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Relaxation Processes of Electronically Excited States in Polypyridine Ruthenium Complexes

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The excited-state properties of several polypyridine ruthenium complexes have been examined. The complexes were selected on the basis of the energy of their low-lying metal-to-ligand charge-transfer (MLCT) state. The dependence of radiative and radiationless rates on the energy of this excited state is discussed. Also, the amount of metal to solvent charge transfer in this lowest state is shown to be independent of the state's energy. Finally, the increase in the activation energy for population of a higher excited ligand field state was directly correlated with the decrease in the MLCT state's energy.

Introduction

In recent years, the photochemistry and photophysics of polypyridine Ru complexes have been extensively examined.[1] In large part this interest stems from the potential use of these complexes in the photochemical decomposition of water. The lowest absorption band (usually around 450 nm) has been assigned to a metal-to-ligand charge-transfer (MLCT) transition.[2–13] It has been suggested that the initially formed state has largely a singlet multiplicity and undergoes very rapid intersystem crossing to the corresponding state having largely a triplet character. The quantum yield for this spin conversion in $Ru(bpy)_3^{2+}$ (bpy = bipyridine) has been evaluated as unity.[14]

The triplet MLCT state undergoes radiative decay with a reasonable quantum yield in the region of 600 nm. The lifetime associated with this emission is approximately 1 μs. Interestingly, numerous studies indicate that there is a symmetry reduction in the ^{3}MLCT state so that it is best described as $(bpy)_2Ru^{3+}[bpy]^-$.[15–17] Furthermore, the emission intensity and lifetime show a large solvent isotope effect in H_2O/D_2O.[18] This led Van Houten and Watts to suggest that this luminescent state has some metal to solvent charge-transfer (MSCT) character.

The temperature dependence of the luminescence has contributed greatly to a further understanding of the photophysics of these complexes. At very low temperatures (<77 K), the observed temperature dependence of the phosphorescence lifetime is best described by a three-state model.[8] That is, the luminescent state is actually composed of three closely spaced states that have widely different lifetimes.

Table I. Emission Maxima, Quantum Yields, and Lifetimes for Ruthenium Complexes

compd	solvent	λ_{max}, nm	ϕ^a	τ,[b] μs	D_2O/H_2O^c
I	H_2O	627	0.053	0.63	1.7
	D_2O	627	0.095	1.07	
II	H_2O	659	0.039	0.62	2.2
	D_2O	659	0.084	1.42	
III	HCl/H_2O	686	0.006	0.29	1.9
	DCl/D_2O	686	0.012	0.50	

[a] I in CH_3CN was the reference. [b] 30 °C. [c] Isotope effect; average based on fluorescence lifetime and quantum yield measurements.

At higher temperatures, all of these closely spaced states are populated, and they can be thought of as an average state. The luminescence from this average triplet state displays an additional temperature dependence in the range of 273–373 K.[18–21] This behavior has led to the postulate that another excited state is approximately 3600 cm^{-1} above the emitting state and that this state can be thermally populated during the lifetime of the ^{3}MLCT state. These conclusions are depicted in Figure 1. The facts that this thermally populated state is nonluminescent, rapidly decays to the ground state, and results in a photosubstitution reaction indicate that its identity is most likely a ligand field (LF) excited state.[19–22]

On the other hand, Fasano and Hoggard have recently studied the quenching of both emission and photosubstitution by ferrocene.[23] Both Sern–Volmer plots were linear but with different slopes. These authors concluded that two excited states are involved but they are not in thermal equilibrium.

In order to gain further insight into the excited-state behavior of these complexes, the photophysics of several closely related complexes has been examined. The complexes were selected on the basis of the expected change in the energy of the MLCT state. In particular, the energy of this state has been systematically lowered and the effect on the excited-state properties determined. The results strongly suggest that the two excited states (MLCT and LF) are indeed in thermal equilibrium.

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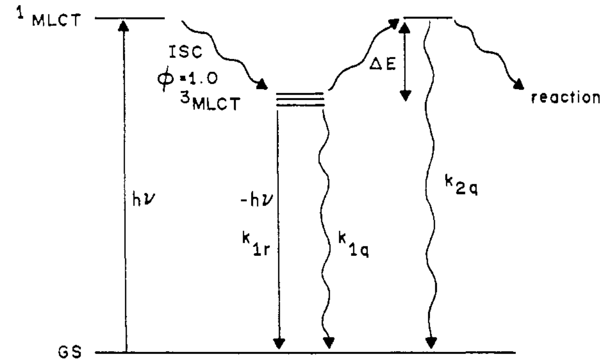


Figure 1. Excited-state processes occurring in polypyridine ruthenium complexes.

Experimental Section

Materials. $[Ru(bpy)_3]Cl_2$ was donated by Professor J. Selbin of this department. The remaining complexes were prepared as described by Sprintschnik et al.[24] The absorption spectra in neutral and acidic H_2O as well as the elemental analysis (Galbraith Laboratories, Knoxville, TN) agreed with the literature.

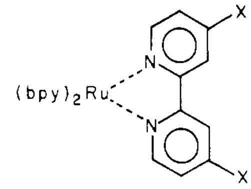
All samples were freshly prepared the day of their use. Typically, a 3-mL sample of the complex ($\sim 5 \times 10^{-5}$ M) was degassed by at least four freeze/pump/thaw cycles (1×10^{-4} torr) and then sealed in a quartz cuvette. For the acidic solutions, the samples were first bubbled with HCl or DCl for several minutes and then degassed.

Spectra. All absorption spectra were recorded on either a Cary 14 or 15 spectrometer. All emission spectra were recorded on an Aminco-Bowman spectrofluorometer. For the fluorescence quantum yield determinations, the standard was $[Ru(bpy)_3]Cl_2$ in CH_3CN. The absolute fluorescence quantum yield for this reference was taken as 0.062.[25]

Lifetime Measurements. All lifetimes were determined by the single-photon counting method.[26] The temperature of the sample was varied by circulating a water/ethylene glycol mixture through a locally constructed cell holder. The temperature was maintained to within 0.5 °C.

Results

The uncorrected fluorescence spectra for I–III are shown in Figure 2. The emission maxima and quantum yields are listed in Table I. The results for I are somewhat higher than those of Van Houten and Watts.[18,19] These authors report quantum yield values of 0.042 and 0.063 and lifetimes of 0.58 and 0.97 μs for I in H_2O and D_2O, respectively. However, Xu and Porter have reported a value of 0.65 μs for the lifetime of I in H_2O.[27] Despite higher quantum yields and lifetimes than Van Houten and Watts, the present value for the isotope effect is identical with that reported by these authors.[18,19]



I, X = H
II, X = CO_2^-
III, X = CO_2H

The quantum yields and lifetimes for II and III are also reported in Table I. Protonation (or deuteration) has a substantial effect on both τ and ϕ, decreasing both by a factor of nearly 2. There are no significant differences in the isotope effects for I–III.

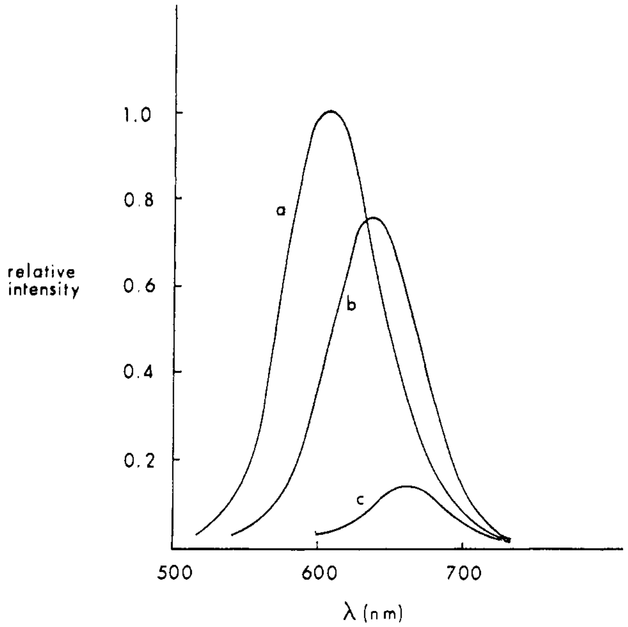


Figure 2. Uncorrected emission specra for (a) I, (b) II, and (c) III.

Table II. Phosphorescence Lifetimes as a Function of Temperatures

	lifetime, ns				
T, °C	I (D_2O)	II (H_2O)	II (D_2O)	III (H_2O)	III (D_2O)
10	1516	636	1503	318	645
20	1392	636	1427	299	572
30	1066	612	1387	292	503
40	907	594	1344	277	453
50	655	581	1278	257	426
60	513	572	1167	250	385
70	332	554	1132	230	355
80	240	514	1033	223	327
90	167	479	870	221	306

Table III. Photophysical Rate Constants for Ruthenium Complexes

	$10^{-5} \times k_{1r}$	$10^{-6} \times k_{1q}$	k_{2q}	ΔE, cm^{-1}	ref
I (H_2O)	0.69	1.22	1×10^{13}	3559	19
	1.37^b		1.7×10^{13}	3673	21
I (D_2O)	0.89	0.23	1×10^{13}	3603	a
	0.69	0.57	1×10^{13}	2568	19
II (H_2O)	0.63	1.54	1×10^{13}	4230	a
II (D_2O)	0.59	0.65	1×10^{13}	4227	a
III (H_2O)	0.21	3.43^c		310^d	a
III (D_2O)	0.24	1.98^c		630^d	a

[a] This work. [b] $k_{1r} + k_{1q}$. [c] At 30 °C. [d] Evaluated by using the usually Arrhenius equation.

The emission quantum yield and lifetime of $Ru(bpy)_3^{2+}$ have been reported to be very temperature dependent.[18-21] In agreement with these reports, we find a strong temperature dependence for this lifetime (Table II). Similarly, the results of Table II also show a dependence for the lifetimes of both II and III. Previously, this temperature dependence has been analyzed within the framework of two closely spaced excited states (Figure 1). The observed temperature dependence is then related to thermal population of the higher excited state. Allsopp et al. have shown that an additional activation energy must be included in order to accommodate the temperature range of 178–370 K.[21] However, reasonable results are obtained in the 273–370 K temperature range by the simpler

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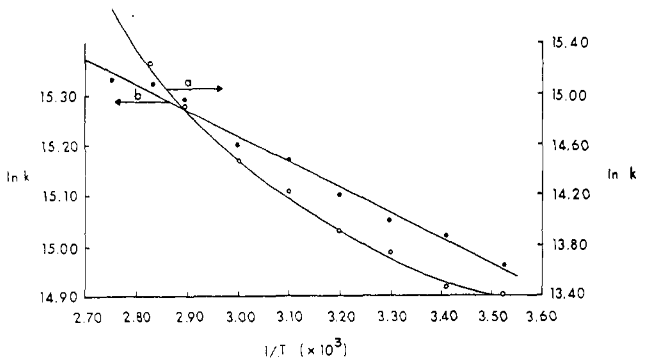

Figure 3. Arrhenius plots for (a) I (in D_2O) and (b) III (in H_2O). The solid lines are either nonlinear or linear least-squares fit of the experimental data.

model involving a single activation energy. Consequently, the luminescence data have been fitted to eq 1,

$$k_{\mathrm{exptl}} = k_{1\mathrm{r}} + k_{1\mathrm{q}} + k_{2\mathrm{q}}e^{-\Delta E/RT} \qquad (1)$$

where the symbolism of Van Houten and Watts has been used and is depicted in Figure 1. Also, the value of $k_{2\mathrm{q}}$ has been fixed as 1×10^{13} s^{-1}, in agreement with previous results.[18-21,22] The results for II in both D_2O and H_2O were also fitted to eq 1, with the values for ΔE being identical in both cases (Table III). The error in these values is less than 100 cm^{-1}.

In contrast to I and II, III displayed normal Arrhenius behavior as shown in Figure 3. The activation energies observed were very small (<1 kcal/mol). Also contrary to the behavior of I and II, the measured activation energy for III is different in H_3O^+ and D_3O^+.

Discussion

There are some major differences in the photophysical properties of I–III. At first sight, little rationale for this behavior seems apparent. However, much of the data can be explained by the model presented in Figure 1 and the fact that the energy of the ^{3}MLCT varies in an orderly fashion for I–III. On the basis of their emission maxima, the energies of the ^{3}MLCT state for I–III are 15 949, 15 175, and 14 575 cm^{-1}, respectively.

As can be seem from Table III, $k_{1\mathrm{r}}$ decreases and $k_{1\mathrm{q}}$ increases as the energy of the emitting state decreases. the decrease in $k_{1\mathrm{r}}$ is due to its dependence on ν^2. This well-known dependence has been predicted theoretically and realized experimentally.[28] The increase in $k_{1\mathrm{q}}$ is expected dut to its dependence upon the energy gap between the initial state (^{3}MLCT) and final (ground) state.[29] Caspar et al. have demonstrated a logarithmic relationship between $k_{1\mathrm{q}}$ and this energy gap for a series of polypyridine Os complexes.[29]

There is a large isotope effect on the phosphorescence of I–III (Tables I and III). The values for $k_{1\mathrm{r}}$ are, within experimental error, independent of solvent deuteration. Furthermore, the decay due to thermal population of the LF state is the same in both H_2O and D_2O. Consequently, the deuterium isotope effect is caused exclusively by a change in $k_{1\mathrm{q}}$. Previously, this has been ascribed to a substantial contribution of a MSCT configuration to the emitting state.[18,19] In fact, by evaluating $k_{1\mathrm{q}}$ for I in different solvents, Nakamuru was able to estimate the relative proportions of MLCT and MSCT in the emitting state.[30] For water, there is approximately a one-to-one admixture of these two states. The similarities of the isotope effect in I–III suggest that the amount of MSCT is also approximately 50% for II and III. This conclusion is surprising since the energy of the MLCT configuration is systematically lower in II and III so that the MLCT contribution to the overall wave function of the emitting state should increase. This increase in MLCT character implies a smaller isotope effect. Further experiments designed to clarify this discrepancy are currently under way.

Above 273 K, a substantial fraction of excited I is dissipated through thermal population of the LF state followed by rapid deactivation to the ground state. The activation energy for this process is simply the energy difference between the ^{3}MLCT and LF states. In I–III, the LF state is expected to be energetically unchanged. On the other hand, the ^{3}MLCT state's energy should decrease as the bipyridine ligand becomes a better acceptor. This is borne out by the emission spectra for I–III that show a systematic red shift. The stabilization of the ^{3}MLCT state should increase the activation energy for population of the LF state. The results of Table III clearly show that this is indeed the case for II. The red shift in the emission is 774 cm^{-1} while the increase in the activation energy is 627 cm^{-1}. The agreement between these two values is reasonable considering the difficulty in determining the activation energy.

For III, the temperature dependence of the lifetime no longer requires eq 1 but rather displays the usual Arrhenius behavior. This can be traced to both the increase in the activation energy for the population of the LF state and the increase in $k_{1\mathrm{q}}$ upon protonation. The activation energy should increase by approximately 1200 cm^{-1} relative to I. With this activation energy, the observed decay rate due to thermal population of the LF state at 373 K can be estimated as 8×10^4 s^{-1}. At this same temperature, the first two terms in eq 1 are approximately 4.5×10^6 s^{-1} so that the second term in eq 1, i.e. decay via the LF state, represents only a 2% change in k_{exptl}. Hence, population of the LF state does not significantly compete with the direct (mostly) nonradiative decay of the ^{3}MLCT state.

There is a small activation energy measured for III that is dependent on the deuteration of water. This might be associated with thermal population of the three closely spaced levels of the ^{3}MLCT state. Harrigan and Crosby have measured several polypyridine Ru complexes and found these states to all be within 80 cm^{-1} of each other.[8] Allsopp et al. have confirmed this result.[21] The observed activation energies in III are all much larger (300–600 cm^{-1}) as well as solvent dependent. These facts suggest that the nonradiative decay of ^{3}MLCT ($k_{1\mathrm{q}}$) may have a small activation energy associated with it.

Summary

The photophysical properties of several polypyridine Ru complexes have been studied. These complexes were selected on the basis of the systematic red shift of their ^{3}MLCT state. The radiative rate constant was shown to decrease as the energy gap between the emitting state and ground state decreased. In agreement with Caspar et al.,[29] the nonradiative decay from the ^{3}MLCT state to the ground state was found to increase as this same energy gap decreased. The nonradiative rate constant for all complexes exhibited a large solvent isotope effect. The similarity of these isotope effects indicates that the amount of MSCT character in the lowest state is the same for I–III.

One major decay pathway for the ^{3}MLCT state of I has been postulated to be thermal population of a higher ligand field state from which photosubstitution and efficient nonradiative decay can occur. However, recent quenching data suggest that these two states are not in thermal equilibrium. The photophysical behavior of I–III is clearly consistent with

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these two states being in thermal equilibrium. Indeed, the stabilization of the ^{3}MLCT state resulted in an equivalent increase in the activation energy for population of the LF state.

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Registry No. I, 15158-62-0; II, 64189-97-5; III, 62207-96-9.

Notes

Contribution from the Department of Chemistry,
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First and Second Ionic Association Constants of Unsymmetrical Metal Chelate Electrolytes from Conductance Measurements: (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Tetraphenylborate, Perchlorate, and Iodide in Nitrobenzene at 25 °C

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Solute–solvent interactions for metal chelate electrolytes with macrocyclic ligands disposed in square-planar fashion about the metal ion have been the subject of considerable investigations: kinetics of axial substitution,[1,2] isomerization,[3,4] and oxidation[5,6] and octahedral–square-planar equilibrium.[7,8]

The effects of the counterion ClO_4^- on the square-planar–octahedral equilibrium for the (1,4,7,10-tetraazacyclotetradecane)nickel(II) cation[9] and on the equilibrium constant for copper(II)–cyclic polythia complexes[10] were observed in aqueous solutions. Bosnich et al.[11] reported that although the conductance of the title complexes, $[Ni([14]aneN_4)]X_2$ (X = halides and perchlorate), in methanol are considerably less than the value expected for a bi-univalent electrolyte and large degree of association is suggested, the spectra are independent of the nature of the anion and not sensitive to the nature of the solvent such as water, methanol, and nitrobenzene, suggesting that the anion is not directly coordinated to the metal ion. However, very little attention has been paid to the quantitative study of ionic association for the unsymmetrically charged metal chelate electrolytes, with the exception of the conductometric study of symmetrically charged (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) sulfate in water–dioxane mixtures.[12]

Table I. Molar Concentrations, C/mol dm^{-3}, and Molar Conductivities, $\Lambda\{^1/_2[Ni([14]aneN_4)]X_2\}$/S cm^2 mol^{-1}, of the Metal Chelate Electrolytes in Nitrobenzene at 25 °C

$[Ni([14]aneN_4)]$-$(BPh_4)_2$		$[Ni([14]aneN_4)]$-$(ClO_4)_2$		$[Ni([14]aneN_4)]I_2$	
$C/10^{-4}$	Λ	$C/10^{-4}$	Λ	$C/10^{-4}$	Λ
0.060 45	28.52	0.036 08	37.33	0.03615	18.65
0.121 92	28.64	0.056 34	36.51	0.12230	14.42
0.222 71	28.50	0.087 10	35.33	0.33444	11.24
0.387 69	28.25	0.165 27	32.88	0.47946	10.16
0.579 50	28.01	0.246 87	31.02	1.4051	7.18
1.144 8	27.44	0.335 77	29.44	2.2365	6.08
2.614 7	26.45	0.475 50	27.55	3.3093	5.24
4.153 0	25.72	0.670 20	25.64	5.0905	4.43
		0.924 95	23.78	7.5715	3.79

In this study conductances for (1,4,8,11-tetraazacyclotetradecane)nickel(II) salts ($[Ni([14]aneN_4)]X_2$; X = BPh_4^-, ClO_4^-, and I^-) were measured in nitrobenzene, which has a moderately high dielectric constant and poor basicity,[13] and analyzed by using the extended Jenkins–Monk method to estimate the second association constant for the bi-univalent electrolytes that we previously proposed.[14] The large association constants for the perchlorate are explained by a hydrogen-bonding interaction of the anion with the N–H protons in the ligand, and those for the iodide are explained by a hydrogen-bonding interaction or a charge-transfer complex.

Experimental Section

Materials. $[Ni([14]aneN_4)](ClO_4)_2$ was synthesized by the published procedure,[15] and the orange crystal was recrystallized from water. Anal. Calcd for $NiC_{10}H_{24}N_4Cl_2O_8$: C, 26.22; H, 5.28; N, 12.24. Found: C, 26.11; H, 5.21; N, 12.29.

$[Ni([14]aneN_4)](BPh_4)_2$ was prepared by mixing equimolar quantities of aqueous solutions of $[Ni([14]aneN_4)](ClO_4)_2$ and aqueous solutions of sodium tetraphenylborate. The yellow precipitate was recrystallized from acetone–water mixtures. Anal. Calcd for $NiC_{58}H_{64}N_4B_2$: C, 77.62; H, 7.19; N, 6.24. Found: C, 77.48; H, 7.16; N, 6.25.

$[Ni([14]aneN_4)]I_2$ was prepared by mixing acetone solutions of lithium iodide and $[Ni([14]aneN_4)](ClO_4)_2$. The pale brown precipitate was recrystallized from methanol–ether mixtures. Anal. Calcd for $NiC_{10}H_{24}N_4I_2$: C, 23.42; H, 4.72; N, 10.93. Found: C, 23.22; H, 4.67; N, 10.88. The perchlorate and tetraphenylborate are easily soluble in nitrobenzene, whereas the iodide is much less soluble. The stock solution (ca. 8 × 10^{-4} mol dm^{-3}) of the iodide was prepared by mixing the crystal with nitrobenzene for 2 h under nitrogen atmosphere.

Nitrobenzene of reagent grade was purified as described previously.[14] The specific conductance (in S cm^{-1}) was less than 2 × 10^{-10}, and water content was 0.0026%. Parameters of the solvent used: density 1.198 25 g cm^{-3} at 25 °C; dielectric constant 34.82; viscosity 0.018 39 Pa s.

Apparatus. The instrumentation and the procedure used for the conductance measurements were described previously.[14,16]

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