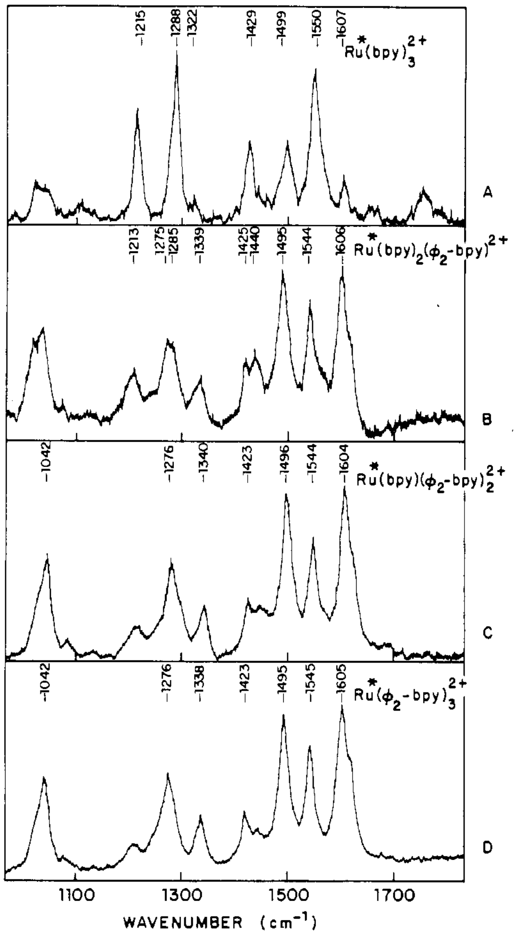

Figure 3. Excited-state resonance Raman spectra of mixed-ligand complexes **3** and **4** and parent tris chelate complexes.

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.

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(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.

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

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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

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

Table I. Solvent Dependence of Absorption and Emission Spectra of *cis*-$Ru(phen)_2(CN)_2$ at 298 K

no.	solvent	AN[a]	$10^{-3}E_{abs}$, cm^{-1}	$10^{-4}\epsilon$, M^{-1} cm^{-1}	fwhm(abs),[b] cm^{-1}	$10^{-3}E_{em}$, cm^{-1}	fwhm(em), cm^{-1}
1	acetone	12.5	19.88		5370	14.31	2780
2	*N*,*N*-dimethylacetamide	13.6	19.84	1.25	5400	14.39	2840
3	pyridine	14.2	19.84		5300	14.53	2720
4	*N*,*N*-dimethylformamide	16.0	19.96	1.28	5330	14.43	2790
5	propylene carbonate	18.3	20.58	1.17	5520	14.62	2910
6	acetonitrile	19.3	20.41	1.16	5530	14.56	2870
7	dimethyl sulfoxide	19.3	20.20	1.13	5410	14.53	2880
8	dichloromethane	20.4	20.33		5340	14.99	2750
9	chloroform	23.1	20.41		5270	15.38	2760
10	*N*-methylformamide	32.1	21.55		5310	15.17	3030
11	2-propanol	33.5	21.28		5720	15.48	2830
12	ethanol	37.1	21.65		5850	15.82	2850
13	formamide	39.8	22.22		5990	15.63	3030
14	methanol	41.3	22.22	1.05	6060	15.55	2880
15	water	54.8	23.81			15.97	3210

[a] Gutmann's solvent acceptor number. See also ref 19. [b] Full width at half-maximum of MLCT absorption (E_{abs}) and emission (E_{em}) of the complex. Error limits are $E_{abs} = \pm 50$ cm^{-1}, $\epsilon = \pm 10\%$, fwhm(abs) = ± 100 cm^{-1}, fwhm(em) = ± 150 cm^{-1}, and $E_{em} = \pm 100$ cm^{-1}.

in the relaxation of excited Ru(II) and Os(II) complexes at low temperature. Previously, we reported that $Ru(bpy)_3^{2+}$ and *cis*-$Ru(bpy)_2(CN)_2$ (bpy = 2,2′-bipyridine) exhibited large time-dependent red shifts of the emission spectra in the temperature region 100–140 K.[6] The observations were explained as due to solvent dipole relaxation in the MLCT excited state of the complex and possibly, in part, to the solvent assisted transition from the charge-delocalized excited state to the localized one.

In these studies, we found that the extent and rate of the time-dependent red shift of emission as well as its apparent activation energy of *cis*-$RuL_2(CN)_2$ (L = bpy or phen (1,10-phenanthroline)) were larger than those of $Ru(bpy)_3^{2+}$.[6] Although complexes of the type $ML_2(CN)_2$ where M is Ru(II), Fe(II), or Os(II) and L is diimine are known to show large solvatochromism,[10] little is known for the solvent effects on the excited-state properties of these complexes. The presently available data are those by Belser et al. on the spectroscopic properties of various *cis*-$RuL_2(CN)_2$ (L = bpy or biquinoline derivatives) in several solvents[11] and those on emission lifetimes of these complexes at low temperature in propionitrile–butyronitrile by Barigelletti et al.[12] However, the detailed information on solvent effects, in particular on the dynamic behaviors of these excited metal complexes, is not available. In order to understand the dynamic behaviors of solvent dipole relaxation processes at low temperature as well as to reveal the role of temperature dependent solvent effects on the excited decay processes, we studied spectroscopic properties of *cis*-dicyanobis(1,10-phenanthroline)ruthenium(II), $Ru(phen)_2(CN)_2$, in 15 solvents. In this report, we demonstrate that donor–acceptor interaction between the cyanide ligands in $Ru(phen)_2(CN)_2$ and solvents is primarily responsible for the large solvent effects on both the ground-state and the excited-state properties of the complex.

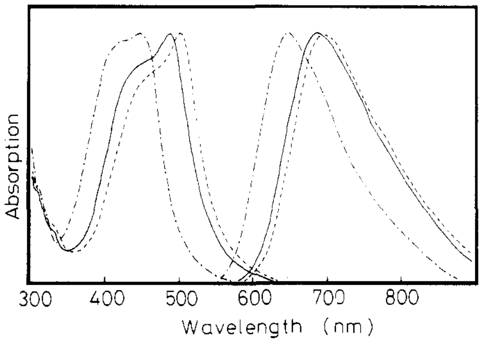

Figure 1. Absorption (left) and emission (right) spectra of $Ru(phen)_2(CN)_2$ in *N*,*N*-dimethylacetamide (- - -), acetonitrile (—), and methanol (-·-·).

Experimental Section

Materials. *cis*-Dicyanobis(1,10-phenanthroline)ruthenium(II), $Ru(phen)_2(CN)_2$, was prepared and purified according to the literature.[13] Elemental analysis of the complex gave satisfactory results.[14] Spectroscopic grade acetone (Dojin Chem.), 2-propanol (Kanto Chem. Ind.), and ethanol (Nakarai Chem. Ind.) were used as supplied. All other solvents were of reagent grade and purified before use according to the accepted procedures.[15]

Spectroscopic Measurements. Absorption and corrected emission spectra were obtained by a Hitachi 320 spectrophotometer and a Hitachi MPF-4 spectrofluorometer, respectively. For determination of the emission quantum yields of $Ru(phen)_2(CN)_2$ in various solvents (ϕ_{em}) at 25 °C, the variation of the refractive index of the solvent was corrected for. The emission yield of $Ru(bpy)_3^{2+}$ in water (0.042) was used as the standard.[16] The absorbance of each sample solution was adjusted to 0.05 at the excitation wavelength (450 nm). The sample was deaerated by Ar gas purging over 20 min. For the emission lifetime measurements, the laser photolysis system described previously was used[17] and the sample solutions were degassed by several freeze–pump–thaw cycles. The emission from $Ru(phen)_2(CN)_2$ obeyed a single exponential function in the temperature range examined in this study (5–65 °C). Temperature was controlled by circulating a water–ethylene glycol mixture using a Yamato-Komatsu Coolnics CTE-220 and CTR-220.

Photochemical Reaction of Ruthenium(II) Complexes. For photochemical reaction of $Ru(phen)_2(CN)_2$ and $Ru(bpy)_3^{2+}$ in several solvents, the sample solutions containing 4.7×10^{-5} M of Ru(II) and 0.1 M of KSCN were irradiated at 450 nm by using a JASCO CRM-FA spectroirradiator. The sample solutions were thoroughly deaerated by Ar gas purging over 20 min.

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Table II. Redox Potentials of *cis*-$Ru(phen)_2(CN)_2$ in Various Solvents at 298 K[a]

		$E_{1/2}$,[b] V vs SCE (vs Fc^+/Fc^0)					
no.	solvent	Ru^+/Ru^0	Ru^0/Ru^-	Ru^-/Ru^{2-}	Fc^+/Fc^0	E_{abs},[c] eV	E_{em},[c] eV
4	*N*,*N*-dimethylformamide	0.87 (0.40)	-1.57 (-2.04)	-1.82 (-2.29)	0.47	2.475	1.789
5	propylene carbonate	0.84 (0.46)	-1.60 (-1.98)	-1.84 (-2.22)	0.38	2.550	1.812
6	acetontrile	0.83 (0.43)	-1.65 (-2.05)	...	0.40	2.531	1.805
7	dimethyl sulfoxide	0.87 (0.42)	-1.55 (-2.00)	-1.79 (-2.24)	0.45	2.505	1.802
8	dichloromethane	0.96 (0.46)	...	...	0.50	2.521	1.859

[a] In the presence of 0.1 M of tetra-n-butylammonium perchlorate. [b] Potential vs. ferrocene/ferrocenium couple. [c] From Table I. Errors limits in determining the potentials are ±0.01 V.

Cyclic Voltammetry. The redox potentials of $Ru(phen)_2(CN)_2$ were determined by cyclic voltammetry with a Hokuto Denko HB-104 function generator and a HA-301 potentiostat.

Results and Discussion

Absorption and Emission Spectra. $Ru(phen)_2(CN)_2$ shows broad absorption and emission around 400–500 nm and 600–700 nm, respectively, and the spectra have been assigned to a metal to ligand charge-transfer (MLCT) transition.[18] Figure 1 clearly shows that both absorption and emission spectra of $Ru(phen)_2(CN)_2$ strongly depend on the nature of the solvent. The most pronounced effect of solvents is the shift of the absorption and emission maximum energies. The absorption (E_{abs}) and emission energies (E_{em}) of $Ru(phen)_2(CN)_2$ in various solvents are listed in Table I. In the present experiment, we could not find any correlations of both absorption and emission energies with dielectric constant (D_s), refractive index (n) of the solvent, or the solvent parameter expressed by $(1/n^2 - 1/D_s)$.

Previously, Burgess et al. explained the solvent dependence of the absorption spectra of $ML_2(CN)_2$ (M = Fe(II) or Ru(II) and L = bpy, phen, or its derivatives) based on the Reichardt E_T value as a solvent parameter.[19] Belser et al., on the other hand, studied solvent effects on the excited-state properties of $RuL_2(CN)_2$ complexes with various diimine ligands and concluded that good linear relationships were obtained when E_{abs} or E_{em} was plotted against Gutmann's solvent acceptor number, AN.[11] A similar relation between the present spectroscopic data and AN or E_T was obtained. It has been reported, however, that the E_T values often result in two separate correlations for a given spectroscopic data set; one is with hydroxylic solvents and another with nonhydroxylic solvents.[10] Furthermore, since the solvent dependence of the excited-state properties of $Ru(phen)_2(CN)_2$ is understandable by assuming donor–acceptor interaction between the cyanide ligands of the complex and solvent molecules, as described later, we will discuss the data based on Gutmann's solvent AN number.[20]

Figure 2 shows the correlations of the absorption and emission energies of $Ru(phen)_2(CN)_2$ with AN. The absorption energies of the cyanide complex in 15 solvents fall on a single line. It is obvious that both absorption and emission spectra shift to higher energy with increasing AN.

Beside the spectroscopic properties of $Ru(phen)_2(CN)_2$, the oxidation ($E_{1/2}(Ru^+/Ru^0)$) and reduction ($E_{1/2}(Ru^0/Ru^-)$) potentials are dependent on the solvents as well (Table II). The absorption/emission energies of $Ru(phen)_2(CN)_2$ are plotted against $E_{1/2}(Ru^+/Ru^0)$ in Figure 3. Although we can confirm the broad trend that the transition energies shifted toward high energies with an increase in the oxidation potentials, detailed discussion of Figure 3 is not warranted, in part owing to the relatively large errors in $E_{1/2}(Ru^+/Ru^0)$.[21] No systematic variation of the reduction potential with solvents was observed.

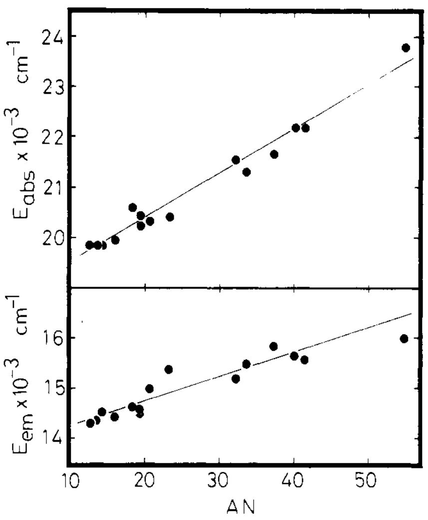

Figure 2. Correlations between E_{abs} (upper trace) and E_{em} (lower trace) of $Ru(phen)_2(CN)_2$ and Gutmann's solvent acceptor number (AN).

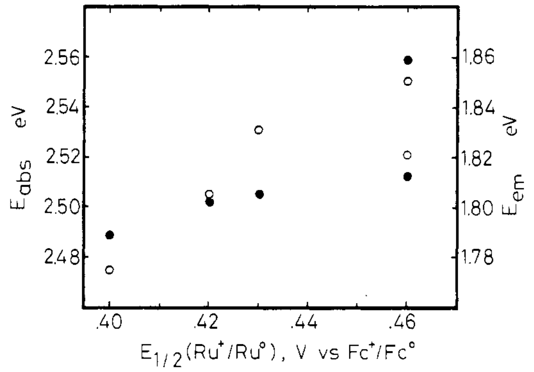

Figure 3. Relationship between E_{abs} (○) or E_{em} (●) and the oxidation potential of $Ru(phen)_2(CN)_2$.

The increase in the MLCT transition energies (E_{abs}/E_{em}) with an increase in the electron-accepting ability of the solvent (i.e., AN) provides clear evidence that the donor (Ru(II) complex)–acceptor (solvent) interaction is the origin of the spectral shifts. Namely, the interaction between the cyanide ligands of the complex and solvent molecules brings about a decrease in the σ-donating ability of the cyanide ligands and, thus, an increase of the nuclear effective charge of the metal ion. Since the oxidation potential of the complex is determined by the level of filled metal orbitals, a change in the σ-donor strength of the cyanide ligands with solvents reflects directly on the oxidation potential in ac-

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(21) Experimental errors in determining redox potentials are in general 10–20 mV, while the overall changes of the potentials are ~60 mV in Figure 3.

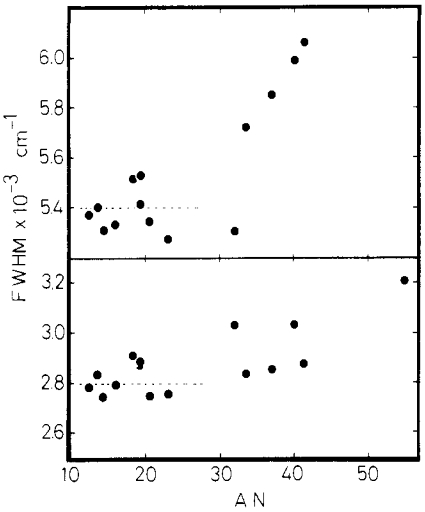


Figure 4. Solvent effects on fwhm of absorption (upper trace) and emission (lower trace) spectra of $Ru(phen)_2(CN)_2$.

Table III. Solvent Effects on the Emission Lifetime of *cis*-$Ru(phen)_2(CN)_2$

solvent[a]	τ,[b] ns	$10^2\phi_{em}$	$10^{-4}k_r$, s^{-1}	$10^{-5}k_{nr}$, s^{-1}	k', s^{-1}	ΔE_a, cm^{-1}
1	900	4.68	5.20	5.22	5.93×10^7	970
2	940	5.42	5.75	5.31	8.81×10^7	1080
3	1190	7.18	6.05	4.55	6.74×10^7	1100
4	1000	4.90	4.88	5.32	1.14×10^8	1180
5	1180	6.37	5.21	4.14	2.21×10^8	1320
6	1220	5.36	4.39	4.97	1.36×10^8	1280
7	1260	6.36	5.03	4.62	2.61×10^8	1410
8	1560	5.83	3.74	3.26	9.15×10^7	1200
9	2050	5.84	2.85	2.71	3.69×10^8	1580
10	1600	6.61	4.12	4.29	1.09×10^{11}	2790
11	1610	6.04	3.75	3.75	3.33×10^9	2000
12	1570	6.15	3.91	4.13	2.96×10^{10}	2470
13	1380	6.76	4.91	3.29	2.47×10^{11}	2790
14	1420	5.37	3.78	4.28	1.11×10^{11}	2700
15	680	1.98	3.13	2.85	1.78×10^{12}	2470

[a] For the numbering of the solvents, see Table I. [b] At 298 K. Error limits are as follows. $\tau = \pm 10\%$, $\phi_{em} = \pm 10\%$, $k_r = \pm 15\%$, $k_{nr} = \pm 5\%$, $k' = \pm 20$–30%, and $\Delta E_a = \pm 100$–200 cm^{-1}.

cordance with the correlation in Figure 3. Dependence of the emission energies on $E_{1/2}(Ru^+/Ru^0)$ can be similarly explained. However, a change in the emission energy with solvents is smaller than that of the absorption energy, so that the correlation is less clear. Such a tendency for a less precise dependence of emission energy on ligand property has been reported for the correlation between absorption/emission energies of a series of ruthenium(II) complexes and $[E_{1/2}(Ru^{3+}/Ru^{2+}) - E_{1/2}(Ru^{2+}/Ru^+)]$.[3]

Another important point is the change in full width at half-maximum (fwhm) of the spectra. The fwhm values listed in Table I were plotted against AN as shown in Figure 4. At AN < 30, the fwhm of the MLCT absorption and emission spectra are almost constant at 5400 ± 150 and 2800 ± 100 cm^{-1}, respectively, whereas further increase in AN brings about the broadening of the spectra. Close inspection of Table I reveals that all of the solvents having AN > 30 are of the hydrogen-bonding type. The relative order of hydrogen bonding ability has been reported to be in the following sequence: H_2O = methanol (1.0) > formamide (0.08) > *N*-methylformamide (0.02) ≫ *N*,*N*-dimethylformamide = acetone (8×10^{-7}), where the number in the parentheses represents the strength of hydrogen bond relative to water.[22] Since $RuL_2(CN)_2$ is easily protonated to give $RuL_2(CN)(CNH)^+$ in acidic media,[22] the broadening of the absorption and emission spectra in these solvents can be ascribed to a hydrogen-bonding effect. The smaller effects of the hydrogen-bonding solvents on the fwhm of the emission spectrum relative to that of absorption coincide with the fact that the excited state of $RuL_2(CN)_2$ is more acidic than the ground state.[23] The hydrogen-bonding interaction between the cyanide ligands and solvents is supposed to alter the Ru—CN and/or C≡N bond length. The change in the hydrogen-bonding effects between the ground and excited states will result in variation of the equilibrium nuclear distances between the two states and, thus, a relative shift of the ground and excited state potential surfaces. This will cause the broadening of both absorption and emission spectra (discussed again later).

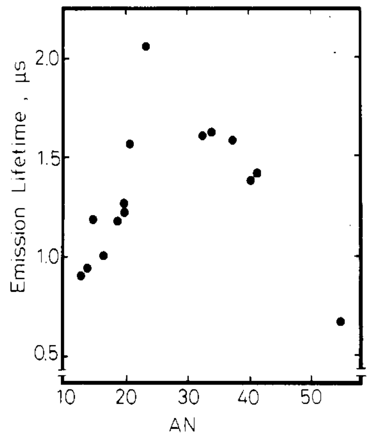


Figure 5. Solvent effects on the emission lifetime of $Ru(phen)_2(CN)_2$.

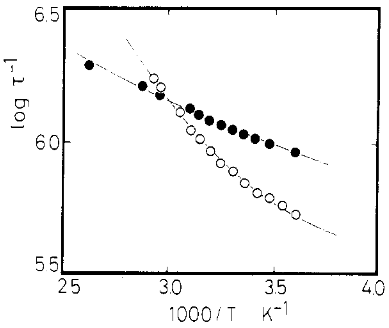
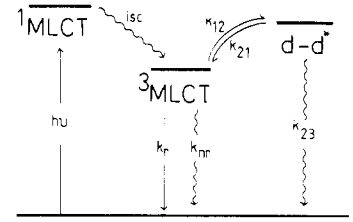


Figure 6. Temperature dependence of the emission lifetime of $Ru(phen)_2(CN)_2$ in *N*,*N*-dimethylacetamide (●) and in methanol (○).

Scheme I. Photophysical Processes of RuL_3^{2+} Complexes[a]



[a] ^{1}MLCT represents the singlet excited state.

Solvent Effects on the Emission Lifetime. The emission lifetimes (τ) and quantum yields (ϕ_{em}) of $Ru(phen)_2(CN)_2$ in 15 solvents were determined as summarized in Table III. With increasing AN, τ increases from 0.9 μs in acetone (AN = 12.5) to the maximum value of 2 μs in chloroform (AN = 23.1). Further increase in AN, however, results in the decrease of τ to 0.6 μs in water (AN = 54.8) as shown in Figure 5. Since the decay of excited Ru(II) complexes represented by $Ru(bpy)_3^{2+}$ is known to involve thermal population from the lowest emitting MLCT excited state (^{3}MLCT) to the nonemitting d–d excited state (d–d*),[4c-e,16] the solvent effects should also be examined at various temperatures.

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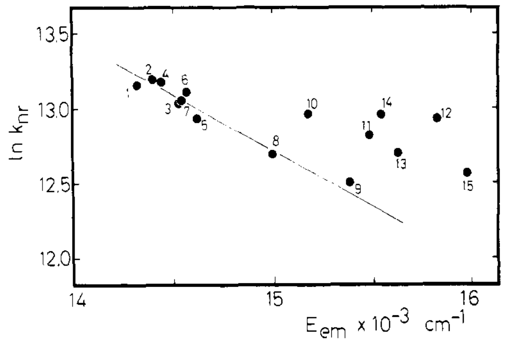

Figure 7. Application of the energy gap law to solvent effects on the nonradiative rate constant of $Ru(phen)_2(CN)_2$ (the numbering corresponds to that in Table I).

Figure 6 shows the temperature effects on τ of $Ru(phen)_2(CN)_2$ in *N*,*N*-dimethylacetamide (AN = 13.6) and in methanol (AN = 41.3). The lifetime decreases with increasing temperature, similar to $Ru(bpy)_3^{2+}$, and is strongly dependent on the solvents as demonstrated in Figure 6. The results in Figure 5 were analyzed by (1) based on Scheme I involving the ^{3}MLCT and d–d* states,[4c,d]

$$\tau^{-1} = k_r + k_{nr} + k' \exp(-\Delta E_a/RT) \quad (1)$$

where k_r and k_{nr} are temperature-independent radiative and nonradiative rate constants from the ^{3}MLCT state, respectively. The meaning of k' and ΔE_a will be discussed later. Employing computer simulation of the temperature-dependent lifetime of $Ru(phen)_2(CN)_2$ in the temperature range 5–65 °C by using nonlinear least-squares procedures, we obtained ($k_r + k_{nr}$), k', and ΔE_a. Furthermore, k_r and k_{nr} were calculated by the relation in (2). All of the data obtained by the analysis of the temperature-dependent emission lifetime of $Ru(phen)_2(CN)_2$ in 15 solvents are included in Table III.

$$k_r = \phi_{em}(k_r + k_{nr}) = \phi_{em}/\tau \quad (2)$$

Application of the Energy Gap Law to the Solvent Effects on k_{nr}. Solvent effects on k_{nr} of Ru(II) and Os(II) complexes have been frequently discussed based on the energy gap law, which predicts a linear decrease in ln k_{nr} with increasing energy gap between the ground and emitting excited states.[4d,e,24] To test applicability of the energy gap law, we plotted ln k_{nr} against E_{em} as shown in Figure 7. A linear ln k_{nr} vs E_{em} plot in a series of non-hydroxylic solvents except for formamide and *N*-methylformamide indicates that the solvent effects on k_{nr} of $Ru(phen)_2(CN)_2$ are explicable within the assumptions of the energy gap law. The slope of the plot, −1100 L cm^{-1}, is almost identical with the values reported previously for the solvent effects on $Ru(bpy)_3^{2+}$ emission,[4e] counteranion effects on $Os(4,4'\text{-}Ph_2phen)_3^{2+}$ emission,[25] and so forth.[26] The similarities of the slope with the reported values indicate that the most important factor contributing to nonradiative decay is the acceptor vibrations of the phen ligands of the complex. Also, the linear relationship in Figure 7 indicates that the solvent interaction with $^*Ru(phen)_2(CN)_2$ does not change appreciably with the nature of the solvent. The deviation of the data in formamides and hydroxylic solvents from the linear ln k_{nr} vs E_{em} relation in Figure 7 will be explained by the hydrogen-bonding interaction between the cyanide ligands and solvents. Namely, as manifested by the broadening of the absorption and emission spectra in hydrogen-bonding solvents, the equilibrium nuclear distances in the ground and excited states are influenced by the hydrogen-bonding interaction. It is apparent that an explanation of k_{nr} as a function of the Franck–Condon factor alone is not valid for $Ru(phen)_2(CN)_2$ in the hydrogen-bonding solvents.

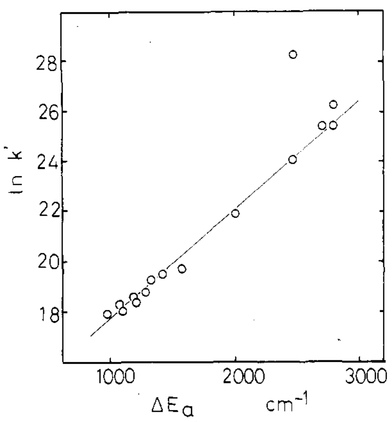

Figure 8. Correlation between ΔE_a and ln k': the Barclay–Butler plot.

Temperature Effects on Emission Lifetime. The MLCT excited-state lifetime of $Ru(bpy)_3^{2+}$ exhibits a large temperature dependence. According to Meyer and co-workers, a large temperature dependence of the emission lifetime of $Ru(bpy)_3^{2+}$ (and thus k' and ΔE_a in (1)) is explained as follows (Scheme I).[4c–e] When the decay of d–d* (k_{23}) is slow compared with the k_{21} process (i.e., $k_{21} \gg k_{23}$), the emitting excited MLCT state and the d–d* state are in equilibrium. In this limit (case I), k' and ΔE_a in (1) correspond to k_{23} and the energy difference between two excited states, respectively. On the other hand, if the decay of the d–d excited state is very rapid (i.e., $k_{23} \gg k_{21}$), k' and ΔE_a are the frequency factor and the activation energy relevant to the k_{12} process, respectively (case II). For the limiting case of $k_{21} \gg k_{23}$ (case I), characteristic values of the parameters are $k' = 10^9$–10^{10} s^{-1} and ΔE_a = 2000 cm^{-1}. For case II ($k_{23} \gg k_{21}$), on the other hand, k' and ΔE_a are reported to be in the ranges 10^{12}–10^{14} and 3000–4000 cm^{-1}, respectively.[4d] Temperature dependence of the emission lifetime of $Ru(bpy)_3^{2+}$ including its solvent effects has been studied by Caspar and Meyer, and they demonstrated that the excited lifetime of $Ru(bpy)_3^{2+}$ was subjected to only small solvent effects on k' (2×10^{12} to 4×10^{13} s^{-1}) and ΔE_a (3100–3800 cm^{-1}).[4c,d]

In marked contrast to the results for $Ru(bpy)_3^{2+}$, both k' and ΔE_a of $Ru(phen)_2(CN)_2$ showed very large solvent dependences as manifested by the variation of k' (6×10^7–2×10^{12} s^{-1}) and ΔE_a (1000–2800 cm^{-1}) with solvents (Table III). A large increase in ΔE_a with solvents accompanies an increase in ln k' as shown in Figure 8, the Barclay–Butler plot. Allosopp[27] et al. and Milder[28] reported analogous linear Barclay–Butler plots for solvent effects on temperature-dependent emission lifetimes of several Cr(III) and Rh(II) complexes, and these authors have claimed that a nonradiative deactivation path does not change appreciably in a series of solvents. However, the compensation of unfavorable activation energy (activation enthalpy, $\Delta H^{\ddagger}$) with favorable activation entropy ($\Delta S^{\ddagger}$) or vice versa, rendering a linear $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ plot, is a common trend. An example is the photoredox quenching of $^*Ru(bpy)_3^{2+}$ by various neutral electron acceptors in acetonitrile. We found that $\Delta H^{\ddagger}$ linearly correlates with $\Delta S^{\ddagger}$ (correlation coefficient = 0.96 for 16 experimental points[29]) in the ΔG (free energy change of the quenching) range of −15 to +5 kcal/mol. Since we[29] and Bock et al.[30] have already demonstrated that the quenching mechanism varies with ΔG (case I and II in ref 29 and 30), the linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ does not necessarily imply that the reaction proceeds via single mechanism. In the present case, the results are best explained by dual mechanism, as described below.

(i) The energy difference between the ^{3}MLCT and d–d* excited

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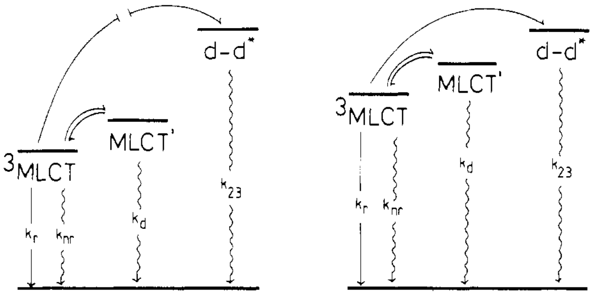
Scheme II. Solvent Effects on the Excited-State Energy Levels of $Ru(phen)_2(CN)_2$



a) in low AN b) in high AN

states ($\Delta E(^3MLCT–d–d^*)$) is very large in low AN solvents. Indeed, Belser et al. reported that $\Delta E(^3MLCT–d–d^*)$ was ~5000 cm^{-1} in a *N,N*-dimethylformamide (AN = 16.0)–dichloromethane (AN = 20.4) mixture.[11] With increasing solvent AN, the emitting MLCT excited state moves to higher energy as evidenced by the higher energy shift of the emission.[31] Recently, Winkler et al. reported picosecond transient absorption spectra of $Fe(bpy)(CN)_4$ in acetone and water.[32] They demonstrated that the lowest excited state of the complex possessed MLCT character in low AN solvents like acetone (12.5) while the MLCT and d–d excited states were almost equal in energy in water (AN = 54.8). Since the solvent interactions with $Fe(bpy)(CN)_4$ are similar to those with $Ru(phen)(CN)_2$, it is easily understood that $\Delta E(^3MLCT - d–d^*)$ is smaller in high AN solvents when the d–d excited state energy is independent of solvents (discussed later). As a consequence, the observed ΔE_a should decrease with increasing AN if thermal activation to the d–d excited state alone is important for a series of solvents. However, ΔE_a increases with AN as clearly seen from Figure 9.

(ii) The observed ΔE_a values of ~1000 cm^{-1} in low AN solvents are in contradiction with $\Delta E(^3MLCT - d–d^*)$ ~5000 cm^{-1}. The three-state model in Scheme I indicates that ΔE_a and k' range 2000–4000 cm^{-1} and 1×10^9–4×10^{13} s^{-1}, respectively. The ΔE_a vaues in low AN solvents are too small to be ascribed to the thermal activation to the d–d excited state.

(iii) The correlation of E_{abs}/E_{em} energies with the oxidation potential of the complex indicates that the d–d excited state energy varies with solvents as well. Namely, the larger the stabilization of the filled metal orbital by solvent interactions with the cyanide ligands (i.e., in high AN solvents), the larger the ligand field splitting. This causes the higher energy shift of the d–d excited state with increasing AN. Phenomenologically, the trend agrees with the gradual increase in ΔE_a with AN (Figure 9) provided the thermal activation from ^{3}MLCT to d–d* is the main deactivation path regardless of solvents. Nonetheless, the small ΔE_a of ~1000 cm^{-1} in low AN solvents can never be explained by this model.

The observed ΔE_a ~ 1000 cm^{-1} in low AN solvents can be explained neither as the energy difference between two excited states (case I) nor as the activation energy of the k_{12} process (case II), while those in high AN solvents could be attributed to the thermal activation to the d–d excited state. The present solvent effects on temperature-dependent emission lifetime of $Ru(phen)_2(CN)_2$ should be thus discussed based on two different mechanisms with solvent AN as described below.

Scheme II displays the mechanisms of the temperature dependence of the emission lifetime of $Ru(phen)_2(CN)_2$ in low (Scheme IIa) and high AN solvents (Scheme IIb). $\Delta E(^3MLCT - d–d^*)$ in low AN solvents is so large that thermal activation from the ^{3}MLCT state to the d–d* state is unlikely ($\Delta E(^3MLCT - d–d^*)$ ~ 5000 cm^{-1}). Contrarily, since the variation of the d–d excited-state energy with solvents is supposed to be relatively small compared with that of the MLCT excited state due to the charge-transfer nature of the latter state, the increase in the acceptor strength of solvents (AN) decreases the energy difference between the emitting ^{3}MLCT state and the d–d* state as discussed above (Scheme IIb).[31,32] Thermal activation to the d–d* state thus becomes facile with increasing AN of the solvents. Temperature dependence of τ (i.e., the apparent ΔE_a value) is large in high-AN solvents as compared with that in low-AN solvents.

Small but finite temperature dependences of τ similar to the present data in low AN solvents (~1000 cm^{-1}) have been reported for several Ru(II) complexes such as RuL_3^{2+}, where L is 3,3′-bipyridazine,[33] 4-(2-pyridyl)pyrimidines,[33] or 4,4′-dicarboxy-2,2′-bipyridine[34] and $RuL_2L'^{2+}$ where L or L′ is 2,2′-bipyridine, 2,2′-bipyrazine, 2,2′-bipyrimidine, and so forth.[4b,35] In every case including the present results, the emitting ^{3}MLCT state is located far below the d–d* state. Recently, Meyer reported that the small temperature dependence of τ of $RuL_2L'^{2+}$ could be attributed to thermal activation to the fourth excited MLCT state[4c] (MLCT′), which had been predicted theoretically to lie at 600–1000 cm^{-1} above the lowest ^{3}MLCT state.[4c,36] Wacholtz et al. also presented similar interpretation for the small activation energy of the emission lifetime of $Ru(bpy)_2$(4,4′-bis(diethylcarboxy)-2,2-bipyridine)$^{2+}$.[35] The present small ΔE_a, which agrees phenomenologically with the energy difference between the lowest and the fourth MLCT excited states (~1000 cm^{-1}), will be in support of the participation of the fourth excited MLCT state as well. Since we suppose that the MLCT′ state also moves to higher energy with the increase in AN owing to the charge-transfer nature of the state, the gradual increases in k' and ΔE_a with AN (Figure 9) will be responsible for the continuous increase in the contribution of the thermal activation from the lowest MLCT excited state to the d–d* state to τ with the decrease in the energy difference between two excited states and, therefore, with the increase in AN.

Photochemical Reaction of $Ru(phen)_2(CN)_2$. The explanations mentioned above are well supported by the solvent dependence of photochemical ligand substitution reaction of $Ru(phen)_2(CN)_2$. For $Ru(bpy)_3^{2+}$, the ligand substitution reaction with KSCN has been known to proceed via the d–d* state with a quantum yield of 0.1 in dichloromethane (degassed solution).[4c] Photoreaction of $Ru(phen)_2(CN)_2$ with 0.1 M of KSCN in several solvents will inform us of the nature of the excited state. Participation of the d–d* state should increase the quantum yield of photodecomposition. Although the product analysis has not been conducted at the present time, the quantum yield of photodecomposition of the cyanide complex was estimated spectroscopically (i.e., absorption change) as listed in Table IV. Table IV clearly demonstrates that the photoreaction with KSCN is favored in a solvent having a high AN number such as *N*-methylformamide (AN = 32.1) or methanol (AN = 41.3), while a photoreaction was scarcely observed in *N,N*-dimethylacetamide (AN = 13.6). The results indicate that the thermal activation from the ^{3}MLCT state to the d–d* state is a major path for the excited decay of $Ru(phen)_2(CN)_2$ in high AN solvents but not in low AN solvents as evidenced from the lack of photodecomposition of the complex.[37]

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(31) Since E_{em} is less sensitive to solvent AN relative to E_{abs} (Figure 2), one may expect that the higher energy shift of the emission with increasing solvent AN corresponds to the lower energy shift of the ^{3}MLCT excited state. However, the radiative decay from the ^{3}MLCT excited state produces the ground state whose solvent configurations are in equilibrium with the excited state (unrelaxed state), and this state relaxes to the solvent-oriented ground state (relaxed state). The energy difference between the unrelaxed and relaxed ground states becomes larger with increasing solvent AN, since the dipole moment of the (relaxed) ground state is larger than the excited state.[11] The high-energy shift of E_{em} with solvent AN is thus not explicable assuming the low-energy shift of the ^{3}MLCT excited state with solvent AN.

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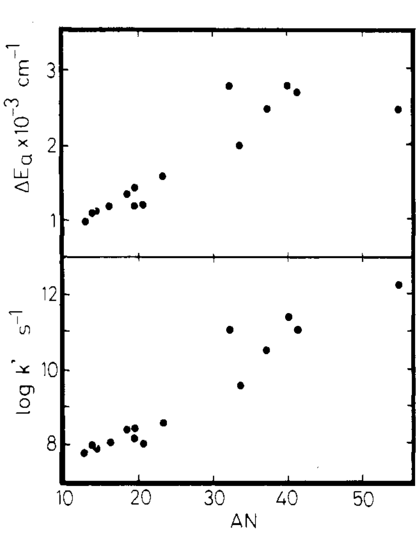

Figure 9. Solvent effects on the temperature-dependent emission lifetime of Ru(phen)$_2$(CN)$_2$: ΔE_a (upper trace); k' (lower trace).

Table IV. Solvent Effects on the Photoreaction of *cis*-Ru(phen)$_2$(CN)$_2$ in the Presence of KSCN (0.1 M)

no.	solvent	AN	Φ_{rel},^{a} %
2	*N*,*N*-dimethylacetamide	13.6	0.0
7	dimethyl sulfoxide	19.3	13.7
10	*N*-methylformamide	32.1	14.5
14	methanol	41.3	27.4

^{a}Relative to the yield of Ru(bpy)$_3^{2+}$ in water. See also ref 4c.

The photochemical quantum yields, although the data are still limited, increase with increasing AN in accord with the solvent dependence of the k' and ΔE_a values.

All data obtained in the present study are interpreted along the single context of the donor–acceptor interaction between the cyanide ligands and solvents, which is primarily controlled by the acceptor strength of solvents, AN.

Control of the Excited Lifetime and Its Temperature Dependence for the Ruthenium(II) Complex. The fine tuning of the redox and spectroscopic (E_{abs} and E_{em}) properties of Ru(II) complexes can be achieved by modulating the ligand propertie such as π-acceptor and σ-donor strength of the ligand.[1-3,4b] The nonradiative rate constant of the Ru(II) complex (k_{nr}) obeys the energy gap law for a series of structurally analogous complexes of the type RuL$_{n-3}$L′$_n$ where L and L′ are diimine ligands or nonchromophoric ligands.[4b] Nevertheless, synthetic control of the lifetime of Ru(II) complex is complicated due to the large temperature-dependent activation term. While the control of electronic coupling parameters between the ground and excited states determining k_{nr} is still difficult, the control of energy levels of ^{3}MLCT and/or d–d* is possible, and consequently, the temperature dependence of τ as well as the photostability can be also controlled by an appropriate choice of ligands and solvents.

The RuL$_3^{2+}$ complexes with strong π-accepting and moderate σ-donating ligands such as 4-substituted pyrimidines possess a relatively low-energy MLCT excited state, and the thermal activation of d–d* does not contribute to the nonradiative decay.[29] These complexes show a small temperature dependence of the emission lifetimes (ΔE_a = 400–1200 cm^{-1}) as expected.[3,33] For RuL$_2$L′$^{2+}$, on the other hand, the use of strong σ-donating ligands such as L′ (i.e., cyanide ligands) brings about a large energy difference between the ^{3}MLCT and the d–d* excited states (~5000 cm^{-1} for Ru(phen)$_2$(CN)$_2$ in low AN solvents) as compared with that for Ru(bpy)$_3^{2+}$ (3000–4000 cm^{-1}), so that the deactivation via the d–d excited state is unlikely as discussed in the previous sections. The MLCT excited states of these complexes will be subjected to deactivation to the ground state directly or via the fourth MLCT excited state, rendering a small temperature dependence of τ. Furthermore, since the MLCT excited energy of RuL$_2$L′$^{2+}$ is largely influenced by the solvent properties, the contribution of the thermal activation from ^{3}MLCT to d–d* can be controlled by the solvent properties as well. Solvent dependent ΔE_a of Ru(phen)$_2$(CN)$_2$ in Figure 8 presents a general principle for fine tuning of the excited lifetime of Ru(II) complexes as a function of ligand structures and solvent properties.

Implication of the Solvatochromism with Low-Temperature Emission of Ru(phen)$_2$(CN)$_2$. Ru(phen)$_2$(CN)$_2$ shows an emission spectrum at 17.06 cm^{-1} (2.115 eV) in an ethanol–methanol mixture at 77 K, while it possesses an emission maximum at 15.55 cm^{-1} (1.927 eV) in methanol at room temperature. Although it is a general trend that the emission of Ru(II) complexes shift to higher energy upon cooling,[6,38,39] the fact that the shift of the emission spectrum of Ru(phen)$_2$(CN)$_2$ is twice as large as of that of Ru(bpy)$_3^{2+}$ has been rarely discussed (E_{em} at 77 K and room temperature are 17.24 cm^{-1} (2.137 eV) and 16.39 cm^{-1} (2.031 eV), respectively). For Ru(phen)$_2$(CN)$_2$, since hydrogen-bonding interactions between the cyanide ligands and solvents are frozen in low-temperature alcohol glass, the excited-state properties of the cyanide complex at low temperature will be greatly different from those at room temperature even in the same alcoholic solvent system. At low temperature, we previously reported that solvent dipole relaxation played a crucial role in the excited relaxation of Ru(bpy)$_3^{2+}$ and RuL$_2$(CN)$_2$ as demonstrated by time-resolved emission spectroscopy.[6] Besides solvent dipole relaxation, the formation and destruction of the hydrogen-bonding interaction between the cyanide ligands in Ru(phen)$_2$(CN)$_2$ and alcoholic solvents will also affect E_{em}. All aspects of solvent effects are dependent on the motion of solvent dipoles. If the solvent (dipole) motion is frozen, no solvent effects can be seen. On the other hand, when the solvent dipole reorientation is much faster than the excited lifetime, time-resolved observation of relaxation processes is not possible. Consequently, a sudden change of solvent effects near T_g of the medium provides valuable information on the dynamic behaviors of solvent relaxation. Indeed, E_{em} of Ru(phen)$_2$(CN)$_2$ in an ethanol–methanol mixture (T_g = 130 K) shifts very sharply (~40 nm) around 110–130 K.[6,38] A larger temperature-induced shift of E_{em} of the cyanide complex relative to that of Ru(bpy)$_3^{2+}$ (~20 nm shift from 110–130 K)[34] in alcoholic glass matrix suggests the participation of the hydrogen-bonding interaction in the excited Ru(phen)$_2$(CN)$_2$.

From the above discussion, it is apparent that the excited state energy of Ru(phen)$_2$(CN)$_2$ cannot be determined from the emission of 77 K. Recently, we estimated the MLCT excited-state energy of Ru(phen)$_2$(CN)$_2$ to be 1.83 eV based on the emission quenching experiments and the ground-state redox potentials of the complex in acetonitrile at 298 K.[40] The estimated value contrasts with that determined from the low-temperature emission at 77 K (2.115 eV). Since Bock et al. reported that the MLCT excited-state energies of Ru(bpy)$_3^{2+}$ estimated from both quenching experiments in acetonitrile and low-temperature emission in an ethanol–methanol mixture satisfactorily agree with each other (2.1 eV),[30] the discrepancy between the values for Ru(phen)$_2$(CN)$_2$ is concluded to be, in part, due to the strong interaction between the cyanide ligands and alcoholic solvents. Further studies on time, temperature, and solvent dependence of

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(37) An alternate explanation is to assume the competition between geminate recombination of CN$^-$ and capture of a solvent molecule by the Ru(phen)CN$^+$ intermediate. In methanol, which is more reactive than *N*,*N*-dimethylacetamide in this context, this may play a role in part in the photodecomposition of the complex. However, since thermal activation to the d–d excited state does not participate in the excited-state reactions in low AN solvents like *N*,*N*-dimethylacetamide as evidenced by small ΔE_a, the formation of the intermediate Ru(phen)$_2$CN$^+$ is not expected. The explanation is not applicable for the reactions in low AN solvents. Product analysis will be necessary to confirm the mechanism.

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emission behaviors of RuL_3^{2+} and $RuL_2(CN)_2$ are necessary to fully understand the excited-state properties of these complexes.

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Registry No. *cis*-Ru(phen)$_2$(CN)$_2$, 112087-85-1; *cis*-Ru(phen)$_2$(CN)$_2^+$, 112087-86-2; *cis*-Ru(phen)$_2$(CN)$_2^-$, 112087-87-3; *cis*-Ru(phen)$_2$(CN)$_2^{2-}$, 112087-88-4; KSCN, 333-20-0.

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Vapor-Phase Electronic Absorption Spectra and Solution Magnetic Circular Dichroism and Absorption Spectra for Dihalo- and Halomethylmercury(II)

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Vapor-phase electronic absorption spectra in the UV region (3.0–5.2 μm^{-1}) are reported for HgI_2, $HgBr_2$, and $HgCl_2$ at temperatures between 130 and 150 °C and for CH_3HgI, CH_3HgBr, and CH_3HgCl at temperatures between 65 and 85 °C. Absorption and magnetic circular dichroism (MCD) spectra are also presented for room-temperature cyclohexane solutions of HgX_2, CH_3HgI, and CH_3HgBr. Several bands in the vapor-phase spectra of the iodo and bromo complexes reveal weak vibrational structure. In particular bands at 4.45 μm^{-1} for HgI_2 and 4.97 μm^{-1} for CH_3HgI show long progressions in the bending mode of the complex and indicate excitation to bound molecular excited states. The solution MCD spectra show two prominent positive pseudo A terms for the two lowest energy band systems at 3.62 and 4.47 μm^{-1} for HgI_2, and a similar positive pseudo A term is also found for the lowest band at 4.32 μm^{-1} for CH_3HgI. The absorption and MCD spectra for the iodo complexes are interpreted by means of a ligand to metal charge-transfer (LMCT) model involving states of the $I^- \rightarrow$ Hg 6s excited configurations. The model includes the effects of halide spin–orbit coupling on the excited LMCT states and can account for differences observed between the absorption intensity and MCD pattern for the iodo complexes and for the bromo complexes.

Introduction

Dihalo- and halomethylmercury(II) complexes, HgX_2 and CH_3HgX, X = Cl^-, Br^-, and I^-, exhibit linear two-coordination both in the vapor and in a variety of solution environments.[1] In spite of this simple coordination geometry and the closed-shell diamagnetic $5d^{10}$ electronic configuration of Hg(II), the description of the lowest energy excited electronic states of these compounds and the assignment of their UV spectra has been lacking in detail and is not free of disagreement. This situation may be partly due to some experimental difficulties in obtaining reliable spectroscopic data under conditions where the two-coordinate species are well-defined. For example, there have been a number of solution spectral studies for HgX_2 in a wide range of solvents[2–6] (comparatively few have been reported for CH_3HgX[7,8]). However, the interpretation of these spectra may be questioned in some cases because dissociation occurs in aqueous solutions in the absence of added halide[5] and the solubility is low in nonaqueous solvents, where solvolysis can also be a complication if the solvent is a potential ligand (e.g. alcohols, acetonitrile, ethers, etc.). In the presence of added halide, species such as HgX_3^- or HgX_4^{2-} form and free halide absorptions tend to dominate the UV spectra in the region 250–190 nm. Further, spectra obtained for HgX_2 in aromatic solvents show differences compared to those obtained in nonaromatic solvents, and these differences have been interpreted as the formation of intermolecular solvent–HgX_2 charge-transfer complexes in the aromatic solvents.[1f,2] All of these complications are expected to lead to Beer's law failure and make questionable any interpretation based on simple linear HgX_2 or CH_3HgX species. In the vapor the simple complexes should be well-defined, but because of their low vapor pressure, elevated temperature and long-path cells are required to obtain reasonable spectra in the UV region.

The solution difficulties notwithstanding, the lowest energy bands for HgI_2, $HgBr_2$, and $HgCl_2$ in nonaromatic hydrocarbon solvents (where complications appear to be minimized) are found near 266, 225, and 200 nm, respectively. A similar blue shift from CH_3HgI to CH_3HgBr to CH_3HgCl has also been observed in methanol,[8] but Beer's law compliance and lack of solvolysis was not reported. The blue shift from I^- to Cl^- has been offered as evidence for a ligand to metal charge-transfer (LMCT) process.[4–6] Consistent with this assignment, photoelectron spectra for HgX_2 and CH_3HgX show that the lowest energy ionizations (9–14 eV) are from the halo ligands.[9] Ionization from the Hg(II) 5d orbitals is found at higher energy (>15 eV). Even though the LMCT assignment of the UV spectra seems reasonable, there remains disagreement as to detail. For example, the lowest energy bands in HgX_2 (and also in several mixed dihalo complexes HgXY) have been assigned as ${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$, a halide to Hg(II) 6p LMCT.[4,6] Since a transition to a ${}^1\Delta_u$ state is electric-dipole-forbidden in $D_{\infty h}$, the observed intensities ($\epsilon \approx 1000$–$3000\ M^{-1}\ cm^{-1}$) were explained by assuming a bent (C_{2v}) upper state (${}^1\Delta_u$ correlates with an electric-dipole-allowed ${}^1B_2$ state in C_{2v} symmetry). However, some recent MO calculations[10] that utilized a relativistic core potential for Hg(II) have been used to interpret the two lowest energy absorption bands in $HgCl_2$ and $HgBr_2$ as dipole-allowed LMCT to ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ states of halide to Hg 6s configurations. The

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