Specific Role of Water in Radiationless Transition from the Triplet MLCT States of Tris(polypyridine) Complexes of Osmium(II)

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The solvent effect on the radiationless transition rates from the excited triplet MLCT (metal-to-ligand charge-transfer) states of tris(bipyridine)osmium(II) ($Os(bpy)_3^{2+}$; bpy = 2,2′-bipyridine) and tris(phenanthroline)osmium(II) ($Os(phen)_3^{2+}$; phen = 1,10-phenanthroline) was investigated in water−methanol mixed solvent and its deuterated analogues at various temperatures. Similar measurements were carried out in H_2O-D_2O and H_2O−dioxane mixed solvents. A significant isotope effect of the solvent on the rate constant of the radiationless relaxation to the ground state was observed in water, while only a small one was recognized in methanol. The radiationless transition rate in the H_2O-D_2O mixture depends linearly on the mole fraction of D_2O, while that in the H_2O−methanol mixture shows no linear dependence on the mole fraction of methanol. Those solvent effects of the radiationless transition are described as the energy transfer from the metal complex to the water molecule included in the Os(II) complex. It was suggested that the observed radiationless transition rates were strongly affected by the microscopic environment around the Os(II) complex from the results in the mixed solvents.

Introduction

The photophysics and photochemistry of Ru(II)−polypyridine complexes (RuL_3^{2+}; L = bpy and phen) have been studied extensively by a number of researchers.[1−3] The phosphorescence from the triplet excited state of the Ru(II) complexes, i.e., ^{3}MLCT (metal-to-ligand charge-transfer) state, is observable even in the liquid phase at room temperature. It was reported that there was a large difference between the radiationless transition rate in H_2O and D_2O[4−6] and that the lifetime of the lowest excited state does not show a linear dependence on the mole fraction of alcohol in water−alcohol mixtures.[7] On the basis of qualitative discussion, it has been proposed that the deuteration effect of water is ascribed to the contribution from the intramolecular vibration mode of the OH bonds[4,5,8] and that the viscosity of the solution is responsible for the nonlinear dependence of the relaxation rate on the mole fraction of alcohol.[7] There are two kinds of radiationless decay paths from the ^{3}MLCT states for the Ru(II) complexes, i.e., the path of direct recovery to the ground state (ISCP: intersystem crossing path) and a path through the (d,d*) excited state (MCP: metal center path).[6,9,10] Since these paths compete with each other, the details of the solvent effect on each path are not still completely elucidated.

Os(II)−polypyridine complexes (OsL_3^{2+}) are also known to be luminescent from the ^{3}MLCT state in liquid solutions at room temperature. Since the metal−ligand distance is estimated to be identical for the Ru complex and the Os complex,[1,11,12] the steric and solvation effects should be very similar for those complexes. On the contrary, these electronic structures are different:[1,13] the ligand field parameter for the Os(II) complexes (10*Dq*) is larger than that for the Ru(II) complexes, which indicates that its (d,d*) excited state is located higher than that of the Ru(II) complex. Moreover, the emission spectra of the Os(II) complexes are red-shifted with respect to those of the analogous Ru(II) complexes, which means that the energy gap between the (d,d*) state and the ^{3}MLCT state is larger for the Os(II) complex. Therefore, the metal-centered (d,d*) states of the Os(II) complexes should be thermally inaccessible from the ^{3}MLCT state at room temperature,[14] and the only possible radiationless decay path from the ^{3}MLCT state is the direct relaxation to the ground state in the Os(II) complexes.

The purpose of this paper is to investigate details of the solvation and the solvent isotope effects on the radiationless decay rates of ISCP from the ^{3}MLCT state by the use of the Os(II) complexes. The role of the solute−solvent interaction and of the hydrogen bond network of the solvent was also examined in water−methanol and water−dioxane mixtures. These results are discussed regarding the radiationless process as energy transfer from the Os(II) complex to the adjacent solvent molecules.

Experimental Section

Materials and Sample Preparation. A. $Os(bpy)_3(ClO_4)_2$ and $Os(phen)_3Cl_2$. The bpy and phen ligands were from Wako Pure Chemical Industries, Ltd., and were used as received. The iodides of the Os(II)

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complexes were prepared according to the literature method from the ligand and $(NH_4)_2OsCl_6$.[15] The obtained iodide complex was converted to the perchlorate or the chloride as follows. The iodide was dissolved in a minimum volume of hot water, and a concentrated aqueous solution of $NaClO_4$ was added to it. The black perchlorate was obtained by filtration and was dried over $CaCl_2$. The perchlorate was purified by recrystallization from water three times. The chloride was prepared by metathesis from the iodide dissolved in a minimum volume of hot water and by addition of freshly prepared AgCl. The solution was filtered, and the filtrate was concentrated to a volume of 5 mL and purified by liquid chromatography on a 2 cm diameter × 20 cm length column of Sephadex LH-20. Elution with absolute ethanol resulted in a dark-green band, and the main part of the band was collected. Finally, the chloride was purified by recrystallization from water two times.

Solvents. D_2O (99.8 atom % D, Merck) and methanol-d_1 (MeOD, 99.5 atom % D, Aldrich) were used without further purification. H_2O was distilled twice. Methanol (MeOH) purchased from Wako Pure Chemical Industries, Ltd., was purified by distillation followed by a second distillation to remove water over freshly prepared magnesium alcoholate just before use for measurements.

Apparatus and Measurements. The absorption and the emission spectra were obtained by use of Hitachi spectrophotometer model 220 and Hitachi 850 and F-4500 fluorescence spectrophotometers, respectively. The temperature was controlled (±0.1 K) with a circulating water flow by use of a thermostat (Tokyo Rika Kikai, EYELA Digital Uni Ace UA-10G) and a cooler (Tokyo Rika Kikai, EYELA Cool ECS-0). The emission spectra were corrected with reference to a standard solution of *N*,*N*-dimethylnitroaniline and 4-methylamino-4′-nitrostilbene.[16]

For $Os(phen)_3^{2+}$, the emission lifetime measurements were performed by use of the second harmonics (532 nm, fwhm 7 ns) from a Nd^{3+}:YAG laser (Spectron Laser Systems SL401) as the exciting pulsed light source. The emission was detected by a photomultiplier (Hamamatsu Photonics R928) through a monochromator (Nikon P250), accumulated by a storage oscilloscope (LeCroy model 9450), and transferred to a microcomputer (NEC PC-9801 VM). The decay curve was analyzed as a single-exponential decay based on a nonlinear least-squares method.

For $Os(bpy)_3^{2+}$, sub-nanosecond pulses from a nitrogen-dye laser (Laser Photonics, LN120C NitroDye laser) were used for excitation incorporated with a C500 (Exciton Chemical Co.) laser dye generating 495 nm pulses. The light was introduced to an apparatus for lifetime measurements (Hamamatsu Photonics, HAMAMATSU C4780 picosecond fluorescence lifetime measurement system) through an optical fiber (Sumitomo Denko Co., MS-300; core diameter is 300 μm). In the present system, emitting light was detected by a polychrometer (Chromex 250IS imaging spectrograph) combined with a streak scope (Hamamatsu Photonics, HAMAMATSU C4334). The time profile of the emission was accumulated and was also transferred to a microcomputer (Apple Macintosh 7100/80AV). The decay curve was analyzed as a single-exponential decay by a nonlinear least-squares iterative convolution method.[17] The temperature was controlled by use of a thermostat (Komatsu-Yamato, Coolnics Thermo-Bath CTE-21). The concentration (about 10^{-5} M) of sample solutions of Os(II) complexes was estimated from the absorption intensity after the bubbling of argon gas.

The tris(polypyridine) Os(II) complexes emit from the triplet MLCT (^{3}MLCT) state rapidly generated from the singlet (^{1}MLCT) state in water−alcohol mixed solvents at room temperature.

Results and Discussions

Emission Quantum Yields and Decay Rates. The emission decays single-exponentially in all solvents at the temperature region of this work. Since the quantum yields of the intersystem crossing from ^{1}MLCT to ^{3}MLCT are supposed to be unity for both Os(II) complexes, the rate constants of nonradiative relaxation from the ^{3}MLCT excited states, k_{nr}, are estimated from the experimental results of the phosphorescence quantum yields, ϕ_r, and the lifetimes, τ_{obs} (eq 1).

$$k_{nr} = 1/\tau_{obs} - \phi_r/\tau_{obs} \tag{1}$$

The emission quantum yields of $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ were 4−15 × 10^{-3} at room temperature in aqueous solution. Therefore, the observed decay rates can be regarded as the radiationless decay rates ($1/\tau_{obs} \approx k_{nr}$). The observed decay rates for $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ are listed in Table 1. Because of the large spin−orbit coupling of the Os(II) ion, transition to the ^{3}MLCT state from the ground state is partially allowed and the lifetime is very short compared with the ruthenium analogues. The oscillator strength of the transition from the ground state to the ^{3}MLCT was estimated as 2.2 × 10^{-3} and 1.5 × 10^{-3} for $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$, respectively. As shown in Table 1, the radiationless transition rate of the Os(II) complexes is accelerated specifically in H_2O.

Table 1. Observed Decay Rates of the ^{3}MLCT States of $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ in Water−Methanol Solutions at Various Temperatures

solvent	$k_{obs}/10^6$ s^{-1}					
	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
			$Os(bpy)_3^{2+}$			
H_2O	43.33	46.00	46.73	47.89		54.64
D_2O	23.00	24.14	24.76	26.10	26.82	27.33
23.5 mol % MeOH[a]	27.33	28.39	30.97	32.52	31.30	34.14
38.9 mol % MeOH[a]	23.37	25.41	25.41	27.07	28.12	28.12
68.8 mol % MeOH[a]	20.48	21.78	22.38	21.53	24.55	24.55
MeOH	20.48	20.89	21.00	21.67	22.13	22.64
22.6 mol % MeOD[b]	17.81	18.62	19.14	20.28	21.00	22.13
38.9 mol % MeOD[b]	16.79	17.66	19.14	20.48	20.79	20.08
68.5 mol % MeOD[b]	16.39	17.22	18.13	18.62	19.50	21.00
MeOD	17.07	17.51	17.66	18.29	18.62	19.50
			$Os(phen)_3^{2+}$			
H_2O	11.23	11.73	12.32	13.04	13.47	13.54
D_2O	5.66	5.93	6.15	6.37	6.61	6.82
20.6 mol % MeOH[a]	7.20	7.47	7.68	7.92	8.19	8.38
29.8 mol % MeOH[a]	6.49	6.80	6.87	7.24	7.42	7.79
68.6 mol % MeOH[a]	5.47	5.62	5.69	6.02	6.09	6.32
MeOH	5.08	5.19	5.26	5.51	5.60	5.62
18.2 mol % MeOD[b]	4.67	4.80	5.02	5.18	5.31	5.48
36.2 mol % MeOD[b]	4.38	4.55	4.70	4.86	5.05	5.14
60.3 mol % MeOD[b]	4.34	4.49	4.59	4.66	4.84	4.98
MeOD	4.57	4.63	4.63	4.71	4.76	4.86

[a] MeOH fraction of MeOH−H_2O mixed solvent. [b] MeOD fraction of MeOD−D_2O mixed solvent.

Solvent Dependence of the Radiationless Transition Rate in Mixed Solvents. Since the ISCP is predominant for these two Os(II) complexes as described above, the observed solvent effect for the Os(II) complexes is mainly caused in the ISCP from the ^{3}MLCT state.

Figure 1 shows the radiationless transition rates of the $Os(phen)_3^{2+}$ as a function of H_2O fraction in H_2O−D_2O mixture. The rate decreases linearly by the addition of D_2O. Figure 2 shows the radiationless transition rates of $Os(phen)_3^{2+}$ in the water−methanol mixed solvent plotted against the mole fraction of methanol at various temperatures. (The analogous figure for $Os(bpy)_3^{2+}$ is available in the Supporting Information as Figure S1.) In contrast to the observations made for H_2O−D_2O mixed solvents, the radiationless rates decreased nonlinearly with an increase in the alcohol mole fraction. Figure 3 shows the radiationless transition rate of $Os(phen)_3^{2+}$ in H_2O−dioxane

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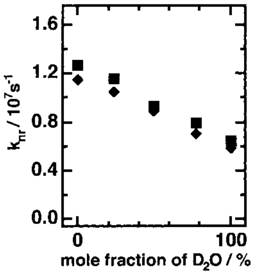

Figure 1. D_2O mole fraction dependence of the radiationless decay rate of $Os(phen)_3^{2+}$: ■, 25 °C; ◆, 13 °C.

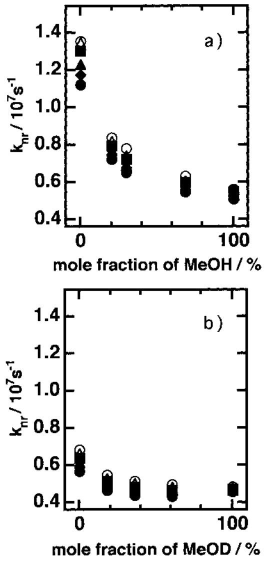

Figure 2. Alcohol mole fraction dependence of the radiationless decay rates for the ^{3}MLCT state of $Os(phen)_3^{2+}$ (a) in H_2O−MeOH solution; (b) in D_2O−MeOD solution: ○, 35 °C; △, 30 °C; ■, 25 °C; ▲, 20 °C; ◆, 15 °C; ●, 10 °C.

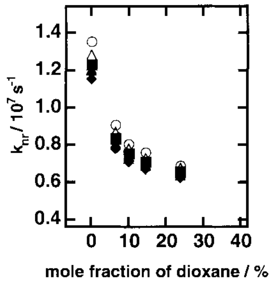

Figure 3. Dioxane mole fraction dependence of the radiationless transition from the ^{3}MLCT state of $Os(phen)_3^{2+}$: ○, 35 °C; △, 30 °C; ■, 25 °C; ▲, 20 °C; ◆, 15 °C.

mixed solvents. The radiationless rate also decreased nonlinearly; the decrease was rapid until 10 mol % dioxane and gradual in larger amounts of dioxane.

There are a number of works on the relationship between the energy of the emission peak and the lifetime of $Ru(bpy)_3^{2+}$ and of analogues.[18,19] For the Os(II) complexes in nonhydroxylic solvents, a correlation between the emission energies and the radiationless rates is also reported and is interpreted by energy gap law:[20] ln k_{nr} approximately varied linearly with the energy gap between the ^{3}MLCT state and the ground state. In contrast with this, the observed radiationless rates in H_2O are extremely large compared with those in D_2O despite the same emission energy of the Os(II) complex both in H_2O and in D_2O. Moreover, in water−dioxane mixtures, the k_{nr} value rapidly decreases with increasing solvent fraction between 0 and 24 mol % dioxane as shown in Figure 3, but nevertheless, the emission energy, E_{em}, was constant at these fractions. The mole fraction dependence of ln k_{nr} in the water−methanol mixed solvents also is not proportional to the value of E_{em} although E_{em} was shifted by changes of the mole fraction of methanol. These results show that there is no simple correlation between ln k_{nr} and E_{em} in the aqueous mixed solvents studied here.

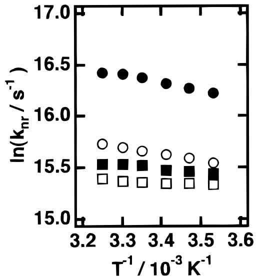

Figure 4. Temperature dependence of the radiationless decay rate of $Os(phen)_3^{2+}$ in water and methanol: ●, H_2O; ○, D_2O; ■, MeOH; □, MeOD.

As shown in Table 1, the value of k_{nr} in H_2O is especially large among solvents used here for both $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$. Moreover, an appreciable isotope effect was observed in water: the rates in H_2O were about twice as fast as those in D_2O, while deuteration of the hydroxy group caused only a slight (about 1.1 times) retardation of the rates in methanol. The characteristic dependence of k_{nr} on the fraction of water and the isotope effect on k_{nr} may originate from the participation of a specific interaction between the Os(II) complexes and water molecule(s) and of the OH vibration of the water molecule.

Temperature Dependence of the Radiationless Transition Rates. The radiationless transition rates of $Os(phen)_3^{2+}$ show a slight temperature dependence as depicted in Figure 4. For $Os(bpy)_3^{2+}$, k_{nr} is also dependent on temperature (as shown in Figure S2 of the Supporting Information). The rate constants are analyzed with a single-exponential function in the temperature region of the present work,

$$k_{nr} = A_{nr} \exp(-\Delta E_{nr}/RT) \tag{2}$$

where A_{nr} and ΔE_{nr} are the pre-exponential factor and the temperature factor for the radiationless transition, respectively. The fitting parameters, A_{nr} and ΔE_{nr}, in eq 2 for $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ are listed in Table 2.

Intramolecular nonradiative decay of the excited electronic states, e.g., ^{3}MLCT → the ground state, can be defined as rapid horizontal transitions from the excited to the ground electronic surfaces. Therefore, such an intramolecular process does not usually depend on temperature.[21] On the contrary, the observed values of k_{nr} clearly show the temperature dependence of the ISCP. The estimated values of ΔE_{nr} are in almost the same range between $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ complexes within experimental error as shown in Table 2.

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Table 2. Preexponential Factors, A_{nr}, and Temperature Factor, ΔE_{nr}, for the Intersystem Crossing Path to the Ground State Assuming Single-Exponential Decays of the Experimental Data

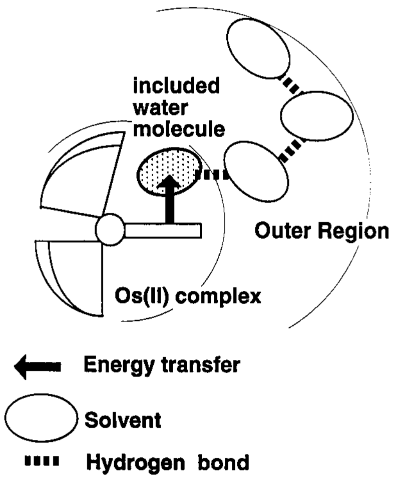
solvent	$A_{nr}/10^8\ s^{-1}$	ΔE_{nr}/kJ mol^{-1}
	$Os(bpy)_3^{2+}$	
H_2O	6.5 ± 1.5	6.3 ± 0.6
D_2O	2.3 ± 0.9	5.2 ± 1.0
23.5 mol % MeOH[a]	4.2 ± 1.6	6.2 ± 1.0
38.9 mol % MeOH[a]	2.6 ± 1.0	5.5 ± 1.0
68.8 mol % MeOH[a]	2.0 ± 0.7	5.1 ± 1.0
MeOH	0.80 ± 0.3	3.0 ± 1.0
22.6 mol % MeOD[b]	2.8 ± 1.1	6.3 ± 1.0
38.9 mol % MeOD[b]	2.6 ± 1.0	6.2 ± 1.0
68.5 mol % MeOD[b]	3.3 ± 1.3	6.9 ± 1.0
MeOD	1.1 ± 0.4	3.7 ± 1.0
	$Os(phen)_3^{2+}$	
H_2O	1.5 ± 0.5	6.0 ± 0.8
D_2O	0.65 ± 0.2	5.5 ± 0.8
20.6 mol % MeOH[a]	0.53 ± 0.2	4.5 ± 1.0
29.8 mol % MeOH[a]	0.64 ± 0.2	5.2 ± 1.0
68.6 mol % MeOH[a]	0.37 ± 0.1	4.3 ± 1.0
MeOH	0.23 ± 0.1	3.3 ± 1.0
18.2 mol % MeOD[b]	0.39 ± 0.2	4.8 ± 1.0
36.2 mol % MeOD[b]	0.37 ± 0.1	4.8 ± 1.0
60.3 mol % MeOD[b]	0.25 ± 0.1	3.9 ± 1.0
MeOD	0.10 ± 0.04	1.7 ± 1.0

[a] MeOH fraction of MeOH−H_2O mixed solvent. [b] MeOD fraction of MeOD−D_2O mixed solvent.

Alternative models are considered for temperature dependence. One is the existence of the fourth MLCT state, and another is intermolecular quenching.[21,22b] In the single crystal or the solid of the Os(II) complex at low temperature, a slight temperature dependence of k_{nr} was observed.[22] The temperature dependence was assigned to the thermal activation to the fourth MLCT state from the lower-lying ^{3}MLCT state, and the activation energy was considered to correspond to the energy gap between the fourth MLCT and the ^{3}MLCT states.[22] The energy of the MLCT states depends on the dielectric constant and the refractive index of the solvent in dielectric continuum theory.[23] If k_{nr} originates in the thermal activation to the fourth MLCT state, k_{nr} in H_2O should be the same as that in D_2O because of almost the same dielectric constant and refractive index between H_2O and D_2O. Thus, the intramolecular transition from the ^{3}MLCT to the fourth MLCT state cannot reproduce the large isotope effect of water on k_{nr}. Consequently, it seems reasonable to consider that the temperature dependence of k_{nr} is caused by "intermolecular" quenching by the solvent molecule.[21,24]

Mechanism of the Solvent Effect on the Radiationless Transition. A mechanism of charge transfer to solvent (CTTS) has been proposed for the solvent-dependent radiationless transition of the $Ru(bpy)_3^{2+}$ complex.[25] However, the CTTS model cannot explain the appreciable retardation of the radiationless transition by the deuteration of water beyond a factor of 2. On the other hand, the contribution of the OH vibration of water to the radiationless transition in $Ru(bpy)_3^{2+}$ is pointed out.[4,5,8] However, detailed discussion about the solvent effect on the ISCP (^{3}MLCT → the ground state) has not been carried out so far since the ISCP and the MCP compete with each other for the radiationless transition of the Ru(II) polypyridine complexes. In the present work, by using the Os(II) complexes, it was clarified that the rate of the ISCP was accelerated vigorously by the existence of H_2O. In order to explain the solvent effect on k_{nr} of the Os(II) complexes, specific quenching by the water molecule must be considered.

Scheme 1. Model of the Energy Transfer from the Os(II) Complex to the Included Water Molecule



In the case of collisional quenching by solvent molecules, k_{nr} depends on the reciprocal of the viscosity of solvent since the collision of solvent molecules is suppressed in viscous solvents. However, the nonlinear dependence of k_{nr} on solvent fraction in water−methanol and water−dioxane mixtures cannot be related to the reciprocal of the viscosity of the mixed solvents. Moreover, the isotope effect on the viscosity of H_2O and D_2O is at most 1.2, which does not agree with the experimental result, that the rate in H_2O is twice the rate in D_2O. Therefore, the solvent molecule as quencher must be beside the Os(II) complex in advance and we present a model for the specific energy transfer from the ^{3}MLCT state to the water molecule as shown in Scheme 1.

Recently, the existence of several hydrating water molecules, which penetrate between the bulky phen or bpy ligands, has been reported, determined by an EXAFS structural analysis of the Ru(II) complexes in aqueous solution.[26] From the results of the EXAFS measurements of the aqueous solution of both $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, the oxygen atom of one or two water molecules exists around 3.5−3.6 Å from the Ru^{2+}; those molecules are called "included water molecules". It was supposed that the included water molecules approached along the C_3 axis of the Ru(II) complex.[26] Considering the similarity of $Os(bpy)_3^{2+}$ and $Os(phen)_3^{2+}$ to the analogues of Ru(II), the included water molecules similarly penetrate the Os(II) complexes. These EXAFS results suggest the existence of a specific interaction between the π electrons of the ligands and the included water molecules. Actually, such an interaction is found between water and benzene and is ascribed to a hydrogen bond between the water proton and the π electron of benzene.[27] The included water molecule seems to participate in a likely type of specific interaction with the polypyridine ring. Therefore, it seems likely that energy transfer from the Os(II) complex to

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the included water molecules takes place. In this case, the OH vibration of the included water molecule is able to play a role as an energy acceptor because of the significant kinetic isotope effect in water ($k_{nr}(H_2O)/k_{nr}(D_2O) \approx 2$). Actually a very large isotope effect of water (>10) on radiationless transitions has been reported for rare earth ions which were coordinated by several water molecules.[28,29] For some rare earth ions such as Sm(III), Eu(III), and Tb(III), the energy gap between the lowest fluorescent level and the highest nonfluorescent level matches the energy of the overtones of the OH or OD vibration of water ($v = 2-5$ for the OH vibration). For the Os(II) complex, the included water molecule will play the same role as the coordinated water of the rare earth ions. The overtones of the vibrationally excited states of H_2O ($v = 3-4$) lie close to the ^{3}MLCT state of the Os(II) complex[29] and are expected to act as energy-accepting levels. For D_2O, the emission energy of the Os(II) complex corresponds to higher overtones of vibration of OD ($v = 5-6$).[30] Since there is a low probability of transition to the higher vibrational quanta, the radiationless rate becomes smaller in D_2O than that in H_2O.

In the case of the energy transfer via dipole−dipole interaction between the transition (^{3}MLCT → the ground state) of the Os(II) complex and that (the vibrational ground state → its excited state) of the included water, the relative orientational change of the included water molecule(s) to the Os(II) complex will vary the k_{nr} value. The orientation of the included water molecule, at least, may be suitable for the energy transfer in water.

In water−methanol mixtures, the observed k_{nr} did not linearly decrease with increasing mole fraction of methanol as depicted in Figure 2. Similar behavior was also found in water−dioxane mixtures. If methanol or dioxane molecules have a greater preference than water molecules to exist near the Os(II) complex, this nonlinear fraction dependence of k_{nr} may be understood because the number of included water molecules decreases faster than that expected from the bulk fraction of water. However, the preferential solvation of methanol or dioxane is excluded since the value of E_{em} in water−dioxane mixtures (0−24 mol % dioxane) is almost constant, and it seems that the included water molecule(s) are difficult to be replaced by dioxane molecule(s).

If one assumes dipole−dipole interaction for the energy transfer as noted above, the k_{nr} value depends on the relative orientational change of the included water molecule(s) to the Os(II) complex. On the basis of the results of the EXAFS measurements, 10 or 11 other water molecules in outer region of the complex were tightly hydrogen bonded to the adjacent water molecules and to the included ones as shown in Scheme 1.[26] Then the orientational change of the included water is caused by a structural change in the hydrogen-bond network in the outer region of the Os(II) complex. If an unfavorable orientation of the included water molecule(s) for the energy transfer arises from the structural change by the addition of methanol or dioxane to the aqueous solution,[31] this orientational change is also responsible for the nonlinear fraction dependence of the observed k_{nr} values.

Thus, the efficiency of the energy transfer is probably affected by the hydration structure as well as the average number of included water molecules per Os(II) complex. Therefore it is possible for the radiationless transition rate of the Os(II) complex studied here to be a specific probe for the microscopic environment in the region around the complex.

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Supporting Information Available: Plots of k_{nr} as a function of the mole fraction of MeOH and MeOD at different temperatures for the ^{3}MLCT state of $Os(bpy)_3^{2+}$ and plots of $\ln(k_{nr})$ as a function of T^{-1} in different solvents for $Os(bpy)_3^{2+}$ (2 pages). Ordering information is given on any current masthead page.

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