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Synthetic Control of Excited-State Properties. Tris-Chelate Complexes Containing the Ligands 2,2′-Bipyrazine, 2,2′-Bipyridine, and 2,2′-Bipyrimidine

George H. Allen, Russell P. White,† D. Paul Rillema,† and Thomas J. Meyer*

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. *Received May 9, 1983*

Abstract: The photophysical and photochemical properties of the series of tris-chelate complexes $Ru(bpy)_n(bpyz)_{3-n}{}^{2+}$, $Ru(bpy)_n(bpym)_{3-n}{}^{2+}$, $Ru(bpym)_n(bpyz)_{3-n}{}^{2+}$, and $Ru(bpy)(bpym)(bpyz)^{2+}$ (n = 0, 1, 2, 3; bpy = 2,2′-bipyridine, bpyz = 2,2′-bipyrazine, bpym = 2,2′-bipyrimidine) are described. From the results of temperature-dependent lifetime (210–345 K) and room-temperature emission quantum yield measurements have been obtained: (1) k_r and k_{nr}, the radiative and nonradiative decay rate constants for the emitting MLCT manifold and (2) kinetic parameters which suggest the intervention of additional excited states. The significant points of the study are the following: (1) trends in k_{nr} properties are understandable based on the energy gap law, (2) low-lying dd states strongly influence lifetimes and photochemical instabilities for the complexes $Ru(bpyz)_3{}^{2+}$, $Ru(bpym)_3{}^{2+}$, $Ru(bpy)(bpyz)_2{}^{2+}$, $Ru(bpy)(bpym)_2{}^{2+}$, $Ru(bpym)(bpyz)_2{}^{2+}$, $Ru(bpym)_2(bpyz)^{2+}$, and $Ru(bpy)(bpym)(bpyz)^{2+}$ at room temperature, and (3) for the complexes $Ru(bpy)_2(bpyz)^{2+}$ and $Ru(bpy)_2(bpym)^{2+}$ there is no evidence for low-lying dd states and these and/or related mixed-ligand complexes may provide a basis for a new series of photochemically stable Ru–polypyridyl chromophores.

The absorption spectra of polypyridyl complexes of Ru(II) and Os(II) are dominated by metal-to-ligand charge-transfer (MLCT) transitions, e.g.,

$$[(bpy)_2Ru^{II}(bpy)]^{2+} \xrightarrow[\text{bpy}=\text{2,2}'\text{-bipyridine}]{+h\nu} [(bpy)_2Ru^{III}(bpy^{-}\cdot)]^{2+*}$$

The results of a series of spectroscopic and theoretical studies suggest that absorption is dominated by transitions to MLCT states which are largely singlet in character[1] and ligand localized on the IR–Raman time scale.[2] Emission appears to occur from states largely triplet in character although the effect of spin–orbit coupling is to mix ^{1}MLCT and ^{3}MLCT states.[1,3]

It has been shown by a series of lifetime (τ_0) and emission quantum yield (ϕ_r) studies that subsequent radiative (k_r) or nonradiative (k_{nr}) decay of the "triplet" state(s) can be accounted for quantitatively[4] by the Einstein equation for spontaneous emission and the energy gap law for nonradiative decay in the form derived by Englman and Jortner[5a] and Jortner and Freed.[5b]

For polypyridyl compounds of Ru(II) an additional feature in the excited-state structure is the appearance of low-lying dd state(s).[4d,e,6] For complexes like $Ru(bpy)_3{}^{2+}$ the dd states are populated by thermal activation from ^{3}MLCT and once formed appear to undergo rapid decay to the ground state, or worse, thermally activated metal–ligand bond dissociation which can lead to relatively efficient photodecomposition, e.g.,

$$[Ru(bpy)_3](NCS)_2 \xrightarrow[CH_2Cl_2]{h\nu} Ru(bpy)_2(NCS)_2 + bpy$$
$$\phi = 0.068^{6a}$$

The existence of low-lying dd states represents a serious limitation to the use of polypyridyl complexes of Ru(II) as photosensitizers both by depletion of the relatively long-lived ^{3}MLCT states and by providing a pathway for photodecomposition. Typically, complications arising from dd states can be avoided by turning to analogous complexes of Os(II) since $10Dq$ is ~ 30% greater for Os, and dd states are not thermally accessible at room temperature and below. However, there are several reasons why Ru(II) polypyridine compounds represent a potentially superior source of photosensitizers.

(a) For equivalent cases where excited-state energies are the same, Ru(II) ^{3}MLCT excited states are longer lived, by a factor of ~3, when compared to their Os(II) MLCT counterparts.[4a]

(b) An extensive background synthetic chemistry exists for Ru(II), and the preparative conditions involved are less demanding.[4c,7]

(c) The background synthetic chemistry to ligand-bridged dimers and oligomers and to intramolecular quencher complexes is known, and the potential clearly exists for designing complex systems where the Ru–bpy chromophore is attached to potential catalytic sites.[8]

However, a severe restriction on the use of such systems is photodecomposition as shown by the loss of pyridine in $Ru(bpy)_2(py)_2{}^{2+}$ which occurs with $\phi \sim 0.3$.[6a]

Clearly it would be desirable to understand and control the factors involved in determining the relative ordering of ^{3}MLCT and dd excited-state energies in Ru(II)–polypyridyl complexes. Recent work[4d] on the series of complexes $Ru^{II}(bpy)_2(L)_2{}^{2+}$ has shown that variations in L can significantly affect the relative position of the dd state as shown by temperature-dependent

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† Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223.

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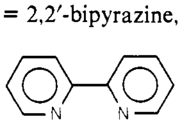
Table I. Kinetic Decay Parameters

complex	T, K[a]	k_{nr},[b] s^{-1}	k_r,[b] s^{-1}	k_1,[c] s^{-1}	k'^0,[c] s^{-1}	$\Delta E'$,[c] cm^{-1}
Ru(bpym)$_3$$^{2+}$	210-322	$(2.1 \pm 0.2) \times 10^6$	$(9 \pm 1) \times 10^4$	$(2.20 \pm 0.01) \times 10^6$	$(6.4 \pm 2.4) \times 10^{13}$	3375 ± 85
Ru(bpy)(bpym)$_2$$^{2+}$	210-295	$(5.1 \pm 0.5) \times 10^6$	$(6 \pm 0.6) \times 10^4$	$(5.10 \pm 0.02) \times 10^6$	$(3.2 \pm 1.4) \times 10^{13}$	3800 ± 110
Ru(bpy)$_2$(bpym)$_2$$^{2+}$	210-345	$(1.24 \pm 0.2) \times 10^7$	$(5 \pm 0.5) \times 10^4$	$(1.2 \pm 0.2) \times 10^7$	$(1 \pm 3) \times 10^7$	400 ± 300
Ru(bpyz)$_3$$^{2+}$	210-295	$(2.4 \pm 0.3) \times 10^5$	$(9 \pm 1) \times 10^4$	$(3.30 \pm 0.03) \times 10^5$	$(8 \pm 2) \times 10^{12}$	3325 ± 60
Ru(bpym)(bpyz)$_2$$^{2+}$	210-345	$(4.0 \pm 0.4) \times 10^5$	$(7 \pm 1) \times 10^4$	$(4.75 \pm 0.07) \times 10^5$	$(8 \pm 2) \times 10^{13}$	3917 ± 48
Ru(bpym)$_2$(bpyz)$^{2+}$	210-345	$(6.6 \pm 0.6) \times 10^5$	$(8.1 \pm 0.8) \times 10^4$	$(7.4 \pm 0.1) \times 10^5$	$(3.5 \pm 1.0) \times 10^{13}$	3850 ± 70
Ru(bpy)(bpym)(bpyz)$^{2+}$	210-345	$(1.0 \pm 0.1) \times 10^6$	$(7.0 \pm 0.7) \times 10^4$	$(1.1 \pm 1.0) \times 10^6$	$(2.8 \pm 0.6) \times 10^8$	1415 ± 55
Ru(bpy)(bpyz)$_2$$^{2+}$	210-345	$(6.7 \pm 0.7) \times 10^5$	$(7 \pm 1) \times 10^4$	$(7.4 \pm 0.1) \times 10^5$	$(4 \pm 3) \times 10^9$	2100 ± 175
Ru(bpy)$_2$(bpyz)$^{2+}$	210-345	$(2.1 \pm 0.2) \times 10^6$	$(5 \pm 0.5) \times 10^4$	$(2.1 \pm 0.2) \times 10^6$	$(3 \pm 9) \times 10^7$	800 ± 600
Ru(bpy)$_3$$^{2+}$ [d]	210-295	$(5.2 \pm 0.5) \times 10^5$	$(8.0 \pm 1.5) \times 10^4$	$(6.10 \pm 0.05) \times 10^5$	$(4 \pm 2) \times 10^{12}$	3275 ± 75

[a] Temperature range studied in lifetime experiment. [b] Calculated from ϕ_r and k_1 data (see text). [c] Obtained from temperature-dependent lifetime measurements in the temperature range given. [d] Data for Ru(bpy)$_3$$^{2+}$ from ref 4e.

lifetime studies, but in all cases studied the dd state remained thermally accessible at room temperature.

An alternate approach to the problem of controlling the accessibility of low-lying dd states is to make variations in the chromophoric ligand(s).[9d] Examples of two such cases have been described on the basis of Ru(bpyz)$_3$$^{2+}$ and Ru(bpym)$_3$$^{2+}$ (bpyz = 2,2′-bipyrazine, bpym = 2,2′-bipyrimidine).[9a-c] Emission and lifetime studies on the two complexes show the existence of relatively long-lived ^{3}MLCT states with properties much like those of the ^{3}MLCT states of Ru(bpy)$_3$$^{2+}$. From spectroscopic and electrochemical measurements it has been shown that the bpyz and bpym ligands have lower lying π^* levels which lead to significant changes in ground- and excited-state redox potentials but to relatively small changes in absorption and emission spectral properties.[9a-c,10]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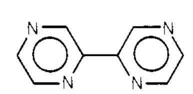
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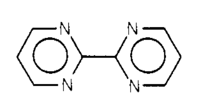
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Recently we reported[10] on the emission and excited-state redox properties of a series of mixed bpy–bpyz and bpy–bpym chelate complexes. The goal of the present work was to investigate the photochemical and photophysical properties of the mixed-chelate complexes in order to explore the following issues. (a) Can the available theory for radiative and nonradiactive processes be applied to MLCT states based on bpyz and bpym as the chromophoric ligands? (b) It is possible to establish in greater detail those factors dictating the relative energies of low-lying dd and MLCT states? (c) Can the availability of such information lead to the synthetic design of a new class of photosensitizers free of the complications caused by low-lying dd states?

Experimental Section

Materials. [AsPh$_4$](NCS) was recrystallized from water and dried under vacuum. Glass-distilled propylene carbonate was purchased from Burdick and Jackson and used without further purification. All other reagents were purchased commercially as reagent grade chemicals and used without further purification.

Preparation of Compounds. The compounds used in this study were prepared as described earlier,[10] and the preparation of the complexes Ru(bpym)(bpyz)$_2$$^{2+}$, Ru(bpym)$_2$(bpyz)$^{2+}$, and Ru(bpy)(bpym)(bpyz)$^{2+}$ will be described in a forthcoming publication.

Physical Measurements. UV–vis spectra were recorded on a Bausch and Lomb 2000 spectrophotometer using matched 1-cm quartz cells.

Lifetime measurements were obtained as described in an earlier paper[6a] with the addition of two devices used for thermal regulation in the temperature range 210–345 K. (1) At room temperature and below an Oxford Instruments liquid N$_2$ Dewar system was utilized with a 6-mm cylindrical Pyrex sample holder. (2) For room temperature and above a water-jacketed sample cell constructed of Pyrex with two quartz windows at right angles was used in conjunction with a large-capacity thermostated circulating water bath. A thermistor, Omega Engineering NaH-106-UUA35J3, attached to the cell, was used to measure the temperature. In regions of temperature overlap results obtained by using either apparatus gave identical results.

Photochemical quantum yields were measured by observing the loss of luminescence as described earlier.[6a]

Corrected emission spectra were obtained with a SLM Instruments, Inc. Model 8000 photon counting fluorimeter. Emission quantum yields in propylene carbonate at 25 °C were determined in deoxygenated solutions (N$_2$ bubbling for 30 min) by a relative method using an aqueous solution containing Ru(bpy)$_3$$^{2+}$ as a standard. Corrections were made for the difference in the refractive indices of the two solvents[11] as shown in eq 1, where ϕ_r^{obsd} is the uncorrected emission quantum yield, n is the

$$\phi_r = \phi_r^{obsd}(n^2/n^2_{H_2O}) \qquad (1)$$

refractive index of propylene carbonate, and n_{H_2O} is the refractive index of water. Emission spectra at 77 K were obtained in 4:1 EtOH/MeOH glasses.

Kinetic and Spectral Fits. Fits of the temperature-dependent lifetime data were made with a PDP 11/34 minicomputer and a Gauss Newton algorithm supplied by Tektronix, Inc.

Spectral fits of the low-temperature emission spectra were made by using a modified version of a two-mode fitting program written by Caspar.[4d,e,12] After converting the wavelength abcissa values to energy, the emission spectral data were corrected for slit-width variations as described by Parker and Rees[13a,b] before fitting.

Results

In the first paper in this series[10] the preparations and characterizations of the mixed bpy–bpyz and bpy–bpym chelate complexes were described. In addition, electrochemical, absorption, and room-temperature emission data were presented. In the present work we have acquired detailed information concerning the photophysical properties of the excited states of these complexes.

Temperature-Dependent Lifetimes. Rate Constants for Excited-State Decay. Temperature-dependent lifetime data were obtained by laser flash photolysis–emission decay measurements using an apparatus described earlier and in brief in the Experimental Section. As for related complexes of Ru(II),[6,12] satisfactory fits of the data were obtained by using the expression in eq 2.

$$[\tau_0(T)]^{-1} = k_r + k_{nr} + k'^0 \exp[-\Delta E'/kT] \qquad (2)$$

As before, the interpretation of the constants is that k_r and k_{nr} are radiative and nonradiative rate constants for decay from

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$$I(E) = \sum_{n_1=0}^{5} \sum_{n_2=0}^{5} \left(\frac{E_{em}(0\text{-}0) - n_1\hbar\omega_1 - n_2\hbar\omega_2}{E_{em}(0\text{-}0)} \right)^4 \left(\frac{S_1^{n_1}}{n_1!} \right) \left(\frac{S_2^{n_2}}{n_2!} \right) \exp\left[-4 \log 2 \left(\frac{E - E_{em}(0\text{-}0) + n_1\hbar\omega_1 + n_2\hbar\omega_2}{\nu_{1/2}} \right)^2 \right]$$

where the summation was carried out over the two sets ($h\omega_1$ and $h\omega_2$, see text) of six vibrational levels. The range for E was 11 000–20 000 cm^{-1}. For explanation of the other variables, see text.

Table II. Emission Data and Emission Spectral Fitting Parameters

complex	$E_{\mathrm{em,\,max}}$,[a] nm	ϕ_r[b]	$E_{\mathrm{em}}(0\text{-}0)$,[c] cm^{-1}	$\hbar\omega_M$,[c] cm^{-1}	S_M[c]	$\hbar\omega_L$,[c] cm^{-1}	S_L[c]	fwhm,[c] cm^{-1}
$Ru(bpym)_3^{2+}$	639	0.011	16 750	1400	1.2	400	1.15	725
$Ru(bpy)(bpym)_2^{2+}$	670	0.011	16 580	1400	1.28	400	1.5	700
$Ru(bpy)_2(bpym)^{2+}$	710	0.004	16 000	1350	1.23	400	1.35	900
$Ru(bpyz)_3^{2+}$	610	0.074	17 600	1325	1.0	400	1.15	650
$Ru(bpym)(bpyz)_2^{2+}$	633	0.074	17 600	1350	1.1	400	1.5	750
$Ru(bpym)_2(bpyz)^{2+}$	655	0.077						
$Ru(bpy)(bpym)(bpyz)^{2+}$	684	0.049	16 150	1350	1.2	400	1.15	700
$Ru(bpy)(bpyz)_2^{2+}$	654	0.079	16 750	1200	1.35	400	1.5	650
$Ru(bpy)_2(bpyz)^{2+}$	710	0.019	15 650	1300	0.9	400	1.25	650
$Ru(bpy)_3^{2+}$	622	0.071	17 380	1400	0.95	400	1.1	575

[a] Wavelength of maximum emission intensity in propylene carbonate at room temperature, corrected for phototube response. [b] Error limits are ±10%. [c] Spectral fitting parameters obtained by using a two-mode fitting procedure on data obtained at 77 K (see text).

low-lying ^{3}MLCT states. The temperature-dependent term has been interpreted as involving thermally activated population of near-lying dd states from the emitting ^{3}MLCT states.[6] As noted earlier and as will be discussed in a later section, a temperature dependence is expected for k_{nr}, but the effect is clearly slight and can be neglected in the data treatment. The temperature-dependent lifetime data were fit to eq 2 in the form,

$$[\tau_0(T)]^{-1} = k_1 + k'^0 \exp[-\Delta E'/kT]$$

utilizing a Gauss–Newton algorithm.[4e,6a] In Figure 1 are shown plots of $1/\tau_0$ vs. $1/T$ in propylene carbonate for $Ru(bpyz)_3^{2+}$ and $Ru(bpy)_2(bpyz)^{2+}$ along with calculated fits using the kinetic parameters in Table I.

It is possible to obtain separate values for k_r and k_{nr} by a combination of temperature-dependent lifetime and quantum yield measurements (eq 3). More generally, ϕ_r is given by eq 4, where

$$\phi_r = \frac{k_r}{k_r + k_{nr} + k'^0 \exp[-\Delta E'/RT]} = k_r\tau_0 \quad (3)$$

$$\phi_r = \eta_{isc} k_r \tau_0 \quad (4)$$

η_{isc} is the efficiency of population of the emitting state(s) following excitation. It is known for $Ru(bpy)_3^{2+}$ that $\eta_{isc} \sim 1.0$ over a wide range of excitation wavelengths,[3b,14] and we have no reason to think otherwise here.

On the basis of the treatments outlined above and $\tau_0(T)$ and ϕ_r measurements, the excited-state kinetic parameters obtained for the series of complexes are shown in Table I. Note that all of the temperature dependence is forced into the single exponential term by the fitting procedure.

Emission Spectra. Room-temperature emission spectra were obtained in propylene carbonate, and the results for the series of complexes are summarized in Table II. In addition, emission spectra were obtained at 77 K in 4:1 EtOH/MeOH glasses. Low-temperature spectra for $Ru(bpy)_2(bpyz)^{2+}$ and $Ru(bpy)(bpym)_2^{2+}$ are shown in Figure 2; spectral fits of the data (discussed below) are also shown in the figure. Even though several of the complexes are mixed chelates containing different chromophoric ligands, no evidence was obtained for multiple emissions either from emission or lifetime measurements. Note that on the basis of electrochemical data[10] and trends in emission energies it has been concluded that in the mixed chelates $Ru(bpy)_n(bpyz)_{3-n}^{2+}$ and $Ru(bpy)_n(bpym)_{3-n}^{2+}$ (n = 0–3) the lowest lying, emitting charge-transfer states are based on the $Ru^{III}(bpyz^{-}\cdot)$ or $Ru^{III}(bpym^{-}\cdot)$ chromophores. This is the expected result since, from electrochemical measurements, the relative ordering of the π^* levels in the free and complexed chelates is $\pi^*(bpyz) < \pi^*(bpym) < \pi^*(bpy)$.

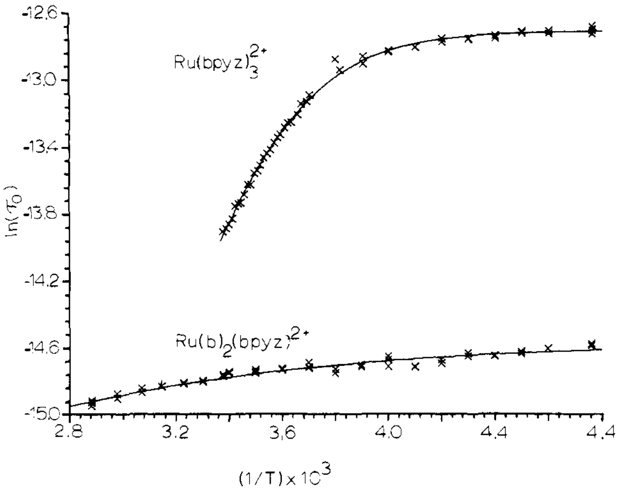

Figure 1. Comparison of the temperature-dependent experimental lifetime data (×) with a computer-generated fit using eq 2 and the parameters in Table I (—) for the complexes $Ru(bpyz)_3^{2+}$ and $Ru(bpy)_2(bpyz)^{2+}$ in propylene carbonate.

As is characteristic of other Ru(II) and Os(II) polypyridine complexes, well-resolved vibrational progressions in the range 1200–1400 cm^{-1} appear in the low-temperature emission spectra.[4d,e,12,15] In complexes where 2,2′-bipyridine or 1,10-phenanthroline is the chromophoric ligand the vibrational structure appears to arise from bpy- or phen-localized vibrations. The ν(bpy) acceptor vibration is no doubt a combination of ring-stretching vibrations. It is worth noting that the pattern of IR bands in the complexes $Ru(bpy)_3^{2+}$, $Ru(bpyz)_3^{2+}$, and $Ru(bpym)_3^{2+}$ in the ring-stretching region (1000–1500 cm^{-1}) is qualitatively the same, although Raman data are not yet available for the series. For example, $Ru(bpyz)_3^{2+}$ shows strong bands in the IR at 1418 cm^{-1} and 1323 cm^{-1}, and $Ru(bpym)_3^{2+}$ shows a strong band at 1410 cm^{-1} and a weak band at 1344 cm^{-1} (all ± 2 cm^{-1}).

Because of the structural similarities amongst the ligands and the common electronic origin of the excited states, the appearance of related vibrational progressions for the bpy-, bpyz-, and bpym-based luminophores is not unexpected.

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$$(dQ/d\nu) = \left(\frac{dQ}{d\lambda}\right)\left(\frac{d\lambda}{d\nu}\right) = -\left(\frac{dQ}{d\lambda}\right)\frac{\lambda^2}{c}$$

since $\nu = c/\lambda$; $d\lambda/d\nu = -c/\nu^2 = -\lambda^2/c$.

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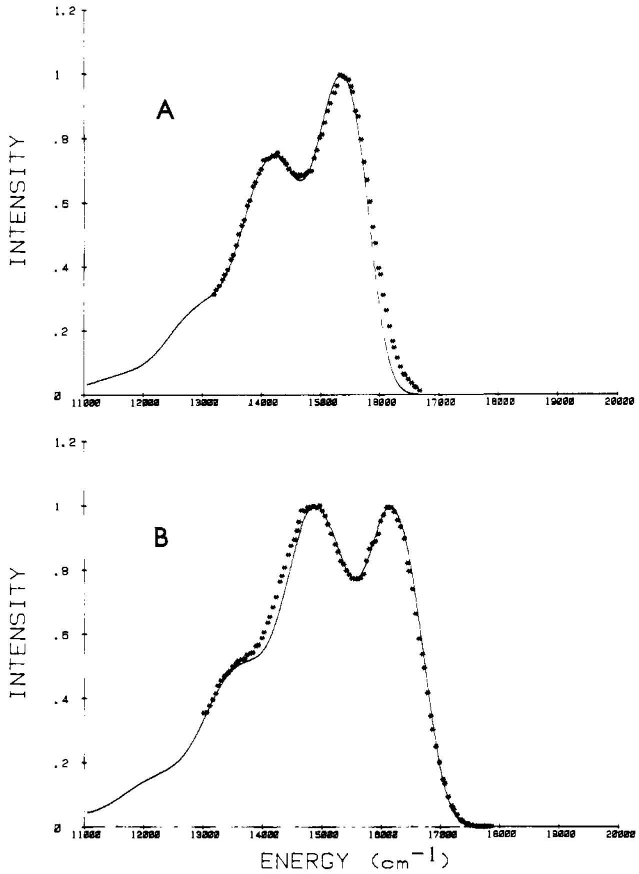

Figure 2. Emission data (*) at 77 K in 4:1 EtOH:MeOH glass at 77 K and calculated fits (—) using the spectral parameters in Table II for (a) $Ru(bpy)_2(bpyz)^{2+}$ and (b) $Ru(bpy)(bpym)_2^{2+}$.

Recent work on spectral fitting of the emission of Os(II)– or Ru(II)–polypyridine-based excited states[4d,e,12] has shown that significant contributions to the observed low-temperature spectra are also made by low-frequency vibrations presumably largely M–L stretching in character. The spectral parameters used in fitting the spectra were S_M, S_L, $E_{em}(0\text{–}0)$, $\hbar\omega_L$, $\hbar\omega_M$ and fwhm. S_M and S_L are measures of the distortion in the high-frequency (1200–1400 cm^{-1}) and low-frequency ($\sim$400 cm^{-1}) acceptor modes of the complexes (see below); $\hbar\omega_M$ and $\hbar\omega_L$ are the energies of the high- and low-frequency acceptor modes; and fwhm is the full width at half maximum in cm^{-1} of the 0–0 vibronic component in the emission spectra. The six parameters were varied systematically (except for $\hbar\omega_L$, a parameter to which the fits are relatively insensitive, and which was held at 400 cm^{-1}), and best fit values for the spectral parameters are shown in Table II for the various complexes. The best fit parameters for $Ru(bpy)_3^{2+}$ under identical conditions are included for purposes of comparison. The data are internally consistent and consistent as well with the parameters for $Ru(bpy)_3^{2+}$ with the exception of $Ru(bpy)_2(bpym)^{2+}$, which required a noticeably larger value for fwhm (900 cm^{-1}) to obtain a satisfactory fit. The fwhm parameter is related to χ_o, the classical outer-sphere trapping energy for the electron-transfer process associated with the excited → ground-state transition,[4e] and there is no obvious reason why χ_o should be abnormally high for $Ru(bpy)_2(bpym)^{2+}$.

Photochemical Quantum Yields. A series of experiments was undertaken to search for photochemical substitution in the mixed-chelate complexes. The medium of choice for the studies was CH_2Cl_2 where ion pairing is expected to be nearly complete even in dilute solution because of its low static dielectric constant (D_s = 9.8) and because of the availability of data in CH_2Cl_2 for $Ru(bpy)_3^{2+}$ and related complexes.[6a,17] Photochemical quantum yields for ligand loss (ϕ_p) for the complexes $Ru(bpy)_2(bpyz)^{2+}$ and $Ru(bpy)_2(bpym)^{2+}$ ($1\text{–}5 \times 10^{-5}$ M) as PF_6^- salts in CH_2Cl_2 but with added NCS^- (2×10^{-3} M) are shown in Table III. Data obtained for $[Ru(bpy)_3](NCS)_2$[6a] under the same conditions are also included for purposes of comparison. The striking point in the comparison is that the photochemistry observed for $Ru(bpy)_3^{2+}$ is quenched for both mixed-ligand chelates containing a single bpyz or bpym ligand.

Table III. Photochemical Quantum Yields

complex	ϕ_p[a]	$\phi_{ic}(dd)$[b]
$Ru(bpym)_3^{2-}$	0.48[a]	0.71
$Ru(bpy)(bpym)_2^{2+}$	$<10^{-3}$ [a]	0.07
$Ru(bpy)_2(bpym)^{2+}$	$<10^{-4}$ [c]	(0.10)[d]
$Ru(bpyz)_3^{2+}$	0.45[a]	0.74
$Ru(bpy)(bpyz)_2^{2+}$	0.035[a]	0.18
$Ru(bpy)_2(bpyz)^{2+}$	$<10^{-4}$ [c]	(0.20)[d]
$Ru(bpy)_3^{2+}$	0.068[e]	
$Ru(bpy)_3^{2+}$	0.029[a]	0.46

[a] Quantum yield for ligand loss for PF_6^- salts in CH_3CN, 2 mM in $[N(n\text{-}C_4H_9)_4]Cl$. The photochemical products are, for example, $Ru(bpyz)_2(CH_3CN)(Cl)^+$ following photolysis of $Ru(bpyz)_3^{2+}$. Error limits are ±10%. [b] Calculated quantum yield of formation of dd state following population of ^3CT state in propylene carbonate at room temperature. [c] As in *a* but in CH_2Cl_2 2 mM in $[As(C_6H_5)_4]NCS$. [d] These values do *not* represent efficiencies for the MLCT → dd transition, see text. [e] From ref 6a. Quantum yield for $[Ru(bpy)_3](NCS)_2$ in CH_2Cl_2. [f] Reference 4e.

Because of limited solubility we have investigated quantum yields for ligand loss for the remaining complexes in acetonitrile solution with complex concentrations in the range $1\text{–}5 \times 10^{-5}$ M with 2 mM added Cl^-. Data for $Ru(bpy)_3^{2+}$ under the same conditions are included for comparison. In agreement with previous work by Lever et al.,[9a] product studies indicate that in acetonitrile solution bpyz or bpym is lost to form the corresponding acetonitrile–chloro complex, i.e.,

$$Ru(bpy)(bpyz)_2^{2+} + CH_3CN + Cl^- \xrightarrow{h\nu} Ru(bpy)(bpyz)(CH_3CN)(Cl)^+ + bpyz$$

This is analogous to results by Cole-Hamilton et al.,[17] where photolysis of $Ru(bpy)_3^{2+}$ in acetonitrile solution in the presence of Cl^- was observed to occur with loss of bpy and the formation of $Ru(bpy)_2(CH_3CN)(Cl)^+$. Clearly there is considerable variation in the experimental ϕ_p values for the series of complexes in CH_3CN and possible origins for the variation will be discussed below, but the enhanced yields compared to $Ru(bpy)_3^{2+}$ for the complexes $Ru(bpyz)_3^{2+}$ and $Ru(bpym)_3^{2+}$ are worth noting.

Discussion

Photophysical Properties of the Emitting MLCT States. As noted above in the bpy–bpyz and bpy–bpym mixed-chelate complexes the available evidence[10] suggests that the luminophores are based on the bpyz or bpym ligands. A considerable amount of photophysical information is available concerning bipyridine-based, emitting MLCT states of Ru(II). That information provides a starting point and a basis for comparison with the data obtained here for the bpyz- and bpym-based luminophores.

Radiative Decay Rate Constants. The radiative rate constant is related to the Einstein coefficient for spontaneous emission[18] as shown in eq 5, in which E_{em} is the emission energy in ergs, ψ_e

$$k_r = \frac{4E_{em}^{\ 3}}{3\hbar^4} |\langle\psi_e|\vec{d}|\psi_g\rangle|^2 \qquad (5)$$

and ψ_g are the wave functions for the excited and ground electronic states, and $\vec{d}$ is the transition dipole moment operator. For either the bpym-based excited states, $(bpym^{-}\cdot)Ru^{III}L_4^{2+*}$, or bpyz-based excited states, $(bpyz^{-}\cdot)Ru^{III}L_4^{2+*}$, the range in k_r values is $k_r = 5 \times 10^4\text{–}9 \times 10^4$ s^{-1} at 25 °C in propylene carbonate. One point

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that follows immediately from the data is that the ratio k_r/E_{em}^3 (taking E_{em} as the energy at the maximum emission intensity) is relatively constant both within a luminophoric series and between the two different ligands. For a series of $Ru^{III}(bpy^{-}\cdot)$ chromophores based on the complexes $Ru(bpy)_2(L)_2^{2+}$ (L = py, ...) values of k_r ranged from 5.7×10^4 to 1.1×10^5 s^{-1}.[4d] The variations in the transition dipole moment, $|\langle\psi_e|d|\psi_g\rangle|$, are small among the three series where the luminophoric ligand is varied among bpy, bpym, and bpyz. It seems clear that the inherent k_r for the Ru-based MLCT excited states is relatively unaffected by substitution of bpy by either bpym or bpyz as the luminophoric ligand.

Nonradiative Decay Rate Constants. Earlier work on MLCT excited states based on 2,2′-bipyridine and 1,10-phenanthroline (phen) complexes of Os(II),[4a,b,12a] on $Ru(bpy)_3^{2+}$ in a series of solvents,[4e] and on the series of complexes $Ru(bpy)_2(L)_2^{2+}$ (L = pyridine and substituted pyridines)[4d] has demonstrated the applicability of radiationless decay theory in accounting for variations in k_{nr} for a series of related complexes.

In the low-temperature limit, for a high-frequency acceptor vibration ω_M ($\hbar\omega_M \gg k_BT$) and assuming weak vibrational coupling (small excited-state distortions) it has been shown that k_{nr} is given by the "energy gap law" in eq 6.[5,12a] In reaching eq

$$\ln k_{nr} = \ln \beta_0 - S_M - \frac{\gamma_0 E_{em}}{\hbar\omega_M} + S_L\frac{\omega_L}{\omega_M}(\gamma_0 + 1) + \frac{b\chi_0}{\hbar\omega_M} \tag{6}$$

6 the following definitions or approximations have been used: (a) $\beta_0 = (C_k^2\omega_k)(\pi/2\hbar\omega_M E_{em})^{1/2}$. (b) $C_k^2\omega_k$ is the vibrationally induced electronic coupling (vibronic) term consisting of the angular frequency of the promoting mode(s) (ω_k) and the nuclear momentum matrix element. (c) $\gamma_0 = \ln(E_{em}(0\text{–}0)/\hbar\omega_M S_M) - 1$. (d) χ_0 is four times the classical solvent reorganizational or trapping energy associated with the transfer of the electron from the ligand to the metal. (e) ω_M is the angular frequency of the high-frequency acceptor vibration(s). (f) $E_{em}(0\text{–}0)$ is the emission energy for the $v'_M = 0 \rightarrow v_M = 0$ vibrational component and is approximately equal to E_{em}, the energy of emission at λ_{max}. (g) $S_M = {}^1/_2\Delta_M^2$ for $\hbar\omega_M \gg k_BT$ is a measure of the extent of excited-state distortion in the acceptor vibration. Δ_M^2 is the dimensionless fractional displacement in the acceptor vibration between equilibrium geometries of the ground and excited states. It is related to the change in equilibrium nuclear coordinate between states (ΔQ_{eq}) by $\Delta_M^2 = (M\omega/\hbar)(\Delta Q_{eq})^2$, where M is the reduced mass. (h) S_L and ω_L are analogous to S_M and ω_M and represent the distortion and angular frequency of low-frequency (~400 cm^{-1}) acceptor modes assumed to be largely M–L stretching in origin. (i) $b = (k_BT/\hbar\omega_M)(\gamma_0 + 1)^2 \approx 1$. The assumptions needed to obtain eq 6 have been outlined previously.[4d] In order for the result to be applied successfully to a series of related excited states, the following conditions must be met. (1) The same type of luminophore in terms of electronic origin must be involved throughout the series. (2) A common pattern of acceptor vibrations, ω_M and ω_L, must exist for all members of the series. (3) The vibrationally induced electronic coupling matrix element between excited and ground states, $C^2\omega_k$, must remain relatively constant. (4) Contributions from the solvent vibrational trapping energy term, χ_0, must also remain relatively constant. From the appearance of vibrational structure as 1200–1400-cm^{-1} vibrational progressions, it has been concluded that for related bpy and phen complexes the principle contribution to vibrational deactivation is from ligand-localized framework stretching vibrations.[4d,12,15] As noted above, vibrational progressions having the same energy spacings appear in the low-temperature emission spectra for the bpyz- and bpym-based luminophores (note Figure 1) suggesting the same conclusion.

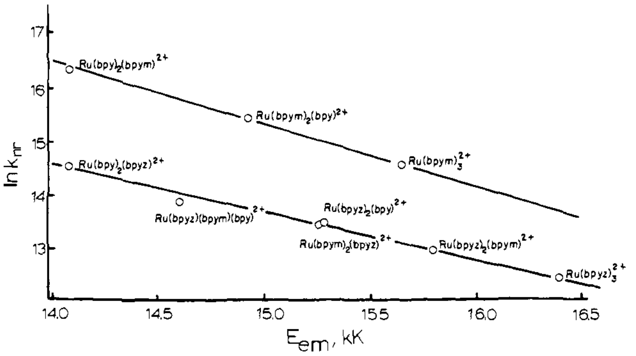


Figure 3. Plots of ln k_{nr} vs. E_{em} for the series of bpyz-based luminophores (lower line) and bpym-based luminophores (upper line) in propylene carbonate. The data were taken from Tables I and II.

Table IV. Values of Slopes and Intercepts from Plots of ln k_{nr} vs. E_{em}

series	slope(ln k_{nr}/E_{em}), eV^{-1}	intercept (E_{em} = 0)
$Ru(bpy)_n(bpyz)_{3-n}^{2+}$ (n = 0, 1, 2)[a]	−7.6	28
$Ru(bpy)_n(bpym)_{3-n}^{2+}$ (n = 0, 1, 2)[a]	−8.1	31
$Ru(bpy)_2L_2^{2+}$ compound series[b]	−7.5 ± 0.7	28.0 ± 1.1
$Ru(bpy)_3^{2+}$ solvent dependence[c]	−7.5 ± 0.7	28.0 ± 1.1
$Os(bpy)L_4^{2+}$ compound series[d]	−7.5 ± 0.7	29.2 ± 1.1
$Os(phen)L_4^{2+}$ compound series[d]	−7.4 ± 0.7	28.1 ± 1.1

[a] In propylene carbonate. [b] In CH_2Cl_2 solution, ref 4d. [c] Reference 4e. [d] In CH_3CN solution, ref 4a, c, 12a.

Turning back to eq 6, since ln β_0 and γ_0 are weakly varying functions of E_{em}, a plot of ln k_{nr} vs. E_{em} is expected to be linear if the conditions outlined above are met. For the individual series of bpyz and bpym complexes it appears that deactivation is dominated by ν(bpyz) or ν(bpym) ring modes and within each series that the electronic structure of the luminophores is also common and either $(bpyz^{-}\cdot)Ru^{III}$ or $(bpym^{-}\cdot)Ru^{III}$ based. Therefore, as shown in Figure 3 and earlier for a series of bpy and phen analogues,[4] it is not surprising that plots of ln k_{nr} vs. E_{em} are linear as predicted by eq 6. Although there are insufficient data for statistically meaningful comparisons, estimated slopes $\partial ln\ k_{nr}/\partial E_{em}$ and intercepts (at E_{em} = 0) for the two plots are listed in Table IV along with values derived from the earlier studies on 2,2′-bipyridine- and 1,10-phenanthroline-based luminophores.[4] From the comparisons it is interesting to note the following observations.

(1) The observed slopes are within experimental error of those found for the series of Os^{II}(bpy) and Os^{II}(phen) complexes alluded to above,[4a,c,12a] for a series of complexes of the type $Ru(bpy)_2(L)_2^{2+}$,[4d] and for $Ru(bpy)_3^{2+}$ where variations in E_{em} were achieved by variations in solvent.[4e] The similarities in slopes for the various cases and the appearance of vibrational structure in low-temperature emission spectra strongly suggest that medium-frequency, ring-stretching vibrations dominate the nonradiative deactivation process.

(2) The difference in intercepts among the various series is probably meaningful and reflects electronic structural differences between Ru and Os and between the different chromophoric ligands. Recall from eq 6 that the term ln β_0 is contained in the intercepts and includes the vibrationally induced electronic coupling term $C_k^2\omega_k$. Assuming that the frequency or average frequency of the promoting mode(s) is the same, the intercept, and presumably C_k^2, is noticeably larger for the bpym- compared to the bpyz-based luminophores. The difference is experimentally meaningful since, for example, they lead to shorter lifetimes for bpym-based luminophores compared to bpyz-based luminophores in cases where the emission energies are the same.

(3) The data clearly fall into two distinct classes based on the presence of the ligand having the lowest π^* level. This fact obviously supports the suggestion that in the mixed chelates, excited-state emission and decay processes are dominated by the lowest lying MLCT states.

^{3}MLCT → dd Interconversion. We now turn to the second major theme of this study—an attempt to uncover the effects of ligand variations on the transition between ^{3}MLCT and dd states and the subsequent photochemical properties of the dd states.

In previous work[6] it was concluded that the temperature dependence observed for the emissive lifetimes of $Ru(bpy)_3^{2+}$ and

Scheme I

$$\mathrm{Ru(bpy)_3^{2+}} \xrightarrow{h\nu} {}^3\mathrm{CT}$$

$${}^3\mathrm{CT} \xrightarrow{k_1} \mathrm{Ru(bpy)_3^{2+}}\ (+\,h\nu \text{ or heat})$$

$${}^3\mathrm{CT} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{dd}$$

$$\mathrm{dd} \xrightarrow{k_3} \mathrm{Ru(bpy)_3^{2+}} \text{ or photoproducts}$$

related complexes arises from thermally activated population of a low-lying dd state or states and that ligand loss photochemistry has its origins in the dd state(s). A kinetic scheme derived from this interpretation is shown in Scheme I using $\mathrm{Ru(bpy)_3^{2+}}$ as the example. On the basis of this scheme the lifetime derived kinetic parameters k', k'^0, and $\Delta E'$ ($k' = k'^0 \exp(-\Delta E'/RT)$) can be interpreted as follows. In general, when the steady-state approximation for $[{}^3\mathrm{CT}]$ is used, k' is related to the constants in the scheme by

$$k' = k_2\left(\frac{k_3}{k_{-2} + k_3}\right)$$

Note that k_2 and k_{-2} are rate constants describing the ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ conversion (k_2) and its reverse, $\mathrm{dd} \rightarrow {}^3\mathrm{CT}$ (k_{-2}). k_3 is a sum of rate constants leading to deactivation of the dd state by decay to the ground state or by following events amongst which are steps leading to ligand loss photochemistry.

In the limit that $k_{-2} \ll k_3$, $k' = k_2$ and the parameters k'^0 and $\Delta E'$ characterize the irreversible ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ surface crossing. In this limit $\Delta E'$ is the energy of activation and k'^0 the preexponential term for the ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ transition, that is, $k_2 = A \exp(-E_a/RT)$ where $k'^0 = \mathrm{A}$ and $\Delta E' = E_a$.

In the remaining limit, $k_{-2} \gg k_3$, ${}^3\mathrm{CT}$ and dd are in equilibrium, and

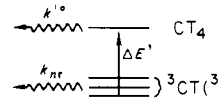
$$k' = \frac{k_2}{k_{-2}}k_3 = k'^0 \exp(-\Delta E'/RT)$$

In this limit, $k_2/k_{-2} = K_2 = \exp[-\Delta E/RT] \exp[\Delta S/R]$, $\Delta E'$ can be interpreted as the internal energy difference between the ${}^3\mathrm{CT}$ and dd states, and $k'^0 = k_3 \exp[\Delta S/R] \sim k_3$. The entropic difference between the two states, ΔS, is expected to be small and has been neglected in the equation above.

The values of k'^0 and $\Delta E'$ obtained for the bpym- and bpyz-based complexes are revealing in the context of the kinetic analysis. Note that k'^0 values (10^{12}–10^{14} $\mathrm{s^{-1}}$) and $\Delta E'$ values ($\sim$3300 $\mathrm{cm^{-1}}$) for $\mathrm{Ru(bpym)_3^{2+}}$ and $\mathrm{Ru(bpyz)_3^{2+}}$ are in the same range as found earlier for $\mathrm{Ru(bpy)_3^{2+}}$,[6a] $\mathrm{Ru(phen)_3^{2+}}$,[6a] and the series of complexes $\mathrm{Ru(bpy)_2(L)_2^{2+}}$[4d] (L = py, substituted pyridines). It is also clear from the photochemical ligand loss quantum yields that as in earlier systems, relatively efficient photochemical ligand loss is observed for these tris chelates. The common pattern in kinetic parameters and the appearance of ligand-loss photochemistry are consistent with a common pattern of excited-state reactivity and, as concluded earlier,[6a] appear to be symptomatic of the irreversible surface crossing limit where $k'^0 = A$ and $\Delta E' = E_a$ for the ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ transition.

In the context of the discussion above, the lifetime and ϕ_p data for the complexes $\mathrm{Ru(bpy)_2(bpyz)^{2+}}$ and $\mathrm{Ru(bpy)_2(bpym)^{2+}}$ are most interesting. For these two complexes drastic decreases occur in both $\Delta E'$ and k'^0. It is also significant that there is an *absence of observable photochemistry* under conditions where $\mathrm{Ru(bpy)_3^{2+}}$ is relatively reactive toward ligand loss. One may conclude that for these complexes the observed temperature dependence is no longer associated with population and/or subsequent reactivity of a low-lying dd state. It should be appreciated that because of the small temperature dependence of the lifetimes for these cases, the kinetic parameters k'^0 and $\Delta E'$ are not as well defined as in the other cases. Nonetheless, the appearance of the temperature dependence is meaningful given the estimated experimental error.

There are at least two reasonable sources for the temperature dependence in these two complexes. (1) The electronic structures of the CT excited states are complicated and consist of several low-lying states. A series of low-lying ${}^3\mathrm{CT}$ states exists,[1] and evidence for them has been obtained by low-temperature lifetime measurements.[15,19] Experimentally, decay data have been obtained as a function of temperature and deconvoluted to give evidence at low temperatures for three-state decay with a spacing between states of $\sim$10 and $\sim$50 $\mathrm{cm^{-1}}$ for $\mathrm{Ru(bpy)_3^{2+}}$. It is important to note here that for $\mathrm{Os(bpy)_3^{2+}}$, evidence has been obtained for a fourth state which is $\sim$600 $\mathrm{cm^{-1}}$ above the closely spaced manifold of lower states.[6d] A recent theoretical treatment[1b,3c] based on a molecular orbital model including spin–orbit coupling has predicted that for $\mathrm{Ru(bpy)_3^{2+}}$, a fourth state should also exist which is appreciably above the lower manifold of three states. The model also predicts greater singlet character for the fourth low-lying MLCT state and therefore a greater value of k_{nr}. If such a state exists for $\mathrm{Ru(bpy)_3^{2+}}$ it is not observable from temperature-dependent lifetime studies because the ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ transition with its large preexponential factor ($\sim 10^{12}$ $\mathrm{s^{-1}}$) dominates the temperature dependence at higher temperatures and would completely mask any contribution from a term arising from population and decay of a fourth MLCT state. For the complexes $\mathrm{Ru(bpy)_2(bpyz)^{2+}}$ and $\mathrm{Ru(bpy)_2(bpym)^{2+}}$ there appear to be no complications arising from low-lying dd states, and the temperature-dependent term may arise from population of an upper ${}^3\mathrm{CT}$ state via,



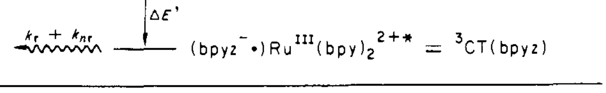
If this interpretation is correct, $\Delta E' \sim 800$ $\mathrm{cm^{-1}}$ for $\mathrm{Ru(bpy)_2(bpyz)^{2+}}$ and $\Delta E' \sim 400$ $\mathrm{cm^{-1}}$ for $\mathrm{Ru(bpy)_2(bpym)^{2+}}$ are at least approximate values for the spacing of the upper CT state above the lower manifold of ${}^3\mathrm{CT}$ states, and $k'^0 = 3 \times 10^7$ $\mathrm{s^{-1}}$ for $\mathrm{Ru(bpy)_2(bpyz)^{2+}}$ and $k'^0 = 1 \times 10^7$ $\mathrm{s^{-1}}$ for $\mathrm{Ru(bpy)_2(bpym)}$ are approximate values for k_{nr} from the upper state. It should be realized that a fourth, low-lying CT state may exist for the other mixed chelates as well. However, as for $\mathrm{Ru(bpy)_3^{2+}}$, their presence would be hidden in the temperature-dependent lifetime experiment because of the temperature dependence of the ${}^3\mathrm{CT} \rightarrow \mathrm{dd}$ transition.

(2) A second possible interpretation arises from the dependence of k_{nr} on E_{em} as predicted by eq 6 and as shown in Figure 2. As described earlier, our fitting procedure for the $\tau_0(T)$ data forces any temperature dependence for nonradiative decay into a single exponential term. From the energy gap law (eq 6), if emission energies for the mono-bpyz and mono-bpym complexes are temperature dependent, k_{nr} would also become temperature dependent and have the form shown in eq 7 where k_{nr}' and k_{nr} are the

$$\ln k_{\mathrm{nr}} - \ln k'_{\mathrm{nr}} = \frac{-\gamma_0(\Delta E_{\mathrm{em}})}{\hbar\omega_{\mathrm{M}}} \qquad (7)$$

nonradiative decay rate constants at two different temperatures and ΔE_{em} is the difference in emission energies at the two different temperatures. It can be predicted that a shift in $\lambda_{\mathrm{em,max}}$ of 5–10 nm over the temperature range studied (210–345 K) would be sufficient to account for the observed effect. In a related study based on temperature-dependent lifetime and E_{em} measurements on $\mathrm{Os(bpy)(L)_4^{2+}}$ complexes, where again there are no low-lying dd states, it has been estimated that the contribution of the temperature dependence of k_{nr} to $\Delta E'$ is probably $\sim$400 $\mathrm{cm^{-1}}$.[20] Nonetheless, high-resolution emission spectra and spectral fitting would be required to rule out or substantiate this possibility.

(3) A third possibility is that the observed temperature dependence represents thermally activated decay from a slightly higher CT state based on a bpy rather than a bpyz or bpym ligand,[21] e.g.,



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If this interpretation were correct, $\Delta E'$ is the internal energy difference between the two CT states. It would also represent the *miniumum* energy of activation for the electron transfer between ligands, and $k^{\prime 0}$ would become the nonradiative decay rate constant for the bpy-localized excited state. This interpretation can probably be ruled out on energetic grounds. Electrochemical measurements[10] show that for the first ligand-based reduction in complexes like $Ru(bpy)_3^{2+}$ and $Ru(bpyz)_3^{2+}$ $\Delta E_{1/2} \sim 0.5$ V, with the bpyz complex being easier to reduce. The difference in potentials for the ligand-based ground states should be a reasonable first estimate for the difference between bpyz- and bpy-based ^3CT states and it is much larger in *magnitude* ($\sim$4000 cm^{-1}) than the experimental values for $\Delta E'$.

On the basis of the analysis developed above, the kinetic decay data for the complexes $Ru(bpy)(bpyz)_2^{2+}$ and Ru(bpy)(bpym)(bpyz)$^{2+}$ are anomalous in that the $k^{\prime 0}$ ($=4 \times 10^9$ and 3×10^8 s^{-1}) and $\Delta E'$ ($=2100$ and 1400 cm^{-1}) values are intermediate between values found for the irreversible surface crossing and small $\Delta E'$ cases. From the data in Table III the ϕ_p value for Ru(bpy)(bpyz)$_2^{2+}$ clearly shows the intervention of ligand-loss photochemistry strongly implicating a low-lying dd state and from qualitative observations, Ru(bpy)(bpym)(bpyz)$^{2+}$, is photolabile as well.

The change in pattern in the kinetic parameters suggests that for the ^3CT excited states of $Ru(bpy)(bpyz)_2^{2+}$ and Ru(bpy)(bpym)(bpyz)$^{2+}$ another kinetic limit has been reached. It is appealing to speculate that for these complexes the actual case, in terms of the reactions in Scheme I, is that in which an equilibrium exists between the ^3CT and dd states. In this limit *direct* information is available concerning the dd state since *$\Delta E'$ becomes the internal energy content of the dd excited state above the ^3CT state and $k^{\prime 0}$ becomes the inverse of the lifetime of the dd state.* Note that the lifetime of the dd state would be determined by the sum of rate constants for radiative and nonradiative decay including subsequent processes which lead to net photochemical ligand loss.

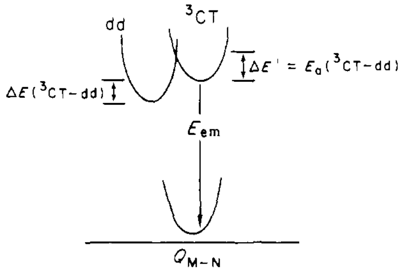
Interestingly, lifetime values for $Ru(bpy)(bpyz)_2^{2+*}$ in CH_3CN decrease linearly with added [Cl$^-$].[22] This observation is in clear contrast to $Ru(bpy)_3^{2+*}$ where τ_0 is [Cl$^-$] independent but photochemistry does occur. The point is worth noting since for $Ru(bpy)_3^{2+*}$ photochemistry appears to occur following an *irreversible* $^3CT \rightarrow$ dd crossing and τ_0 for ^3CT is expected to be independent of [Cl$^-$] since the photochemical step occurs *after* the $^3CT \rightarrow$ dd transition. The observation of a [Cl$^-$] dependence of τ_0 for $Ru(bpy)(bpyz)_2^{2+*}$ suggests that in this complex the ^3CT and dd states are dynamically coupled and Cl$^-$ attack on the dd state influences the ^3CT lifetime. The conclusion reached here is not unequivocal since the lifetime of $Ru(bpyz)_3^{2+*}$[22] is also quenched by Cl$^-$. Initial flash photolysis studies suggest that in the latter reaction an important component of the quenching is by electron transfer, $Ru(bpyz)_3^{2+*} + Cl^- \rightarrow Ru(bpyz)_3^+ + Cl$, and redox quenching by Cl$^-$ may be a major origin of the [Cl$^-$] dependence for $Ru(bpy)(bpyz)_2^{2+}$ as well.

Origin of the Ligand Effects. From the work described here, there appear to be wide variations in the relative energies of the ^3CT and dd states in what are ostensibly closely related complexes. We do not yet understand in a detailed way the factors that lead to the variations, but in these and related complexes, variations in CT absorption band energies and in E_{em} are reconcilable at least qualitatively on the basis of simple bonding arguments. For example, recent work on a series of complexes of the type Os(phen)(L)$_4^{2+}$ (L = py, 1/2bpy, PR_3, CH_3CN, ...)[4c] has shown that linear correlations exist between E_{em} and the difference in reduction potentials for the Os-based oxidation ((phen)Os$^{III/II}$(L)$_4^{3+/2+}$) and phen-based reduction ((phen$^{0/-}$)Os(L)$_4^{2+/+}$), $\Delta E_{1/2} = E_{1/2}(Os^{III/II}) - E_{1/2}(Os(phen^{0/-}))$. From such observations it can be concluded that variations in MLCT excited-state energies depend largely on two factors: (1) the relative energy of the π^* orbital of the luminophoric ligand, and (2) the relative stabilization of oxidation state Ru(II) (or Os(II)) compared to Ru(III) (or Os(III)) by a combination of σ and π effects as L is varied.

Chart I

complex	$Ru(bpym)_3^{2+}$	Ru(bpy)(bpym)$_2^{2+}$	Ru(bpy)$_2$(bpym)$^{2+}$
E_{em}, kK	15.65	14.93	14.08
$E_a(^3CT$-dd), cm^{-1} ($\Delta E'$)	3375	3800	>4500

Scheme II



Turning first to the series of bpym complexes, the order of decreasing emission energy—$Ru(bpym)_3^{2+*} >$ Ru(bpy)(bpym)$_2^{2+*} >$ Ru(bpy)$_2$(bpym)$_2^{2+*}$—is consistent with this idea. As bpym ligands are replaced by bpy, a shift to lower energy is expected. Bpy is a better σ-donor ligand and less effective as a π-acceptor ligand.[10] Replacing bpym by bpy in a series of related complexes is expected to stabilize the (bpym$^-\cdot$)Ru^{III} excited states relative to the ground state by enhanced σ(bpy) donation and by a decreased stabilization of the Ru(II) ground state by dπ–π^* back-bonding.

From the kinetics data for the $^3CT \rightarrow$ dd transition, it is interesting to note that as shown below, the values for *$\Delta E'$ appear to increase as E_{em}* decreases (Chart I). Only a lower limit for $E_a(^3CT \rightarrow dd)$ is available for Ru(bpy)(bpym)$_2^{2+}$ because the kinetically derived quantity $\Delta E'$ for this complex from temperature-dependent lifetime measurements appears to refer to a process different from the $^3CT \rightarrow$ dd transition.

The three energy quantities E_{em}, $\Delta E(^3CT$–dd), and $E_a(^3CT$–dd) are shown in Scheme II. Scheme II is a schematic energy-coordinate diagram which illustrates variations in the energies of the ground and ^3CT and dd excited states along a normal coordinate largely M–N in character. Given its $(d\pi)^5d\sigma^*$ electronic configuration, the dd state is expected to be distorted along the M–N normal coordinate(s).[24]

Although the $E_a(^3CT$–dd) or $\Delta E'$ values from the lifetime measurements are not a direct measure of the energy difference between ^3CT and dd, $\Delta E(^3CT$–dd), they are expected to vary in the same sense.[23] As a consequence, the fact that $\Delta E' = E_a(^3CT$–dd) decreases in the sequence $Ru(bpym)_3^{2+} >$ Ru(bpym)$_2$(bpy)$^{2+} >$ Ru(bpym)(bpy)$_2^{2+}$ suggests that ^3CT is stabilized relative to dd through the series. Electronically, the origin of the effect may be in enhanced ligand $\rightarrow$ Ru(III) donation in ^3CT compared to dd as bpym is replaced by bpy. The same electronic effect would be expected to contribute to the decreasing E_{em} values along the series.

For the mixed bpyz–bpy series the situation may be analogous, but there are added complications. For the intermediate cases $Ru(bpy)(bpyz)_2^{2+}$ and Ru(bpy)(bpym)(bpyz)$^{2+}$ it appears that the dd state may be in dynamic equilibrium with ^3CT. Presumably, destablization of the ^3CT states by exchanging bpy or bpym

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(23) If the $^3CT \rightarrow$ dd transition is viewed as an intramolecular electron transfer reaction $d\pi^5\pi^*(bpy)(^3CT) \rightarrow d\pi^5d\sigma^*(dd)$, it is expected that $\Delta E'$ ($=E_a$) should be related to the $^3CT \rightarrow$ dd energy gap, ΔE(dd) in the classical limit, by

$$\Delta E' = E_a = (\chi + \Delta E(dd))^2/4\chi$$

where χ is four times the classical intramolecular and solvent vibrational trapping energy.[4e]

ligands for a bpyz ligand has the effect of bringing the relative energies of the states into an appropriate juxtaposition for a dynamic equilibrium to exist. Recall that $\Delta E'$ for this case cannot by compared directly to $\Delta E'$ values for the other two complexes. For $\mathrm{Ru(bpyz)_3}^{2+}$, $\Delta E'$ is E_a for the ^{3}CT $\rightarrow$ dd surface crossing and for the intermediate case $\Delta E'$ reflects the difference in internal energy between the ^{3}CT and dd states.

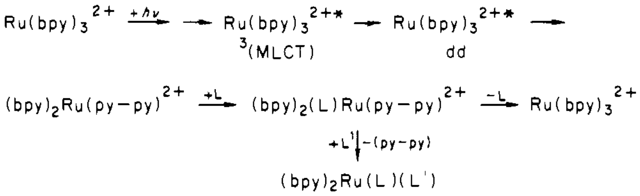
Photochemical Quantum Yields. The data we have acquired on quantum yields for loss of a chelate ligand are not sufficient to establish the photochemical mechanisms in detail, but several comments can be made. From our results the complexes can be separated into several different classes in terms of photochemical behavior. (1) The complexes $\mathrm{Ru(bpy)_2(bpyz)}^{2+}$ and $\mathrm{Ru(bpy)_2(bpym)}^{2+}$ display an absence of photochemistry, and the decay kinetics data are consistent with a large ^{3}CT–dd energy gap, ΔE(dd). Because of the magnitude of ΔE(dd), the dd state is not appreciably populated during the lifetime of ^{3}CT. (2) For the tris-chelates $\mathrm{Ru(bpym)_3}^{2+}$ and $\mathrm{Ru(bpyz)_3}^{2+}$, ligand-loss photochemistry not only exists but it has efficiencies ($\phi_p = 0.48$ and 0.45, respectively) that are notably higher than those for $\mathrm{Ru(bpy)_3}^{2+}$ under identical conditions. Crutchley and Lever[9a,b] report a quantum yield for $\mathrm{Ru(bpyz)_3}^{2+}$ ($\phi_p = 0.37$) under similar conditions which is in reasonable agreement with our value. It should be noted that their experimental method of measurement differed from ours. In making comparisons between complexes the most valuable parameter is the efficiency of ligand loss from the dd state once populated, ϕ_p(dd). ϕ_p(dd) is given by eq 8, where

$$\phi_p(\mathrm{dd}) = \phi_p/\phi_{ic}(\mathrm{dd}) \tag{8}$$

ϕ_{ic}(dd) is the efficiency of population of the dd state from ^{3}CT. From Scheme I it is given by

$$\phi_{ic}(\mathrm{dd}) = k'^0 \exp(-\Delta E'/kT)/[k_1 + k'^0 \exp(-\Delta E'/kT)] \tag{9}$$

Values for ϕ_{ic}(dd) in propylene carbonate calculated by using eq 8 are listed in Table III. Unfortunately, our lifetime data are in propylene carbonate and the photochemical quantum yield data in acetonitrile so that values for ϕ_p(dd) are not available. Nonetheless, it is evident that the three tris-chelates $\mathrm{Ru(bpy)_3}^{2+}$, $\mathrm{Ru(bpym)_3}^{2+}$, and $\mathrm{Ru(bpyz)_3}^{2+}$ are all quite active toward ligand loss once the dd states are populated. The origin of the enhanced reactivity for the bpym and bpyz complexes may lie in the lowered σ-donor ability of the bpym and bpyz ligands compared to bpy. Weaker σ-donor ligands might be expected to dissociate more easily from an excited state of configuration $(\mathrm{d}\pi)^5\mathrm{d}\pi^*$ where $\mathrm{d}\pi$–π^* back-bonding is expected to be small.[24] In support of this idea is the fact that in the mixed-chelate complexes, where both bpyz or bpym ligands are present, it appears that the weaker σ-donor ligands bpyz or bpym are lost in preference to bpy, as noted previously. (3) It has already been mentioned that for the complexes $\mathrm{Ru(bpy)(bpyz)_2}^{2+}$ and $\mathrm{Ru(bpy)(bpym)(bpyz)}^{2+}$ the ^{3}CT and dd states may be in dynamic equilibrium. (4) Qualitatively, the mixed chelates $\mathrm{Ru(bpym)(bpyz)_2}^{2+}$ and $\mathrm{Ru(bpym)_2(bpyz)}^{2+}$ undergo relatively efficient ligand-loss photochemistry and in that sense they resemble the tris chelates.[22] The situation is less clear for $\mathrm{Ru(bpy)(bpym)_2}^{2+}$. Here, the kinetic parameters for ^{3}CT decay are consistent with an irreversible ^{3}CT dd surface crossing, and yet loss of bpym is noticeably less efficient ($\phi_p < 10^{-3}$) than in the tris chelates. However, as shown below for $\mathrm{Ru(bpy)_3}^{2+}$, the photochemical ligand-loss mechanism is thought to involve a series of steps,[6a] including chelate ring opening and subsequent capture by the solvent or another entering group; with such a complex mechanism, it is hardly surprising that significant variations in ϕ_p should exist. A full accounting of such variations would demand an extended series of experiments in a series of solvents over an extended temperature range.



$$\mathrm{Ru(bpy)_3}^{2+} \xrightarrow{+h\nu} \;\rightarrow\; \underset{^3(\mathrm{MLCT})}{\mathrm{Ru(bpy)_3}^{2+*}} \rightarrow \underset{\mathrm{dd}}{\mathrm{Ru(bpy)_3}^{2+*}} \rightarrow$$

$$\begin{tikzcd} \mathrm{(bpy)_2Ru(py{-}py)}^{2+} \arrow[r, "+L"] & \mathrm{(bpy)_2(L)Ru(py{-}py)}^{2+} \arrow[r, "-L"] \arrow[d, "+L'"', "-(py{-}py)"] & \mathrm{Ru(bpy)_3}^{2+} \\ & \mathrm{(bpy)_2Ru(L)(L')} & \end{tikzcd}$$

Conclusions

From our results it is clear that the ligands bpyz and bpym join 2,2′-bipyridine and 1,10-phenanthroline and their derivatives as members of a family of related chromophoric ligands. The lower π^* levels for the bpyz and bpym ligands lead to changes in excited- and ground-state redox potentials as a consequence of changes in electronic structure,[10] but the photophysical properties of the emitting ^{3}MLCT states are clearly consistent with properties found earlier for related bpy and phen complexes.[4,6] Variations in radiative and nonradiative lifetimes are systematic and can be rationalized by using available theory and measurements of the electronic and vibrational characteristics of the grund and excited states.

However, our results have led to what may be a far more important observation. Although $\mathrm{Ru^{II}}$–bpy and related complexes are appealing as potential sensitizers in energy conversion processes, their use can be severely circumscribed by photodecomposition induced by thermal population of low-lying dd states.[6] Our results begin to show what factors are involved in determining the ^{3}CT–dd energy gap. One immediate gain is the resulting insight into how synthetic modifications in the basic chromophore can be used to remove low-lying dd states from thermal accessibility in the excited-state manifold. Such work may lead to a family of photostable sensitizers, and we are currently exploring the background synthetic chemistry of systems of the type $\mathrm{(bpy)(bpz)Ru^{II}}<^{\mathrm{L}}_{\mathrm{L}}$ and $\mathrm{(bpy)(bpym)Ru^{II}}<^{\mathrm{L}}_{\mathrm{L}}$ with this goal in mind.

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