $[\mathbf{1a'}]PF_6$), although this did not appear to have any adverse effect on the subsequent hydrolysis step.

Complex **1b**, which is green in the solid state but red−orange in solution, was characterized by ^1H NMR, ^{13}C NMR, ESI-MS, UV/vis spectroscopy, elemental analysis, and X-ray crystallography. All data are consistent with the structure depicted in Scheme 1.

The UV−visible spectrum of **1b** is of note, particularly the two distinct peaks in the visible region (Figure 1). The

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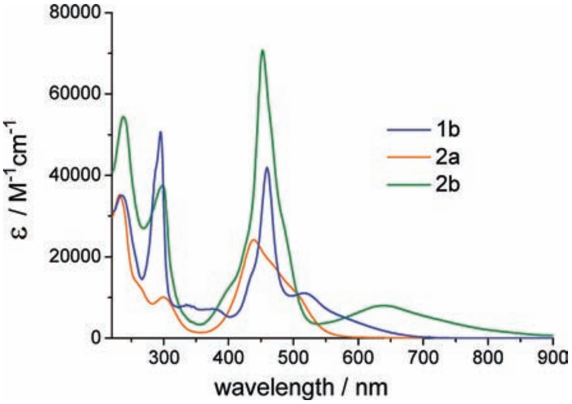

Figure 1. UV/vis spectra of **1b** (in CH_3OH), **2a** (in CH_3OH), and **2b** (in CH_2Cl_2).

intense narrow band with $\lambda_{max} = 483$ nm can be attributed to a $S_o \rightarrow S_1$ ($\pi-\pi^*$) transition of the dipyrrin ligand. Both the relatively narrow bandwidth and the position of this peak, which has been found to be relatively insensitive to the identity of the metal center and coligands, are diagnostic of this type of transition.[7] The broader peak centered at 512 nm presumably originates from a Ru(II)-to-bipy charge transfer (metal-to-ligand charge transfer, MLCT) transition. This transition is red-shifted with respect to $[Ru(bipy)_3]^{2+}$, where it appears at 443 nm.[8] Similar shifts are seen in analogous halide and oxalate complexes[9] and can be rationalized on the basis of anionic, weakly π-accepting ligands raising the energies of the ruthenium(II) d orbitals.

The simple appearance of the absorption spectrum of **1b** as the superposition of a $\pi-\pi^*$ dipyrrin transition and a MLCT transition suggests that the two chromophores are largely uncoupled; that is, the orbitals involved in these transitions are distinct and located in different spatial regions of the complex.

To further probe this behavior, resonance Raman experiments were conducted on complex **1b**. Resonance Raman is a useful technique for assigning electronic transitions as vibrational modes of chromophores that resonate at the Raman excitation wavelength are selectively enhanced. Spectra were acquired at two excitation wavelengths—514 nm (Figure 2a) and 458 nm (Figure 2b)—corresponding to the two bands in the above-mentioned absorption spectrum. The observed Raman spectra are distinctly different. The longer excitation wavelength is associated with vibrational modes of the Ru−bipy MLCT chromophore, as evidenced by the qualitative similarity to the resonance Raman spectrum of $[Ru(bipy)_3]^{2+}$ (Table S1, Supporting Information).[8] Conversely, the shorter excitation wavelength results in resonant enhancement of dipyrrin vibrational modes. These observations confirm the origin of the two absorption bands and lend further weight to a localized, noninteracting depiction of the dipyrrin and MLCT chromophores.

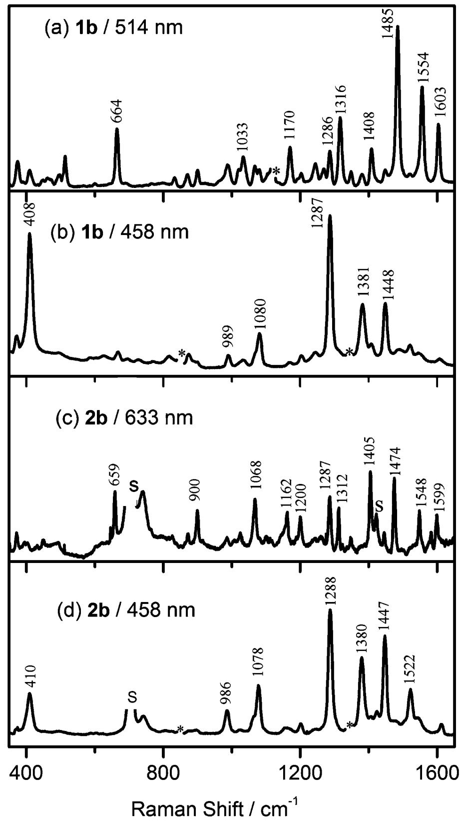

Figure 2. Resonance Raman spectra of **1b** in CH_3OH and **2b** in CH_2Cl_2 at various excitation wavelengths. S denotes a solvent band, and asterisks denote where laser lines have been removed. Tabulated data are available in the Supporting Information.

[**1b**]·(CH_3OH)·$6H_2O$ crystallizes in the space group $P\bar{1}$ with one enantiomer of the complex occupying the asymmetric unit.[10] As anticipated, the geometry at the ruthenium(II) center is distorted octahedral (Figure 3). The $Ru-N^{bipy}$ bond lengths fall in the range 2.047(2)−2.058(2) Å, while the $Ru-N^{dipyrrin}$ bond lengths are marginally longer (2.062(2) and 2.062(4) Å). The phenyl ring is twisted 71.5° out of the plane of the dipyrrin chelate, while the deprotonated carboxylato group twists 15.0° out of the plane of the phenyl ring. The C−O bond distances of the carboxylato group (1.260(8) and 1.263(7) Å) are consistent with it being deprotonated, thus rendering **1b** neutral. The carboxylato groups of neighboring complexes are linked into an infinite network by hydrogen bonds to common H_2O molecules.

Complex **2a** was obtained in good yield by reacting **L** (2 equiv) with $[Ru(dmso)_4Cl_2]$ in absolute ethanol (Scheme 2). Purification via column chromatography on alumina afforded a fine red−brown solid, which was orange-colored in solution. As its monodentate dmso ligands should be readily displaced by chelating ligands, **2a** is expected to be a useful

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(10) Crystal data for **1b**·(CH_3OH)·$6H_2O$: $C_{37}H_{42}RuN_6O_9$, $M = 815.83$, triclinic, space group $P\bar{1}$, $a = 8.76980(10)$ Å, $b = 12.46720(10)$ Å, $c = 17.3089(2)$ Å, $\alpha = 108.0700(10)°$, $\beta = 90.1170(10)°$, $\gamma = 92.8580(10)°$, $V = 1796.58(3)$ Å^3, $T = 150(2)$ K, $Z = 2$, 73 884 reflections measured, of which 10 474 were unique ($R_{int} = 0.039$), refined against 512 parameters to give $R_1 = 0.0472$ ($I > 2\sigma(I)$), GOF = 1.06.

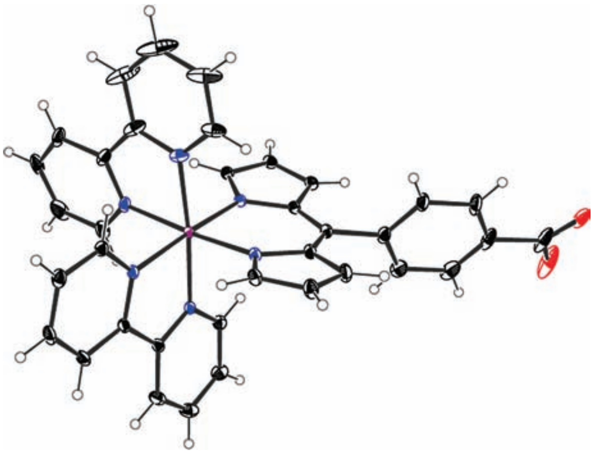
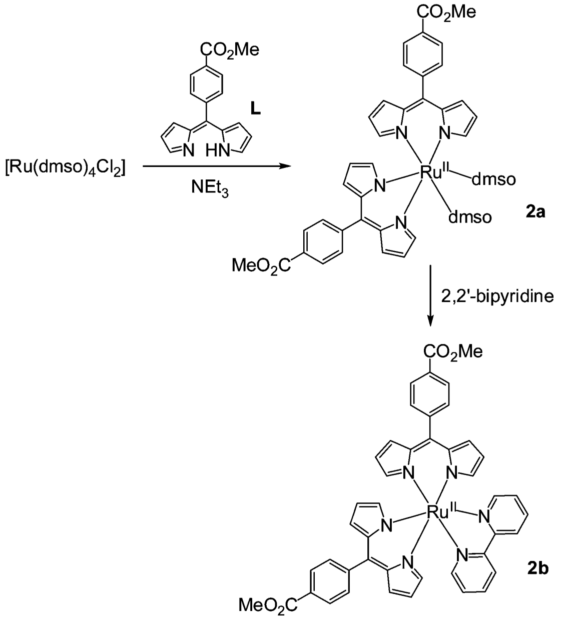


Figure 3. Molecular structure of one of the enantiomers of **1b** in the solid state as determined by X-ray crystallography. Thermal ellipsoids are displayed at the 30% level. Violet = Ru; blue = N; black = C; red = O; gray = H.

Scheme 2. The Synthetic Route to Complexes **2a** and **2b**



intermediate for the synthesis of various bis- and tris(dipyrrinato) complexes of ruthenium(II). Indeed, **2a** could be cleanly converted into **2b** via a direct reaction with 2,2′-bipyridine at elevated temperatures. Complex **2b** was isolated as a metallic green solid and characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS, UV/vis spectroscopy, and elemental analysis.

The most notable feature of the absorption spectrum of **2b** is the broad, intense band at 638 nm (Figure 1). We ascribe this to a Ru → bipy (MLCT) transition on the basis of this band being progressively red-shifted in going from $[Ru(bipy)_3]^{2+}$ to **1b** to **2b**. The peak around 480 nm arises from the intraligand dipyrrin ($\pi-\pi^*$) transition.

This assignment of the absorption spectrum of **2b** is supported by resonance Raman spectroscopy. Remarkably different spectra were observed upon excitation into the low-energy band (λ_{ex} = 633 nm, Figure 2c) versus the band around 450 nm (λ_{ex} = 458 nm, Figure 2d). The former spectrum exhibits distinct parallels with the resonance Raman spectrum of $[Ru(bipy)_3]^{2+}$. This implies that the absorption band of **2b** at 638 nm also involves a Ru → bipy MLCT transition. The 458 nm spectrum of **2b** is nearly identical to that seen for **1b**, strongly suggesting that the absorption bands around 480 nm for **1b** and **2b** originate from similar transitions, namely, dipyrrin $\pi-\pi^*$. As for **1b**, it appears that the dipyrrin and MLCT chromophores in complex **2b** are largely uncoupled.

Preliminary measurements indicate that complexes [**1a**]PF_6, **1b**, and **2b** exhibit either very weak or no fluorescence upon excitation into their dipyrrin absorption bands (λ_{ex} = 460 nm). In the case of **2b**, where the MLCT absorption band is energetically well separated from the dipyrrin band, excitation into the MLCT excited states also does not lead to any emission. As observed for related complexes, the excited states of these complexes may decay via low-lying ligand field states.[11] A full investigation of the emissive properties of these complexes, including any pH-dependent emission from **1b**, is continuing.

Ruthenium(II) complexes are of considerable interest in the context of dyes in dye-sensitized solar cells.[12] Mixed dipyrrin/bipyridine ruthenium(II) complexes are anticipated to be efficient dyes due to the light-harvesting capacity of dipyrrins and metal-mediated energy transfer between dipyrrin-localized excited states and (lower-energy) MLCT excited states. The general synthetic strategies reported herein should provide a route to analogues of **1b** and **2b** that feature carboxyl functional groups on the bipyridyl ligands, hence enabling efficient binding and electron transfer pathways to TiO_2. Work toward this goal is continuing, along with a full experimental and computational analysis of the fascinating spectroscopic properties of this family of compounds.

Supporting Information Available: Synthetic procedures and analytical data for **1b**, **2a**, and **2b**. Raman spectroscopy details including data in tabulated form. X-ray crystallographic data for complex **1b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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