experiments, and the 3537-cm^{-1} band could be a hydrogen-bound OH stretch. A molecule that matches these characteristics is the radical **5**, which would be formed by breaking both the NH and NN bonds; however, this might be expected to be photosensitive and to be destroyed on photolysis.

Class III absorptions, which are destroyed on photolysis, include bands at 1438 and 1382 cm^{-1}, which became multiplets in mixed oxygen isotope experiments, and bands at 1525, 1517, and 535 cm^{-1}, which displayed no ^{18}O shifts. Possible products, involving only NN bond dissociation, are the peroxyamine and nitroxide radicals.

Conclusions

The infrared spectra of hydrazine and its reaction products with HF, F_2, and O_3 have been observed in an argon matrix. Vibrational assignments were made for hydrazine, resolving uncertainties in the assignments of the NH_2 wag (ν_6), the antisymmetric NH_2 scissors motion (ν_{10}), and the second harmonic of the torsion ($2\nu_7$).[2,6] Introducing HF into the matrix caused the formation of a hydrogen-bonded complex between the two reagents, involving a primary interaction between the nitrogen lone pair and the acid and a secondary interaction between a hydrogen atom on the adjacent amine group and the fluorine. This is similar to the chelated structure found for the NH_2OH–HF complex.[9]

Hydrazine and F_2 reacted on deposition to form the N_2H_3F–HF complex, which represents the first spectroscopic evidence for the monofluorohydrazine molecule. The fact that the reaction did not require photolysis corresponds with dissociation energy data[1] that show hydrazine to be more reactive than ammonia, which required photolysis to react with fluorine to give the NH_2F–HF complex.[10]

Hydrazine and O_3 reacted during condensation to give three sets of products, the major one being hydroxyhydrazine, NH_2NHOH. Evidence for an intramolecular hydrogen bond between the hydroxyl hydrogen and the lone pair on the α-nitrogen was seen from a large red-shift in the OH stretching frequency. Unlike most molecules, hydrazine did not require photolysis to react with ozone, demonstrating its high reactivity. As for N_2H_3F, this is the first evidence for NH_2NHOH.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE 85-16611 and preliminary spectra of hydrazine in an argon matrix from W. B. Person.

Registry No. N_2H_4, 302-01-2; NH_2NHF, 36336-10-4; NH_2NHOH, 112296-53-4; HF, 7664-39-3; F_2, 7782-41-4; O_3, 10028-15-6; $^{18}O_2$, 14797-71-8; D_2, 7782-39-0.

Contribution from the Departments of Chemistry, Columbia University,
New York, New York 10027, and Saint Michael's College, Winooski, Vermont 05404

Energy Redistribution and Localization in the Excited States of Ruthenium(II) Polypyridyl Complexes

Challa V. Kumar,[†] Jacqueline K. Barton,*[†] Ian R. Gould,[†‡] Nicholas J. Turro,*[†] and J. Van Houten[§]

Received May 5, 1987

Excited-state absorption and resonance Raman spectra of the mixed-ligand complexes $Ru(bpy)_2phen^{2+}$ (**1**) and $Ru(bpy)_2DIP^{2+}$ (**2**) (DIP = 4,7-diphenylphenanthroline) are reported. The excited-state spectra of these mixed-ligand complexes show that the excited-state electron is localized on individual ligands but show nonstatistical contributions from states corresponding to each of the ligands present in the coordination sphere. On the basis of the excited-state absorption spectra, the bpy* contribution to **1*** is twice as much as that of phen*, whereas in case of **2*** the contribution of DIP* is much more than that of bpy*. Excitation of the mixed-ligand complexes at different wavelengths gave identical spectra, showing that the initial excited-state population relaxed quickly to an equilibrium mixture, which depends very much on the type of ligand. Intramolecular energy transfer is rapid. Excited-state absorption spectra of mixtures of parent tris chelates, in contrast, which depend upon the wavelength of excitation, show that intermolecular energy transfer is very slow. Excited-state localization and rapid relaxation to an equilibrium distribution is further supported by excited-state resonance Raman spectra of these mixed-ligand complexes. Vibrational transitions corresponding to bpy* dominate the spectrum of **1*** whereas the vibrational bands of DIP* dominate in case of **2***. Consistent with these results are the resonance Raman spectra of the excited states of the mixed-ligand complexes $Ru(bpy)_2(4,4'\text{-}Ph_2\text{-}bpy)^{2+}$ (**3**) and $Ru(bpy)(4,4'\text{-}Ph_2\text{-}bpy)_2^{2+}$ (**4**). These spectra clearly indicate preferential localization of excited-state energy on the 4,4'-Ph_2-bpy ligand. Thus, it may be possible to design systematically mixed-ligand complexes that would absorb light at a wavelength of choice but would funnel the energy onto a desired ligand.

The photophysics and excited-state redox properties of ruthenium complexes have received considerable attention due to the rich chemistry of their luminescent excited states.[1] Excited-state resonance Raman experiments show that the lowest excited state is a metal-to-ligand charge transfer (MLCT) state, and in the case of $Ru(bpy)_3^{2+}$, the excited-state electron is localized on one of the three bipyridyl ligands.[2] In mixed-ligand complexes of the type $Ru(bpy)_2L^{2+}$, two such states might be expected to be present: one, in which the excited-state electron is localized on the bpy ligand, and the other, in which the electron is localized on the second ligand L.[3,4] These states may exist in a rapid thermal equilibrium, leading to an effective averaging of the excited-state properties. Indeed the excited states of mixed complexes of Ru(II) with the ligands 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) show monoexponential decay in single-photon counting experiments,[4a] and the excited-state lifetimes of these mixed complexes are statistical averages of the parent tris chelates. These observations are consistent with several other excited-state

---

[†] Columbia University.

[‡] Present address: Eastman Kodak Co., Corporate Research Laboratories, Rochester, NY 14650.

[§] Saint Michael's College.

(1) For a review on photophysics of ruthenium(II) polypyridyl complexes, see: Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(2) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *102*, 4391. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (c) Woodruff, W. H. In *Inorganic Chemistry*: Toward *the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983. (d) Woodruff, W. H.; Dallinger, R. F.; Hoffman, M. Z.; Bradley, P. G.; Presser, D.; Malvey, V.; Kessler, R. J.; Norton, K. A. In *Time-Resolved Vibrational Spectroscopy*; Atkinson, G. H., Ed.; Academic: New York, 1983.

(3) (a) Smother, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 106. (b) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526. (c) Forster, M.; Hester, R. E.; *Chem. Phys. Lett.* **1981**, *81*, 42.

(4) (a) Crosby, G. A.; Elfring, W. H., Jr. *J. Phys. Chem.* **1976**, *80*, 2206. (b) Blakley, R. A.; Myrick, M. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1986**, *108*, 7843. (c) Myrick, M. L.; Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 2841. (d) Anderson, S.; Seddon, K. R.; Wright, R. D ; Cocks, A. T. *Chem. Phys. Lett.* **1980**, *71*, 220. (e) Tait, C. D.; Mac Queen, D. B.; Donohoe, R. J.; DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *J. Phys. Chem.* **1986**, *90*, 1766. (f) Ferguson, J.; Krausz, E. *Inorg. Chem.* **1987**, *26*, 1383.

properties, such as the emission quantum yields and emission spectral maxima, which also suggest such a rapid thermal equilibration.

This equilibration of the excited-state electron among the ligands in a mixed chelate may be exploited to localize preferentially the electron onto one of the three ligands by shifting the equilibrium in favor of the desired ligand. The relative populations of such localized states may be determined in part by their relative solvation energies and ligand reduction potentials.[5] In this paper we present evidence for a nonstatistical distribution of localized excited states from time-resolved absorption (TRA) and excited-state resonance Raman (TR^3) spectra of two sets of mixed-ligand complexes, Ru(bpy)$_2$phen^{2+} (**1**), Ru(bpy)$_2$DIP^{2+} (DIP = 4,7-diphenyl-1,10-phenanthroline) (**2**), Ru(bpy)$_2$(4,4′-Ph$_2$-2,2′-bipyridine)$^{2+}$ (**3**), and Ru(bpy)(4,4′-Ph$_2$-2,2′-bipyridine)$_2{}^{2+}$ (**4**) in aqueous solution.

Experimental Section

Excited-State Absorption Spectrometer. Time-resolved absorption spectra were obtained by using a homemade optical multichannel absorption spectrometer. The samples were excited by a QuantaRay, Q-switched, Nd-YAG laser (DCR-2, FWHM = 6 ns, 5 mJ per pulse at 355 nm). Excitation at 308 nm was accomplished by using a Lambda Physik EMG-201MSC Excimer laser. A xenon lamp (150 W, Oriel Corp.) powered by a PRA Model M301 power supply and M305 pulser was used as the monitoring source. The lamp was pulsed to produce very bright, 1 ms wide, spectrally broad and highly reproducible lamp profiles. The monitoring light after passage through the sample was collimated and focused onto the entrance slit of an ISA Model HR-320 spectrograph. The light was dispersed by a grating onto a PARC Model 1420, gated (10 ns), intensified diode array (512 elements) detector. The detector was controlled by a PARC Model 1461 controller that in turn was interfaced to a PDP-11/23 computer. The monitoring beam was intercepted by the laser pulse at right angles in the sample. The lamp profile with and without the laser excitation was recorded, and then the data were converted to absorbance. Timing of the various events was controlled by a California Avionics Digital Delay generator (Model 111AR) and a homemade pulse generator. A Stanford Instruments Model SR 250 computer interface along with a homemade pulse generator was used to produce various trigger signals needed for the experiment. The entire experiment was computer controlled through a homemade, menu-driven software with extensive graphics, written in Tektronix SPS basic language. The spectrograph was calibrated with a low-pressure mercury lamp. Typical resolution of the spectrograph was better than 0.5 nm under the experimental conditions.

Excited-State Raman Spectrometer. The excited-state resonance Raman experiments were conducted by using a homemade laser Raman spectrometer. The samples were excited by a Nd-YAG laser, as previously described. The laser power was high enough to saturate the excited-state population and also to scatter off from the excited state formed during a single laser pulse. The sample solution was pumped through a nozzle to form a smooth thin jet, which was intercepted by the laser. The back-scattered light was collected at a small angle to the pump beam and focused onto the entrance slit of the Spex Triplemate spectrograph. The third stage of the spectrograph contained a 2400 groove/mm grating to provide high resolution for all the Raman experiments. This grating covers a range of ~900–1800 cm^{-1} in the Raman spectrum with ~2-cm^{-1} resolution. The dispersed light was detected by a PARC Model 1420 gated (10 ns), intensified diode array detector (1024 elements) that was interfaced to a PARC Model 1460 controller. The entire experiment was run by a homemade, menu-driven program with special graphics, written in Heminway Basic operating system. The Raman spectrum of water was routinely subtracted from the data, and occasionally a two-point smoothing was performed to minimize the noise of the OMA amplifiers. The spectra were calibrated by using the published Raman spectrum[2] of Ru(bpy)$_3{}^{2+*}$.

Metal Complexes. The mixed complexes [Ru(bpy)$_2$phen]Cl$_2$ and [Ru(bpy)$_2$(DIP)]Cl$_2$ were prepared as described in ref 4a. The ^{13}C NMR spectrum of the mixed complexes **1** and **2** showed that the two bpy ligands are magnetically equivalent with no plane of symmetry bisecting the ligand. A total of 15 resolvable signals were observed for **1** at 121.9, 123.6, 124.9, 125.0, 125.9, 128.8, 134.6, 135.5, 135.6, 145.3, 149.4, 149.7, 150.0, 155.0, and 155.3 ppm. Similarly, a total of 17 resolvable signals were observed for **2** at 125.6, 127.4, 128.0, 129.3, 129.4, 130.1, 130.3, 130.9, 131.1, 136.6, 139.3, 149.2, 150.5, 153.0, 153.1, 157.9, and 158.2 ppm. The fast-atom-bombardment mass spectra of these complexes gave the respective molecular weights of 664 (M$^+$) for **1** and 816 (M$^+$), 781 [(M − Cl)$^+$] for **2**, confirming their identity. Loss of ligands was observed as the major fragmentation pathway in these spectra. The emission lifetimes of these complexes as measured by single-photon counting technique were 450 and 700 ns, respectively, in air-saturated water solutions at 20 °C. The mixed complexes [Ru(bpy)$_2$(4,4′-Ph$_2$-bpy)]Cl$_2$ (**3**) and [Ru(bpy)(4,4′-Ph$_2$-bpy)$_2$]Cl$_2$ (**4**) were prepared in a similar way, and their characterization and photochemistry will be published elsewhere. The luminescence lifetimes for these complexes in degassed CH$_2$Cl$_2$ were 1.45 and 1.36 μs, respectively, at 25 °C.

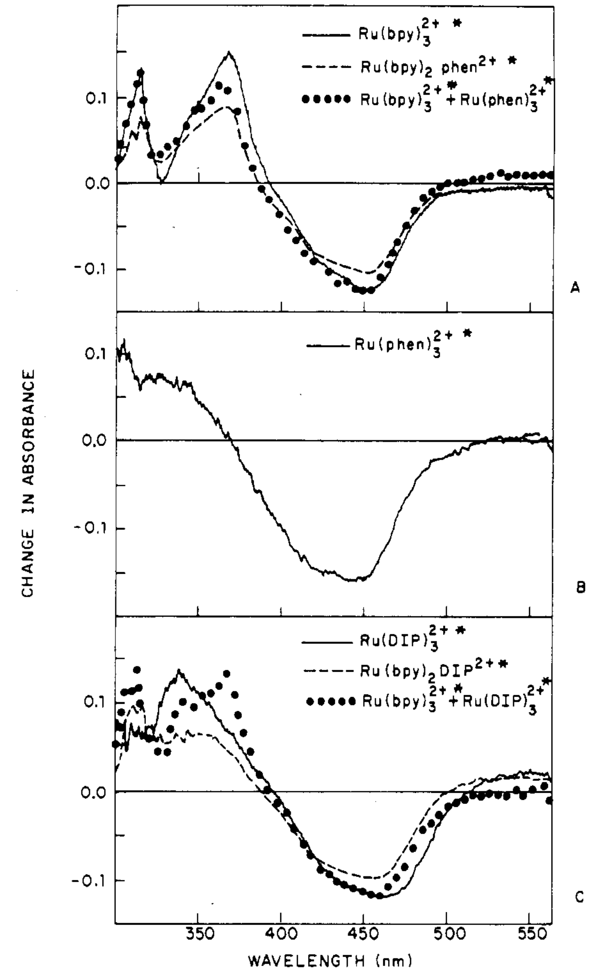

Figure 1. Time-resolved absorption spectra of ruthenium(II) mixed-ligand complexes **1** and **2** and parent tris chelate complexes.

Results and Discussion

The excited-state absorption spectra of the mixed-ligand complexes **1** and **2** along with those of their parent tris complexes, obtained 20 ns after excitation at 355 nm, are shown in Figure 1. The excited-state absorption spectrum of Ru(bpy)$_2$phen^{2+} is similar to that of Ru(bpy)$_3{}^{2+}$ (Figure 1A).[6] In fact, this spectrum is superimposable onto the spectrum obtained when a mixture of Ru(bpy)$_3{}^{2+}$ and Ru(phen)$_3{}^{2+}$, in a 2:1 ratio of their absorbances at 355 nm, is excited (Figure 1A). Therefore, in the excited state of **1**, the energy is nearly statistically (2:1) distributed among the bpy and phen ligands. The absorption spectrum of **1*** is unaffected by the wavelength at which **1** is excited, whereas that of the

---

[5] Solvent reorganization and vibronic coupling have been suggested as two of the main reasons for charge localization. See: (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Chem. Phys.* **1975**, *10*, 361. (c) Launay, J. P.; Babonneau, F. *Chem. Phys.* **1982**, *67*, 295. (d) Cocks, A. T.; Wright, R. D.; Seddon, K. R. *Chem. Phys. Lett.* **1982**, *85*, 369. (e) Barigelletti, F.; Belser, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680. (f) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

[6] Kumar, C. V.; Barton, J. K.; Turro, N. J.; Gould, I. R. *Inorg. Chem.* **1987**, *26*, 1455.

Table I. Excited-State Energy Distribution in Ruthenium(II) Complexes

complex	excitation wavelength, nm	% contribution[a] bpy*	phen*	DIP*
$Ru(bpy)_3^{2+}$	355 or 308	100		
$Ru(bpy)_2phen^{2+}$	355 or 308	~66	~33	
$Ru(bpy)_3^{2+}$ + $Ru(phen)_3^{2+}$	355	>50	<50	
$Ru(bpy)_3^{2+}$ + $Ru(phen)_3^{2+}$	308	>70	<30	
$Ru(bpy)_2DIP^{2+}$	355 or 308	<40		>60
$Ru(bpy)_3^{2+}$ + $Ru(DIP)_3^{2+}$	355	>60		<40
$Ru(bpy)_3^{2+}$ + $Ru(DIP)_3^{2+}$	308	<50		>50

[a] These percentages indicate estimates and are intended only to show trends in equilibria.

mixture critically depends upon the relative absorbances of the two parent complexes at the wavelength of excitation. This clearly indicates that initial population of either bpy* or phen*, in the mixed complex, rapidly equilibrates to a nearly statistical distribution, while in mixtures of tris chelate complexes the initial populations of these states are not equilibrated rapidly. The intramolecular energy redistribution is therefore extremely rapid in these complexes[7] whereas the intermolecular energy transfer is relatively slow. These observations lend support to the earlier suggestions of exciton hopping in these systems.[5]

In contrast, the excited-state absorption spectrum of $Ru(bpy)_2DIP^{2+}$, 20 ns after excitation at 355 nm, is similar to that of $Ru(DIP)_3^{2+}$ and is quite distinct from that of a 2:1 molar mixture (or a 2:1 mixture in absorbance at 355 nm) of $Ru(bpy)_3^{2+}$ and $Ru(DIP)_3^{2+}$ (Figure 1C). Thus, in the mixed complex **2**, the equilibrium distribution favors the population of DIP* over bpy*, in spite of the fact that there are two bpy ligands for every DIP ligand in the coordination sphere. The TRA spectrum of **2*** is also found to be independent of excitation wavelength whereas that of a mixture of the parent complexes is found to depend strongly upon the relative absorbances of the two complexes at the wavelength of excitation. For example, excitation of a molar mixture at 355 nm gave a spectrum that resembled mostly the spectrum of $Ru(DIP)_3^{2+*}$, whereas excitation of the same mixture at 308 nm gave a spectrum with greater contribution from the $Ru(bpy)_3^{2+*}$ species (Table I).

These observations may be explained in terms of rapid intramolecular energy redistribution in the case of the mixed complexes that is independent of diffusion. Irrespective of the initial states that are populated, excitation energy is redistributed rapidly among the ligands, favoring the ligand that can provide the lowest energy state. On the other hand, in the case of molar mixtures of symmetric tris chelate complexes, energy transfer is intermolecular and is diffusion limited; the initial population of the states is directly proportional to the ground-state extinction coefficients at the wavelength of excitation. Here, then, relative populations depend on the wavelength of excitation.

The distribution of excited-state populations observed for these different mixed and tris chelate complexes under various conditions is shown in Table I. The relative populations of the excited states in the case of a mixed complex can be roughly estimated from the contributions of the parent TRA spectra to that of the observed spectrum. Such an estimate for **2** shows that the contribution from $Ru(bpy)_3^{2+}$ is <40%, which is much less than the statistically predicted 66%. The TRA spectra of the mixed complexes therefore not only support the electron-hopping mechanism for these complexes but also support the idea that the energy is localized onto a given ligand and the preferred ligand is the one that can provide the lowest energy state.[5e]

Excited-state energy distribution among the ligands is even more markedly demonstrated by the excited-state resonance Raman spectra of these complexes in aqueous solutions. The excited-state

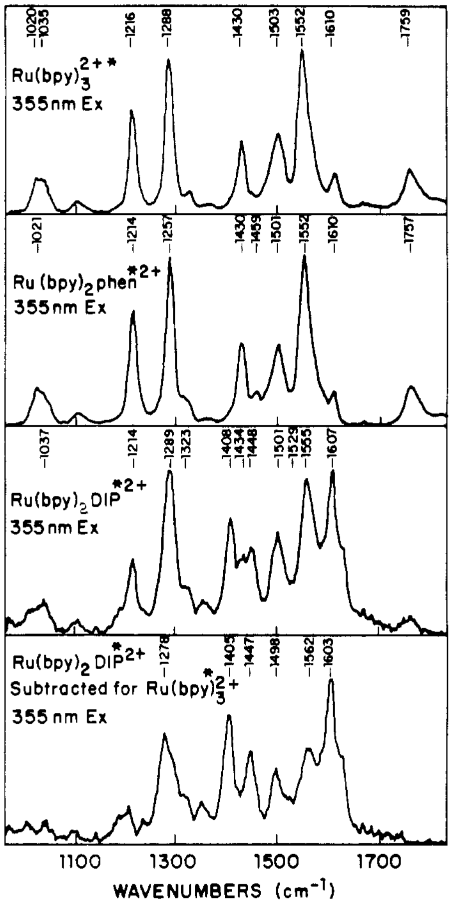

Figure 2. Excited-state resonance Raman spectra of ruthenium(II) mixed-ligand complexes **1** and **2** and parent tris chelate complexes.

resonance Raman spectra of the two mixed-ligand complexes **1** and **2**, along with those of the parent tris chelate complexes, are shown in Figure 2. The spectrum of $Ru(bpy)_2phen^{2+*}$ is clearly dominated by the transitions of $Ru(bpy)_3^{2+*}$. A weak transition at 1459 cm^{-1} corresponding to that of $Ru(phen)_3^{2+*}$ is noticeable in this spectrum. When the spectrum of $Ru(bpy)_3^{2+*}$ is subtracted from that of the mixed complex, the spectrum of $Ru(phen)_3^{2+*}$ is obtained.[6] Thus, the Raman spectrum of **1*** contains two spectra superimposed, one arising from the bpy* state and the other from the phen* state. If these excited states are delocalized or are in very rapid equilibrium, then the Raman frequencies of the mixed complex would be expected to be quite different from that of either parent spectrum. Since this is not true, these states are no doubt localized on the respective ligands and are in a dynamic equilibrium.[7] Factors such as the low resonance enhancements for the phen state at 355 nm may account for the low intensity of its transitions in the spectrum of the mixed complex **1**.

In contrast, the excited-state resonance Raman spectrum of $Ru(bpy)_2DIP^{2+}$ is dominated by features characteristic of the DIP ligand (Figure 2C). The spectrum also reveals transitions from that of the bpy ligand which are less intense. When the spectrum of $Ru(bpy)_3^{2+*}$ is subtracted from that of **2***, a spectrum corresponding to that of $Ru(DIP)_3^{2+*}$ results (Figure 2D). Thus, all the transitions of complex **2** may be assigned to those of the parent complexes, consistent with the localization of the excited-state electron on each of the ligands. Since the transitions corresponding to $Ru(bpy)_3^{2+*}$ are not the most intense transitions, the excitation is preferentially localized on the statistically unfavored DIP ligand.

Another example of energy redistribution and localization into a favored ligand comes from the study of the mixed complexes $Ru(bpy)_2(4,4'\text{-}Ph_2\text{-}bpy)^{2+}$ (**3**) and $Ru(bpy)(4,4'\text{-}Ph_2\text{-}bpy)_2^{2+}$ (**4**). Excited-state resonance Raman spectra of complexes **3** and **4** along with those of the parent tris chelate complexes are shown in Figure 3. The transition at 1215 cm^{-1} is characteristic of the bpy* state, and its intensity is dramatically reduced as this ligand is replaced

---

[7] Excited-state resonance Raman spectra of mixed-ligand complexes **1** and **2** on picosecond time scales, recorded at AT&T Bell Laboratories, in collaboration with Dr. L. E. Brus, were similar to those obtained on nanosecond time scales. Thus, the excited-state equilibration appears to be rapidly attained within ~30 ps (laser pulse width).

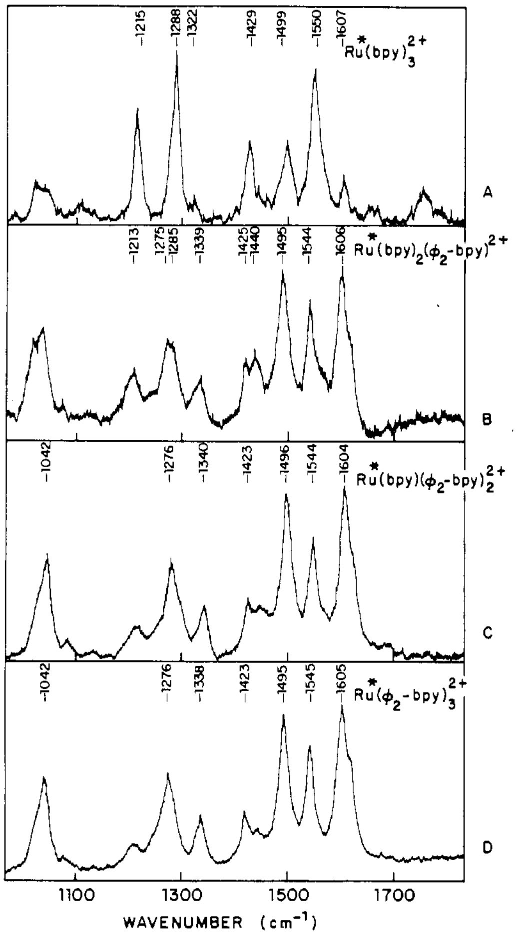

Figure 3. Excited-state resonance Raman spectra of mixed-ligand complexes **3** and **4** and parent tris chelate complexes.

by the 4,4'-Ph_2-bpy ligand, as may be seen in Figure 3B,C. Moreover, the transition at 1605 cm^{-1} in the excited-state resonance Raman spectrum of Ru(4,4'-Ph_2-bpy)$_3^{2+}$ is very strong and is characteristic of this ligand. It is interesting to note that the intensity of the 1605-cm^{-1} transition is increased upon the replacement of a single bpy ligand by 4,4'-Ph_2-bpy, as shown in Figure 3B,[8] in contrast to that found for the substitution of a bpy ligand by a phen ligand, as in Ru(bpy)$_2$(phen)$^{2+}$ (Figure 2B). The preferred localization of the excited state on this ligand is even more prominent in the case of Ru(bpy)(4,4'-Ph_2-bpy)$_2^{2+}$, as shown in Figure 3C. Indeed this spectrum is almost superimposable on that of Ru(4,4'-Ph_2-bpy)$_3^{2+*}$. This result is to be compared with that of **1***, where the spectrum is dominated by the transitions of bpy*. Thus, in fluid solution, localization of the excitation is strongly influenced by the relative excitation energies of the ligands in the coordination sphere.

It may be concluded that for the ruthenium polypyridyl complexes the excited-state energy is localized on the ligands in the lowest MLCT states and is funneled into the energetically favored ligand after initial excitation. With this in mind, it becomes possible to design systematically complexes with specific ligands that would absorb at the wavelength of choice but that would funnel the energy onto a different ligand. Since the relative populations of these states can be influenced by various factors, schemes to direct this localization, such as the effect of binding to nucleic acids,[9] on the energy distribution in these systems are under current investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE-83-51017; J.K.B. is a Presidential Young Investigator) and the Army Research Office (N.J.T.) for their financial support.

---

(8) Photoaquation of Ru(bpy)$_2$(4,4'-Ph_2-bpy)$^{2+}$ gave a product mixture consisting of 70% 4,4'-Ph_2-bpy ligand and 30% bpy ligand: Van Houten, J., manuscript in preparation. This clearly supports the current findings about the preferential localization of excitation on the 4,4'-Ph_2-bpy ligand.

(9) In Ru(phen)$_3^{2+}$ binding to DNA it has been suggested that one of the ligands is intercalated and is in a different environment compared to the other two. This difference in environment for the intercalated ligand may influence the excited-state distribution in a mixed complex such as **2**. See: Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518.

Contribution from the Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Solvatochromism in the Excited State of the *cis*-Dicyanobis(1,10-phenanthroline)ruthenium(II) Complex

Noboru Kitamura, Masami Sato, Haeng-Boo Kim, Ritsuko Obata, and Shigeo Tazuke*

Received April 22, 1987

Solvent effects on spectroscopic properties (i.e., absorption and emission energies and excited lifetime and its temperature dependence) of the *cis*-dicyanobis(1,10-phenanthroline)ruthenium(II) complex were investigated. All spectroscopic properties mentioned above were correlated fairly well with Gutmann's solvent acceptor number (AN), indicating that electron donor–acceptor interaction of the cyanide ligands in the complex (donor) with solvents (acceptor) was responsible for the large solvent effects. The observed linear relationship between the apparent activation energy for the emission decay and AN of solvents was explained as a result of the solvent-dependent energy level of the lowest emitting MLCT (metal to ligand charge-transfer) excited state. The importance of hydrogen-bonding interaction between the cyanide ligands and solvents in the excited relaxation processes is also discussed.

Introduction

Recent studies on various polydiimine ruthenium(II) complexes proved that π-acceptor and σ-donor strengths of the ligand, solvent, and temperature were of primary importance as the factors influencing both redox and excited-state properties of the complexes.[1-5] In addition to these factors, we[6] and several research groups[7-9] recently demonstrated that dominant role of solvents

---

(1) Kitamura, N.; Kawanishi, Y.; Tazuke, S. *Chem. Phys. Lett.* **1983**, *97*, 103.

0020-1669/88/1327-0651$01.50/0