Synthesis of Polypyridyl Complexes of Ruthenium(II) Containing Three Different Bidentate Ligands

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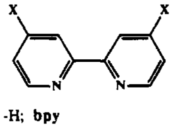
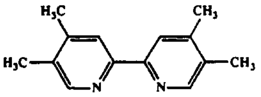
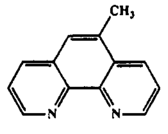
The metal-to-ligand charge transfer (MLCT) excited states of polypyridyl complexes of Ru(II) have provided a basis for the study of photoinduced electron or energy transfer in solution and in molecular assemblies.[1-5] The properties of these excited states can be varied systematically by varying the ligands.[6-9] We describe here a general synthetic procedure which extends the coordination chemistry to heteroleptic tris-bidentate polypyridyl (pp) complexes, $[Ru(pp)(pp')(pp'')]^{2+}$, based on the ligands and opens new possibilities for the design of specific excited-state properties.



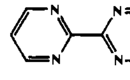
X = -H; bpy
X = $-CH_3$; 4,4'-$(Me)_2$bpy
X = -COOEt; 4,4'-$(CO_2Et)_2$bpy
X = $-NH_2$; 4,4'-$(NH_2)_2$bpy



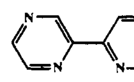
4,4',5,5'-$(Me)_4$bpy =
4,4',5,5'-tetramethyl-2,2'-bipyridine



5-Me-phen =
5-methyl-1,10-phenanthroline



bpm = 2,2'-bipyrimidine



bpz = 2,2'-bipyrazine

Earlier attempts to develop general synthetic routes to heteroleptic tris-bidentate complexes have met with limited success.[10] Our procedure was adapted from the method of Deacon and Thomas[11-13] and uses $[Ru(CO)_2(Cl)_2]_n$ as the precursor.[14] When $[Ru(CO)_2(Cl)_2]_n$ and a bidentate polypyridyl ligand (pp) were heated at reflux in EtOH or MeOH for 15 min, the yellow solids *trans*-(Cl)-$[Ru(pp)(CO)_2Cl_2]$ (pp = bpy or 4,4'-$(Me)_2$bpy) precipitated and were isolated as fine yellow crystals on recrystallization from MeOH in 80–90% yield. They were converted into the corresponding triflato species, $[Ru(pp)(CO)_2(CF_3SO_3)_2]$ by heating at 105–110 °C for 90 min in trifluoromethanesulfonic acid in a stream of N_2 and collected after precipitating the white product by the addition of ethyl ether at 0 °C. The white to pale yellow cations $[Ru(pp)(pp')(CO)_2]^{2+}$ (pp = bpy, 4,4'-$(Me)_2$bpy; pp' = bpy, 4,4'-$(Me)_2$bpy, 4,4'-$(CO_2Et)_2$bpy, bpm, 5-Me-phen) were formed by dissolving the triflato complexes and an excess of a second polypyridyl ligand (pp') and heating in ethanol at reflux for 90 min. They were isolated as PF_6^- salts in 70–80% yield upon addition of a saturated aqueous solution of NH_4PF_6 and recrystallization from ethanol. The tris-bidentate cations $[Ru(pp)(pp')(pp'')]^{2+}$ were formed by heating the dicarbonyl cations $[Ru(pp)(pp')(CO)_2]^{2+}$ with a 3-fold excess of the decarbonylating reagent trimethylamine *N*-oxide in 1,2-dimethoxyethane at reflux in the presence of an excess of the third polypyridyl ligand (pp'') (pp'' = bpy, 4,4'-$(Me)_2$bpy, 4,4'-$(CO_2Et)_2$bpy, bpm, 5-Me-phen, 4,4'-$(NH_2)_2$bpy, 4,4',5,5'-$(Me)_4$bpy, bpz). Purification was achieved by Sephadex (SP-

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Table I. Ground and Excited State Properties in CH_3CN at 298 K

	$E_{1/2}$, V vs SSCE[a]		λ_{max}, nm (±2 nm) ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})	λ_{em},[b] nm (±3 nm)	ϕ_{em}[c] ±5%	τ,[b] ns (±5%)	ϕ_{dec},[d] (±10%)
	oxidn	redn					
$[Ru(bpy)_3]^{2+}$	+1.29	−1.33 −1.52 −1.78	285 (87.0)[e] 323 (6.5) 345 (6.5) 451 (14.0)	626	0.062	920	0.029
$[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(5\text{-}Me\text{-}phen)]^{2+}$	+1.24	−1.37 −1.56 −1.81	268 (68.8) 286 (68.5) 385 (sh) (8.96) 429 (20.1) 453 (17.2)	627	0.069	1115	0.011
$[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(bpm)]^{2+}$	+1.37	−1.03 −1.49 −1.74	269 (50.7) 286 (62.9) 395 (sh) (9.59) 429 (13.2) 448 (13.1)	665	0.007	67	<0.001
$[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(4,4'\text{-}(CO_2Et)_2bpy)]^{2+}$	+1.35	−1.01 −1.48 −1.69	286 (56.7) 309 (34.4) 366 (9.63) 399 (sh) (9.19) 426 (10.3) 483 (10.7)	702	0.055	772	<0.001

[a] Acetonitrile/0.1 M $[N(n\text{-}C_4H_9)_4]PF_6$ at a Pt-button working electrode (0.4 cm^2) at a scan rate of 100 mV/s. [b] In ~1 × 10^{-5} M Ar-sparged CH_3CN solutions at 298 K. [c] Emission quantum yields (ϕ_{em}) by using $[Ru(bpy)_3](PF_6)_2$ in CH_3CN (ϕ_{em} = 0.062) as the standard, as described previously. Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448. [d] Quantum yields for decomposition measured relative to $[Ru(bpy)_3](PF_6)_2$ (ϕ_p ~ 0.029) at ~2 × 10^{-5} M in a freeze–pump–thaw degassed (4×), stirred 0.2 M $[N(n\text{-}C_4H_9)_4]Cl/CH_3CN$ solution at 295 K by measuring the decrease in emission intensity as a function of time (12 h). A collimated 75-W Xe lamp was used as the source, with the intensity of irradiation measured using Reincke salt as a chemical actinometer. Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803. [e] Rillema, D. P.; Allen, G. H.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

C25) cation-exchange chromatography with 0.2 M NaCl in H_2O as the eluent. The complexes were isolated from the eluent as PF_6^- salts by addition of a saturated aqueous solution of NH_4PF_6. The purities of the samples were established by ion-exchange HPLC on a Brownlee AX-100 "Prep 10" column following procedures described elsewhere.[15]

The compounds and salts were characterized by ^1H-NMR spectroscopy, electrochemical measurements and elemental analysis.[16] Corroborating evidence that the products were the tris-heteroleptic chelates $[Ru(pp)(pp')(pp'')]^{2+}$ (rather than a statistical mixture of complexes with varying ligand distributions) was obtained by fast atom bombardment mass spectrometry (FAB) in a 3-nitrobenzyl alcohol matrix.[17] Appearing in the spectra were the ion pairs, $\{[Ru(pp)(pp')(pp'')](PF_6)\}^+$, and fragment ions corresponding to the loss of the second PF_6^- and sequential loss of the remaining polypyridyl ligands. Parent ions for the tris-heteroleptic chelates were not observed.

The photophysical and electrochemical properties of some of these complexes have been investigated in detail; those for $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(5\text{-}Me\text{-}phen)]^{2+}$, $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(bpm)]^{2+}$, and $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(4,4'\text{-}(CO_2Et)_2bpy)]^{2+}$ are summarized in Table I. They include $E_{1/2}$ values for the $Ru^{III/II}$ and the one-electron ligand-based couples, absorption and emission spectral maxima, MLCT excited state lifetimes, and quantum yields for emission and ligand loss relative to $[Ru(bpy)_3]^{2+}$. Excitation spectra acquired at the emission maximum overlay the absorption spectra within experimental error. On the basis of transient resonance Raman spectra of the excited states, emission originates from MLCT states with the excited electron on the ligand having the most positive reduction potential.[18] For $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(bpm)]^{2+}$, where bpm has the lowest lying π^* acceptor level, intense excited-state resonance Raman signals characteristic of $4,4'\text{-}(Me)_2bpy$ in $[Ru(4,4'\text{-}(Me)_2bpy)_3]^{2+*}$ at 1202, 1321, 1445, and 1624 cm^{-1} and bpy in $[Ru(bpy)_3]^{2+*}$ at 1211, 1321, and 1624 cm^{-1} were not observed, while bands for bpm at 766, 1012, 1034, 1174, 1249, 1421, 1490, and 1560 cm^{-1} were observed. Compared with $[Ru(bpy)_3]^{2+}$, all of the mixed ligand complexes are much less prone to undergo photochemically induced ligand loss. From this observation and the fact that emission lifetimes (τ) for $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(5\text{-}Me\text{-}phen)]^{2+}$ and $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(4,4'\text{-}(CO_2Et)_2bpy)]^{2+}$ in 4:1 (v/v) EtOH:MeOH are only slightly temperature dependent over the range 160–298 K, the dd states in these complexes appear to be relatively inaccessible in these ligand environments at room temperature.[19,20]

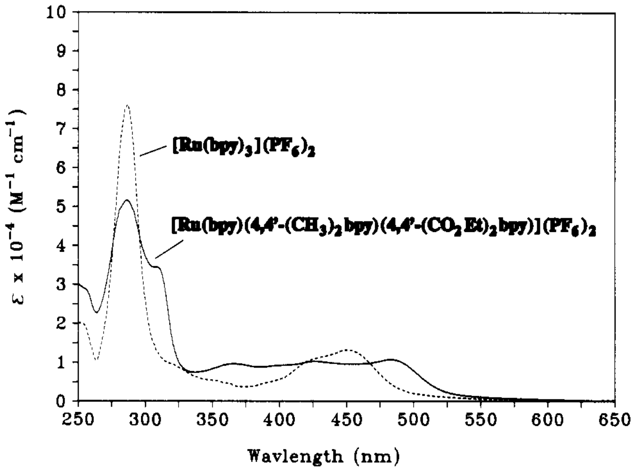

Figure 1. Absorption spectra in CH_3CN at 298 K.

The synthetic method described here is general. It opens new strategies for the design of molecular assemblies and visible light

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sensitizers based on tris-bidentate complexes of Ru^{II}. For example, by proper exploitation of the substituents on the polypyridyl ligands and by taking advantage of the existence of $d\pi \rightarrow \pi^*$ transitions to the lowest two acceptor levels at the polypyridyl ligand, it is possible to "fill in" large portions of the visible spectrum of these complexes compared to $[Ru(bpy)_3]^{2+}$. This can be seen in Figure 1 where spectra for $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)(4,4'\text{-}(Me)_2bpy)(4,4'\text{-}(CO_2Et)_2bpy)]^{2+}$ are compared. For the mixed-ligand complex bands arising from $d\pi \rightarrow \pi_1^*(4,4'\text{-}(CO_2Et)_2bpy)$ and $d\pi \rightarrow \pi_2^*(4,4'\text{-}(CO_2Et)_2bpy)$ transitions appear at 520 and 380 nm, the former extending to 580 nm with appreciable absorption. The region between 450 and 460 nm is filled in by $d\pi \rightarrow \pi_1^*$(bpy, $4,4'\text{-}(Me)_2bpy$) absorptions while the $d\pi \rightarrow \pi_2^*$(bpy, $4,4'\text{-}(Me)_2bpy$)) absorption appears at $\lambda < 350$ nm, overlapped with $\pi \rightarrow \pi^*$ transitions at the polypyridyl ligands.

We are currently exploring the use of multiple ligands to prepare complexes with even lower energy absorptions, with the ultimate goal of designing "black absorbers" which will exhibit high absorptivity throughout the visible and near-UV region, be photostable, and retain appreciable excited-state lifetimes.

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