Excited-State Properties of a (2,2'-Bipyridine)ruthenium(II) Complex, $[Ru(CN)_{4}(bpy)]^{2-}$, a Model of Localized Excitation

Masako Kato, Seigo Yamauchi, and Noboru Hirota*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan (Received: March 22, 1988; In Final Form: July 18, 1988)

The excited-state properties of a mono complex, $[Ru(CN)_4(bpy)]^{2-}$, have been investigated as a model of a tris complex, $[Ru(bpy)_{3}]^{2+}$, with completely localized excitation. The mono complex shows strong solvent dependence in both absorption and emission spectra. Larger temperature and time dependences of the emission spectrum were observed in the range 100-150 K. The emission spectrum shifts to a longer wavelength side at higher temperatures or at later times. An edge excitation red shift was also observed in this system. These results are mostly interpreted by solvent reorientation in the excited states. The decay rate constant of the mono complex was found to be remarkably dependent on temperature $(1.3 \times 10^4 \text{ s}^{-1} \text{ at } 4.2 \text{ c}^{-1})$ K and 3.0×10^5 s⁻¹ at 77 K), which can be analyzed in terms of the three emitting states separated by 8 and 53 cm⁻¹ from the lowest one. It was found that the properties of the mono complex are very similar to those of the tris complex. From these results, it is concluded that the excitation is localized on a single bpy ligand for the tris complex not only in liquid solutions but also in rigid media.

1. Introduction

The excited emitting states of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine; tris complex) and related complexes have attracted much interest in recent years, and various techniques have been employed to investigate their properties. One of the important points at issue now is whether an excited electron is localized on a single bpy ligand or delocalized over all three bpy ligands in a solid phase, though in a fluid solution a localized state is generally recognized as a proper description.¹ Many studies have been devoted to clarifying the difference between these two cases, but the problem still seems to remain unsolved. Ferguson et al. proposed that an excitation in the emitting state of $[Ru(bpy)_3]^{2+}$ is delocalized in a rigid glass, but a localization process takes place at a temperature where a glass-fluid transition of a solution occurs.² They observed spectral shifts with temperature and delay time and interpreted these results by the localization process. Yersin's group has supported the delocalization model from the results of the polarization³ and the Zeeman effect⁴ on the absorption and emission spectra in the single crystal. But several groups have favored the localized model (vide infra).⁵⁻⁷

In order to solve this problem, it is useful to observe emitting properties of a complex containing only one bpy ligand (mono complex), as a model of the localized state, and compare them with those of the tris complex. Several studies on such mono complexes have been reported: Crosby et al. investigated luminescence properties of a series of $[Ru(bpy)_n(N-N)_{3-n}]^{2+}$ (n =0-3; N-N = 1,10-phenanthroline (phen), substituted phen, and substituted bpy) and interpreted the similarities of the spectra among all the mixed-ligand complexes in terms of the delocalization of the excitation over the nonequivalent ligands.⁸

DeArmond et al. studied the photoselection spectrum of a mono complex, $[Ru(bpy)(py)_4]^{2+}$ (py = pyridine), as well as those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, and proposed that the symmetries of the excited states of the tris complexes are lower than D_3 in a glassy solution. Balzani et al. measured emission spectra and lifetimes of $[Ru(bpy)_n(N-N)_{3-n}]^{2+}$ [n = 1, 2; N-N = 2,2'-biquinoline (biq), 2,2'-biisoquinoline (*i*-biq), 4,4'-dimethyl-3,3'dimethylene-2,2'-biquinoline (DMCH)] in a temperature range 84-250 K and concluded that the excitation is localized on a single bpy ligand in the systems including *i*-biq ligand, while it is not fully localized in other systems.⁹ On the basis of the observation of the time-dependent shift of the emission peak in a mono complex of osmium(II), Meyer et al. opposed the proposal that the spectral shift in a glass-fluid transition region is due to the localization process.⁷ On the other hand, Ferguson et al. compared magnetic circular polarized luminescence (MCPL) of the mono complexes containing dicarbethoxy derivatives of bipyridine with that of the tris complex and supported an occurrence of the localization process.¹⁰ Therefore, these studies of the mono complexes did not provide a definitive answer to the question of whether the excitation is localized or delocalized. This is mostly due to the similarities of the mixed ligands studied.

In this work, we have investigated the properties of a mono complex in which a very weak interligand interaction is expected. We selected a new type of bpy complex of ruthenium(II), [Ru-(CN)₄(bpy)]²⁻, as a model of completely localized character and studied spectral features and decay rate constants of the luminescence over the wide temperature range 4.2-295 K. We have found that the luminescence properties of the mono complex are very similar to those of the tris complex, showing marked temperature and time dependences of the emission spectrum at the rigid-fluid transition temperature. The temperature-dependent decay rate constants can also be analyzed in terms of the three low-lying emitting levels as in the tris complex. These results give a strong support to the localized model of the tris complex, $[Ru(bpy)_3]^{2+}$, in rigid media.

2. Experimental Section

In order to obtain higher solubilities in organic solvents, a tetramethylammonium salt of the mono complex $[N(CH_3)_4]_2$ - $[Ru(CN)_4(bpy)]$ ·4H₂O was prepared by a method similar to that for the potassium salt.¹¹ [RuCl₄(bpy)] $_n^{11,12}$ (2.5 g) and an excess

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Figure 1. Absorption spectra of [Ru(CN)₄(bpy)]²⁻ in ethanol-methanol (4:1 v/v) at room temperature (solid lines) and 77 K (dotted line; arbitrary unit).

TABLE I: Absorption and Emission Data (103 cm⁻¹) of [Ru(CN)4(bpy)]2- in Various Solventsa

solvent	absorption		emission	
	$^{1}d\pi_{1}^{*}$	$^{1}d\pi_{2}^{*}$	$^{3}d\pi^{*}$	
H ₂ O	25.0		16.4	-
CH ₃ OH	22.5	30.7	15.1	
С,Й,ОН	21.9	30.0	14.9	
CH ₃ CN	19.5	28.3	16.2	
DMF	18.1	25.9		

^aAt room temperature.

amount of N(CH₃)₄CN¹³ (1.4 g) in water-ethanol (4:1 v/v; 200 mL) were refluxed for 4 days. The dark orange solution was filtered and evaporated to dryness. The residue was first purified by alumina column chromatography. The main band eluted with ethanol was collected and evaporated to dryness. The dark red solid was then treated with acetonitrile several times, and the mono complex was separated from a byproduct, $[Ru(CN)_2(bpy)_2]$, having a higher solubility in acetonitrile. A dark red crystal of the mono complex was obtained by recrystallization from methanol-nitromethane. Anal. Calcd for RuN₈C₂₂H₃₂·4H₂O: C, 45.43; H, 6.93; N, 19.26. Found: C, 45.38; H, 6.96; N, 19.36. Trace amounts of impurities $([Ru(CN)_2(bpy)_2]$ and a few unidentified species) were further removed by DEAE-Sephadex A-25 ion-exchange chromatography according to the method reported by Scandola et al.14

Adsorption spectra were taken with a Shimazu UV-3000 spectrophotometer. Emission spectra were obtained with a Spex 1704 1-m monochromator equipped with an EMI 9502B photomultiplier or a Heath 30-cm monochromator. As excitation sources, a 900-W Xe arc lamp was used for taking steady-state emission spectra and an excimer laser (XeCl; $\lambda = 308$ nm) for time-resolved measurements (spectra and lifetimes). Time-resolved spectra were obtained with a PAR 160 boxcar integrator. Excitation wavelength dependence of the emission spectra was measured with a Shimazu RF-502A spectrofluorimeter. Emission spectra were corrected with respect to the sensitivity of the detector by observing the standard spectra of m-(dimethylamino)nitrobenzene and 4-(dimethylamino)-4'-nitrostilbene.15 The temperature was monitored by immersing an Au/Fe-chromel thermocouple directly into the liquid and solid solutions and was controlled by an Oxford Instrument CF 204 cryosystem.

3. Results

The absorption spectrum of [Ru(CN)₄(bpy)]²⁻ in ethanolmethanol (4:1 v/v) is shown in Figure 1. The spectrum is typical of that of ruthenium(II)-diimine complexes. Two broad bands are clearly seen in the visible region and are assigned to the metal

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Figure 2. Steady-state emission spectra of [Ru(CN)₄(bpy)]²⁻ in ethanol-methanol (4:1 v/v) at various temperatures: 1, 82 K; 2, 108 K; 3, 120 K; 4, 123 K; 5, 129 K; 6, 135 K; 7, 150 K. These spectra were corrected to the detection sensitivity and were normalized with respect to the peak intensity.



Figure 3. Temperature dependence of the emission maxima of $[Ru(CN)_4(bpy)]^{2-}(O)$ and $[Ru(bpy)_3]^{2+}(\bullet)$.^{2a} Data were taken from the maximum of the second peak.



Figure 4. Time dependence of the emission maximum of [Ru(CN)₄-(bpy)]²⁻ in ethanol-methanol (4:1 v/v) at various temperatures.

to ligand (bpy) charge-transfer (MLCT) $d\pi^*$ bands. The absorption $({}^{1}d\pi^{*})$ and emission $({}^{3}d\pi^{*})$ maxima in various solvents at room temperature are summarized in Table I. They are solvent dependent, but the solvent dependence is quite large for ${}^{1}d\pi^{*}$ and smaller for ${}^{3}d\pi^{*}$. The absorption and emission data at room temperature and 77 K are in agreement with those reported by Scandola et al. who used $K_2[Ru(CN)_4(bpy)] \cdot 2H_2O$ obtained by a photochemical method.14

Figure 2 shows the temperature dependence of the steady-state emission spectra in ethanol-methanol (4:1 v/v). As the spectral profile varied remarkably with temperature, these spectra were corrected with respect to the sensitivity of the detector to obtain the real peak positions. The large temperature dependence of the spectrum was observed in the range 100-150 K, where the peak shifts to red at higher temperatures. Little shift was observed in

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Figure 5. Excitation wavelength dependence of emission spectra for $[Ru(CN)_4(bpy)]^{2-}$ in ethanol-methanol (4:1 v/v) at 77 K. The emission spectra were observed by excitations on the longer wavelength side at A, 450 nm; B, 530 nm; C, 540 nm; and D, 550 nm.



Figure 6. Temperature dependence of the decay rate constants of $[Ru(CN)_4(bpy)]^{2-}$ in ethanol-methanol (4:1 v/v). A simulation curve (solid line) was obtained by using the values summarized in Figure 7.

other temperature regions except a slight red shift (ca. 300 cm^{-1}) below 30 K. In Figure 3, the result for the temperature dependence of the emission peaks (70–170 K) is summarized, together with that of the tris complex. It is seen that a drastic change takes place in the range 110–130 K. We also observed the time-dependent spectral shift in the temperature range 110–140 K. The emission peak shifts to a longer wavelength side at later times as shown in Figure 4. The emission spectra observed at various excitation wavelengths and 77 K are shown in Figure 5. The emission spectrum shifts to a longer wavelength region when the complex is excited at a longer wavelength side. Such a shift is clearly seen when the excitation wavelength is longer than 520 nm, which is an absorption edge of the low-lying triplet states.

Figure 6 shows the temperature dependence of the emission lifetimes in the ethanol-methanol solution. The lifetime of the mono complex decreased remarkably from 75 μ s at 4.2 K to 3 μ s at 77 K, which is similar to the case of the tris complex.⁸ The decays followed single-exponential curves in this temperature range. Plots of log k_0 (k_0 is the obtained decay rate constant) vs 1/T in ethanol-methanol were analyzed by eq 1, which is based

$$k_0 = \frac{k_1 + k_2 \exp(-\Delta E_1/kT) + k_3 \exp(-\Delta E_2/kT)}{1 + \exp(-\Delta E_1/kT) + \exp(-\Delta E_2/kT)}$$
(1)

on the assumption that the emission comes from thermally equilibrated three levels.¹⁶ k_1 , k_2 , and k_3 denote the decay rate constants of the first, second, and third lower levels, respectively, and ΔE_1 and ΔE_2 are the energy differences of the first and second levels and the first and third levels, respectively. The decay becomes much faster and deviates from a single-exponential decay above 120 K, which might be related to solvent reorientation processes as discussed in the next section. Therefore, the data in this region were omitted from this analysis. The obtained values are summarized in Figure 7 together with those of the tris com-



Figure 7. Emitting properties of the three low-lying states of (a) $[Ru(CN)_4(bpy)]^{2-}$ and (b) $[Ru(bpy)_3]^{2+.17}$



Figure 8. Correlations between energies of the ${}^{1}d\pi_{1}^{*}$ states and acceptor numbers (A.N.)¹⁹ of solvents for $[Ru(CN)_{4}(bpy)]^{2-}(\bullet)$, $[Ru(CN)_{2^{-}}(bpy)_{2}](\Delta)$,²⁹ and $[Ru(bpy)_{3}]^{2+}(O)$.^{1e}

plex.¹⁷ The values are found to be very similar between the mono and tris complexes.

4. Discussion

 $[\operatorname{Ru}(\operatorname{CN})_4(\operatorname{bpy})]^{2^-}$ is a typical mono complex with no other aromatic ligands besides bpy. Thus, this molecule can show the properties of the excited state in which a promoted electron is completely localized on one bpy ligand. The properties are compared with those of the tris complex, $[\operatorname{Ru}(\operatorname{bpy})_3]^{2^+}$, and the problem whether the excitation is localized or delocalized in the tris complex is discussed. The mono complex studied belongs to a $C_{2\nu}$ point group.

4.1. Solvent Effect. Due to a central metal cation, Ru²⁺, and ligand anions, 4 CN⁻, a large dipole moment is expected to exist along the C_2 -axis in the ground state of the mono complex. As is usual for these kinds of complexes,¹⁸ very large solvent effects on the MLCT bands are observed in both the absorption and emission spectra (Table I). The MLCT bands shift to higher energies (blue shift) in a more polar solvent. When the band position is plotted against the acceptor number of a solvent,¹⁹ a linear correlation is obtained as shown in Figure 8. From this figure, it is clearly indicated that the solvent effect is much greater in the mono complex than in a bis complex, $[Ru(bpy)_2(CN)_2]^{20}$ and the tris complex.^{1e} This remarkable blue shift is interpreted in the following way: First, a dipole interaction with polar solvent molecules stabilizes the ground state remarkably. A strong hydrogen bonding of this complex with a protic solvent may enhance this interaction. In the excited MLCT states, the dipole moment would be reduced because the dipole moment produced by the transfer of an electron from ruthenium to bpy is in the opposite direction to that of the ground-state dipole moment. Therefore, the extent of stabilization is expected to be larger for the ground state than for the MLCT state, which makes the transition energy of the MLCT states higher in a polar solvent. This is consistent with the experimental results. Considering the large difference

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Figure 9. Schematic potential energy diagram for both the ${}^{3}d\pi^{*}$ and ground states involving a solvent orientation. See the Discussion (section 4.2) for the details.

in the dipole moments, the stable configuration of the complex including solvent molecules in the MLCT states must be different from that in the ground state.

4.2. Spectral Shift at 100-150 K. Since Ferguson et al. proposed that the localization occurs around the rigid-fluid transition temperature of the solvent (100-150 K in this ethanol-methanol case), the temperature and time dependences of the emission spectra of $[Ru(bpy)_3]^{2+}$ and related complexes have been investigated in detail.^{6,7,9,21} But, these foregoing works were not conclusive for this problem. In the mono complex, [Ru(CN)₄-(bpy)]²⁻, we observed larger spectral changes in both temperatureand time-dependent spectra (Figures 2 and 3). This fact clearly indicates that the shifts observed around the transition temperature are not due to the localization of the excitation. It is more likely that the shifts arise from solvent reorientation (relaxation) due to the change in the stable configurations caused by the large difference in the dipole moments between the MLCT and ground states. Although such an interpretation has already been suggested by several groups,^{7,21} our result that the magnitude of the shift is larger in the mono complex (having a larger dipole moment) than those in the bis and tris complexes clearly supports this idea. The potential curves of the two states are schematically shown in Figure 9. When the excitation is made at 77 K, the emission comes from the MLCT state with the same solvent configuration as in the ground state because the solvent molecules cannot move around. As temperature is increased, the solvent becomes less rigid and the solvated complex is allowed to relax to a more stable configuration resulting in the red shift of the emission peak. Ultimately at higher temperatures where the solvent is fluid, the emission comes from the MLCT state with a stable configuration, and the spectrum does not shift any more above some temperature (140 K in the case of EtOH-MeOH). Such an expectation is in agreement with the experimental results (Figure 3).

In the time-resolved experiment, the spectrum is also expected to be red-shifted with time at 110-140 K, because the emission frequency changes with the solvent reorientation and temperature variation brings the solvent reorientation times into the same time domain as the excited-state lifetimes. As the temperature is increased, the fraction of the solvent molecules making the reorientation during the lifetimes increases, shifting the emissions toward longer wavelengths.

Excitation wavelength dependence of the emission spectra at 77 K (Figure 5) is another evidence for the existence of the solvent reorientation process. At this temperature, the solvent reorientation is mostly frozen during the decay of the emission. When the excitation energy is high enough ($\lambda_{ex} < 500$ nm), the observed emission spectrum is an average over the distribution of the different solvent orientations in the ground state (Figure 9). If the excitation energy is selected to be low enough ($\lambda_{ex} > 520$ nm), only the species with smaller energy gaps, i.e., having more stable orientations of solvent molecules in the excited state, will be

excited. In such a situation, the emission peak shifts to a longer wavelength side in proportion to the lower excitation energy as illustrated in Figure 9. This phenomenon is known as an "edge excitation red shift" and has been reported for several organic molecules.²²

Thus, the spectral shift in the temperature region of the rigid-fluid transition of the solution is explained reasonably well in terms of the solvent reorientation. The fact that the mono complex with a larger dipole moment shows larger shifts than the bis and tris complexes strongly supports this conclusion.

In concluding this section, we comment on a temperature-dependent solute-solvent interaction that may cause a large temperature dependence of the emission. In fact, the absorption spectrum of this complex shows a remarkable shift between 77 K and room temperature in aprotic solvents such as DMF (λ_{max} = 467 and 552 nm, respectively) and acetonitrile (λ_{max} = 425 and 513 nm, respectively). This is interpreted by the fact that the magnitude of stabilization in the ground state by solvation is larger at 77 K (i.e., solid phase) than at room temperature (i.e., fluid solution). In the ethanol-methanol system, however, as the shift of the absorption spectrum is much smaller (Figure 1) compared with that of the emission, this effect can be excluded in explaining the temperature- and time-dependent shifts of the emission spectrum.

4.3. Three Emitting States. In the tris complex, the temperature dependence of the decay rate constants has been analyzed in terms of the three emitting states with different decay rate constants¹⁷ as shown in Figure 7b. It is interesting to see whether or not the mono complex also has low-lying three emitting levels. The temperature dependence could be analyzed by the three-level model as in the tris complex. The result of the analysis is summarized in Figure 7a, where it is seen that both the k_i and ΔE values are very similar to those for the tris complex. This result strongly suggests that the emitting states come from essentially the same origin in both the mono and tris complexes in spite of the differences in their geometrical symmetry, ligand field strength, total charge, etc. For the tris complex, presence of the three low-lying levels was experimentally confirmed by the observation of the well-resolved emission spectra in the single crystals of $[Ru(bpy)_3](ClO_4)_2$ and $[Ru(bpy)_3](PF_6)_2$ by Yersin et al.^{3c,d} Although there still remain questions about the assignment of these three levels,^{3,4,8,23-25} similarities in the luminescence properties of the mono and tris complexes indicate that the level schemes of the excited states of both complexes should be similar. From these results, we conclude that the excitation in the tris complex is apparently localized on one of the three bpy ligands.

If the localized nature is correct in solid solutions, all of the three emitting states in the tris complex should not be degenerate. This is different from the assignment by Ferguson's²³ and Yersin's^{4a} groups that assigned these states as the E states. However, the following results are consistent with our localized model. First, the polarization data for the emission can be explained by $C_{2\nu}$ symmetry.²⁶ Second, any degenerate E states were not observed in the recent Zeeman experiments on the two lower lying emitting sublevels.^{4,27} Furthermore, the excitation hopping model based on the photoselection experiment by DeArmond et al.²⁸ is consistent with the localized model. This model is also supported by the MO calculation by Kober and Meyer.²⁶ All of these results seem to support our conclusion that the excitation is localized on a single bpy ligand in the tris complex even in the rigid media.

Registry No. $[Ru(CN)_4(bpy)]^{2-}$, 105206-45-9; $[N(CH_3)_4]_2[Ru-(CN)_4(bpy)]$, 119390-74-8.

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