

5. S. K. Kim, T. H. Joo, S. W. Suh, and M. S. Kim, *J. Raman Spectrosc.*, **17**, 381 (1986).
6. R. P. Cooney, M. R. Mahoney, and M. W. Howard, *Chem. Phys. Lett.*, **76**, 448 (1980).
7. J. H. S. Green and D. J. Harrison, *Spectrochim. Acta*, **32A**, 1279 (1976).
8. G. Varsanyi(Ed.), *Vibrational Spectra of Benzene Derivatives*, Academic Press, New York, 1969.
9. R. K. Goel and M. L. Agarwal, *Spectrochim. Acta*, **38A**, 583 (1982).
10. M. Moskovits and D. P. Dillela, *J. Chem. Phys.*, **73**, 6068 (1980).
11. P. Avouris and J. E. Demuth, *J. Chem. Phys.*, **75**, 4783 (1981).
12. P. Gao and M. J. Weaver, *J. Phys. Chem.*, **89**, 5040 (1985).
13. C. M. Friend, J. Stein, and E. L. Muetterties, *J. Am. Chem. Soc.*, **103**, 767 (1981).
14. C. M. Friend, E. L. Muetterties, and J. Gland, *J. Phys. Chem.*, **85**, 3256 (1981).
15. K. Kishi and S. Ikeda, *Surf. Sci.*, **107**, 405 (1981).
16. B. A. Sexton and N. R. Avery, *Surf. Sci.*, **129**, 21 (1983).
17. R. M. Wexler and E. L. Muetterties, *J. Phys. Chem.*, **88**, 4037 (1984).
18. H. Nichols and R. M. Hexter, *J. Chem. Phys.*, **75**, 3126 (1981).
19. M. Moskovits, *J. Chem. Phys.*, **75**, 3126 (1981).
20. J. A. Creighton, *Surf. Sci.*, **124**, 209 (1983).
21. V. M. Hallmark and A. Campion, *J. Chem. Phys.*, **84**, 2942 (1986).
22. F. R. Dollish, W. G. Fateley, and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York, 1974.
23. Z. Rappoport(Ed.), *Chemistry of Cyano Group*, Wiley, New York, 1970.
24. C. G. Swain and L. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).
25. A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, **77**, 639 (1977).
26. E. R. Vorpagel, A. Streitwieser, Jr., and S. D. Alexandratos, *J. Am. Chem. Soc.*, **103**, 3777 (1981).

Precipitation, Resolubilization and Luminescent Properties of Tris(2,2'-diimine)Ruthenium(II) Complexes in Premicellar Anionic Surfactant Solutions

Joon Woo Park* and Sung Hee Kim

Department of Chemistry, Ewha Womans University, Seoul 120-750. Received June 24, 1988

Premicellar precipitation, resolubilization and luminescing behaviors of RuL_3^{2+} ($L = \text{bpy, phen, Me}_2\text{bpy}$) in aqueous alkylsulfate and sulfonate solutions were studied. Addition of the anionic surfactants to RuL_3^{2+} solutions caused initial precipitation which was redissolved by further addition of the surfactants. The apparent solubility products K_{sp} 's of the precipitates were evaluated assuming 1:2 salt formation. The values were smaller as the ligand is more hydrophobic and the length of hydrocarbon chain of the surfactant is longer. The K_{sp} values for $L = \text{bpy}$ were constant over wide surfactant concentration range. However, those for $L = \text{Me}_2\text{bpy}$ and also for phen, but to less extent, increased with the surfactant concentration. The resolubilization of 1:2 salts was followed by red-shift of emission band and extensive emission quenching above critical concentration of the surfactants. The critical concentration was lower for more hydrophobic surfactant. For $L = \text{Me}_2\text{bpy}$, the blue-shifted emission band with enhanced emission intensity was observed in intermediate surfactant concentration region. The high ionic strength of media prevented the precipitate formation, but facilitated the red-shift of the emission bands. The results support that the precipitate is dissolved by accretion of surfactant anions to the salts to form water-soluble surfactant-rich RuL_3 -surfactant anionic species. These species appeared to aggregate cooperatively to produce large clusters which exhibited the red-shifted emission.

Introduction

In recent years, the photochemical and photophysical behaviors of tris(2,2'-bipyridine)ruthenium(II), $Ru(\text{bpy})_3^{2+}$, and related complex cations have been a subject of intense study.¹ This is primarily due to the promise of a convenient solar energy conversion using the complex cations as a photosensitizer. To increase the energy conversion efficiency, anionic surfactant systems, especially sodium dodecylsulfate (SDS), were extensively employed.²⁻¹⁶ The large changes in the luminescent and photochemical properties of the photosensitizers in the SDS solutions were mainly attributed to the binding of the cations on the anionic micelle. Meanwhile it was noticed that the properties of $Ru(\text{bpy})_3^{2+}$ in the sub-

micellar concentration of SDS are considerably different from those observed in the absence of SDS and in SDS micellar solutions.^{3,6,9,10} When SDS is added to $Ru(\text{bpy})_3^{2+}$ solutions, precipitate is formed at initial stage and the emission band shifts to shorter wavelength region. Further addition of SDS redissolves the precipitate and the red-shift of the emission band is observed. The decay kinetics of the excited $Ru(\text{bpy})_3^{2+}$ in premicellar SDS solutions is much faster than that obtained in the absence of SDS or at higher SDS concentration. This was attributed to the triplet-triplet annihilation due to the formation of the $Ru(\text{bpy})_3^{2+}$ -rich clusters.^{2,6,10} The emission quenching of $Ru(\text{bpy})_3^{2+}$ by methylviologen⁹ and by cationic dyes⁸ was reported to be more efficient in premicellar region of SDS. Similarly, the enhanced energy transfer

in pre-micellar surfactant solutions was reported for dye-surfactant systems and the phenomena were also explained in terms of the formation of dye-rich pre-micellar aggregates.¹⁷

Despite of the apparent importance of pre-micellar interactions of $\text{Ru}(\text{bpy})_3^{2+}$ and other Ru(II) photosensitizers with anionic surfactants in relation to their potential application, little attention has been given to the factors governing the interactions. In this work, the influence of hydrophobicity of the ligands of the Ru(II) complexes and the surfactants on the precipitation and resolubilization of the complexes by anionic surfactants was investigated. The changes in the luminescent behaviors of Ru(II) complexes by the addition of the surfactants were correlated with the structures of the species of Ru(II) complex-surfactant associations.

Experimental

The ligands(L) of Ru(II) complexes used in this study are 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy). These were obtained from Aldrich. Perchlorate salts of RuL_3^{2+} were synthesized by the methods described in literatures.^{18,19} SDS(Fluka) was purified by recrystallization from ethanol after washing with ether. Sodium decylsulfate (SDeS) from Merck and other surfactants from Aldrich were used as received. Deionized distilled water was used. The concentrations of RuL_3^{2+} were determined spectrophotometrically using $\epsilon_{452} = 14600$ for $\text{L} = \text{bpy}$, $\epsilon_{447} = 19000$ for $\text{L} = \text{phen}$, and $\epsilon_{460} = 14300 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{L} = \text{Me}_2\text{bpy}$.²⁰

To study precipitation reactions between RuL_3^{2+} and anionic surfactants, solutions containing both RuL_3^{2+} and surfactants were centrifuged to remove the precipitates and the supernatants were withdrawn. This was repeated several times until no change in absorption spectra was observed by further centrifugation. Filtration was avoided as RuL_3^{2+} are adsorbed on the filter paper. The absorption spectra of the clear solutions were taken from a Beckman DU-8B UV-VIS spectrophotometer using 1 cm cells and the concentrations of the dissolved RuL_3^{2+} were calculated from the absorbance values and the molar absorptivity data.

Uncorrected luminescence spectra were recorded on a Hitachi 650-10S spectrofluorimeter at 25°C. Unless otherwise mentioned, the RuL_3^{2+} -containing surfactant solutions were centrifuged prior to take the spectra. The excitation wavelength was the wavelength of absorption maximum of the respective Ru(II) complex. The concentration of RuL_3^{2+} was kept below $1.0 \times 10^{-5} \text{ M}$ to avoid problems with self quenching.

Results and Discussion

Solubility Products of RuL_3^{2+} -Alkyl Sulfate Salts.

RuL_3^{2+} formed water-insoluble salts with alkyl sulfate anions (C_nOS^-) at low surfactant concentration. Removing the precipitates by centrifugation resulted in clear solutions. No noticeable difference in spectral position and shape between the absorption spectra of the clear solutions and those taken in the absence of surfactant or at high surfactant concentration was observed. This is in good agreement with a previous report.³ This implies that the water-soluble alkyl sulfate associated RuL_3^{2+} species (if any) exhibit the same absorption characteristics as the free RuL_3^{2+} does.

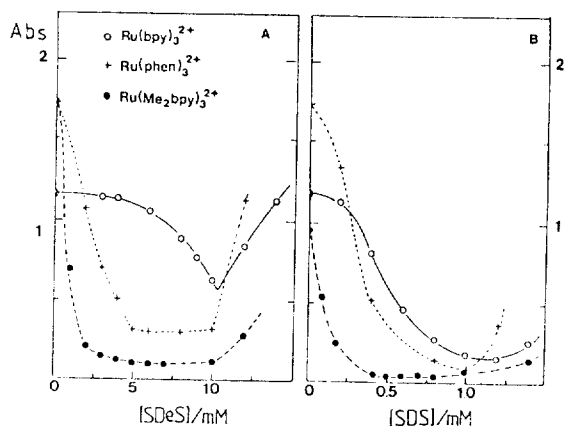
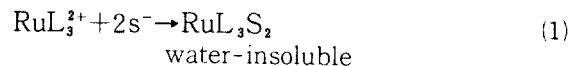


Figure 1. Absorbance values of the centrifuged Ru(II) complex solutions as functions of sodium decylsulfate (A) and sodium dodecylsulfate concentrations (B). The absorbance values were taken at their absorption maxima. The initial concentrations of the Ru(II) complexes were given in Table 1.

Figure 1 shows the absorbance values of the centrifuged solutions as functions of initial concentrations of SDS and SDeS. As the concentration of the anionic surfactant increases, the absorbance values decreased in low surfactant concentration region, and then it increased beyond certain concentration of the surfactant. Evidently the former reflects precipitation of RuL_3^{2+} and the latter indicates resolubilization of the precipitate by the surfactants. The precipitation reaction can be written as equation 1, where S^- stands for surfactant anion in general.



If one assumes that the absorbance in low surfactant concentration region, where the precipitates formed, arises only from the free RuL_3^{2+} , one can calculate the apparent solubility products of the precipitates defined by eq 1. Under the assumption, we calculated the concentration of free RuL_3^{2+} , $[\text{RuL}_3^{2+}]_f$, dividing the absorbance values of the centrifuged solutions by the molar absorptivities of the respective cations. The concentration of free surfactant, $[\text{S}]_f$, was calculated by $[\text{S}]_0 - 2([\text{RuL}_3^{2+}]_0 - [\text{RuL}_3^{2+}]_f)$, where $[\text{S}]_0$ and $[\text{RuL}_3^{2+}]_0$ are initial concentrations of surfactant and RuL_3^{2+} , respectively. The apparent solubility products defined as $(K_{\text{sp}})_c = [\text{RuL}_3^{2+}]_f[\text{S}]_f^2$ were evaluated and listed in Table 1. The apparent solubility products were corrected using the activity coefficients of the ions estimated from Debye-Hückel limiting law and the results are also included in Table 1.

It is obvious from Figure 1 and Table 1 that the Ru(II) complex with more hydrophobic ligand forms less soluble, i.e. smaller K_{sp} , precipitate with a surfactant anion. Also the more hydrophobic SDS forms the precipitate with given RuL_3^{2+} in much lower concentration region than SDeS does. These clearly indicate that the formation of water-insoluble RuL_3S_2 salts is favored by hydrophobic interaction. This is similar to the finding made in cationic dyes-SDS precipitation.²¹

The corrected solubility products for $\text{Ru}(\text{bpy})_3\text{S}_2$ were fairly constant over wide range of surfactant concentration. This is in good agreement with a previous report.³ On the contrary, the apparent K_{sp} values for $\text{Ru}(\text{phen})_3\text{S}_2$ and $\text{Ru}(\text{Me}_2\text{bpy})_3\text{S}_2$ salts were highly dependent on the surfactant

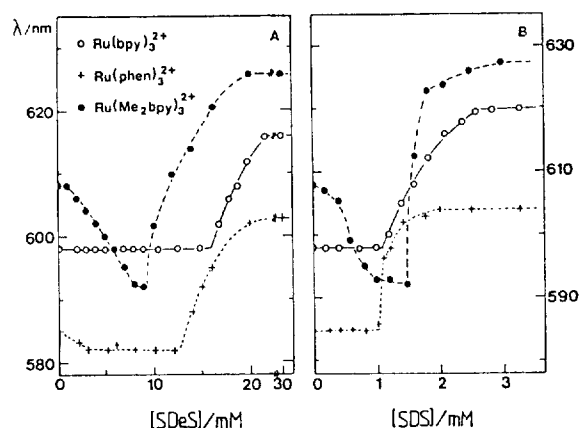
Table 1. Solubility Data of RuL₃²⁺ in SDS and SDeS Solutions

Ligands	[Ru(II)] ₀ × 10 ⁵ /M	[S] ₀ × 10 ³ /M	[Ru(II)] _f × 10 ⁵ /M	(K _{sp}) _c × 10 ¹¹	(K _{sp}) _a × 10 ¹¹
SDeS(C ₁₀ OS)					
bpy	7.9	8.0	6.05	383	203
		9.0	5.26	421	215
		10.0	4.32	426	210
Av. 210					
Phen	9.2	2.0	5.66	21.0	15.2
		4.0	2.66	39.7	25.3
		6.0	1.70	57.9	33.3
		8.0	1.60	98.5	52.2
Me ₂ bpy	12.1	1.0	5.15	3.8	3.0
		2.0	1.69	5.4	4.0
		3.0	1.23	9.5	6.5
		4.0	1.06	15.2	9.7
		5.0	0.86	19.6	11.0
SDS(C ₁₂ OS)					
bpy	8.0	0.40	5.15	0.605	0.516
		0.60	2.59	0.627	0.525
		0.80	1.29	0.573	0.470
		1.00	0.81	0.593	0.476
Av 0.497					
phen	9.0	0.20	7.06	0.182	0.158
		0.39	2.80	0.196	0.169
		0.78	0.79	0.299	0.245
		1.00	0.45	0.306	0.244
Me ₂ bpy	6.2	0.09	3.75	0.0098	0.0089
		0.18	1.77	0.0148	0.0133
		0.42	0.41	0.0382	0.0331
		0.50	0.31	0.0713	0.0603

#Ru(II) and S stand for RuL₃²⁺ and surfactant, respectively.
##. Subscripts o and f denote the initial and final concentrations of respective species. ### (K_{sp})_c is defined in terms of concentrations as [Ru(II)]_f[S]_f², while (K_{sp})_a is defined in terms of activities.

concentration. This was reproducible and too large to be attributed to the experimental error. The dependence of the K_{sp} values was much more pronounced for Ru(Me₂bpy)₃S₂ than for Ru(phen)₃S₂. Also it was greater with SDS than SDeS. The simple precipitation reaction defined by eq 1 cannot explain the behavior. For these complexes, the presence of water-soluble Ru(II) complex-bearing species other than the free RuL₃²⁺ is speculated even at low surfactant concentration. Discussion on this is made in the following sections.

Resolubilization of RuL₃S₂ Precipitates and Luminescence Properties. Unlike the absorption spectra, the luminescent spectra of RuL₃²⁺ solutions depend strongly on the concentration of the anionic surfactants.^{3,9,10,16} The emission spectra of the uncentrifuged turbid solutions were blue-shifted about 25 nm. However, the centrifuged Ru(bpy)₃²⁺ solutions of low surfactants concentration exhibited their emission maxima at the same wavelength with that of the surfactant free solutions. This is clear indication that the emission band observed at shorter wavelength region in the uncentrifuged solutions arise from the suspended Ru(bpy)₃S₂ particles.⁹ In case of Ru(Me₂bpy)₃²⁺, the emission spectra of the centrifuged solutions appeared still blue-shifted in the in-

**Figure 2.** Changes of the wavelength of emission maxima of the centrifuged RuL₃²⁺ solutions by the addition of sodium decylsulfate (A) and sodium dodecylsulfate (B).**Table 2. Critical Concentrations of Surfactants [S]_{es} for the Red Shift of Emission Bands in Water and in 0.1 M NaCl and the Maximum Magnitude of the Shift^a for RuL₃²⁺ in Anionic Surfactants Solutions at 25°C**

L	Surf. ^b	CMC ^c × 10 ³ /M	[S] _{es, water} × 10 ³ /M	[S] _{es, NaCl} × 10 ³ /M	Δλ _{max} /nm	ΔE _{em} /cm ⁻¹
bpy	C ₈ S	140	160	130	14	-380
	C ₁₀ S	41	38	19	16	-440
	C ₁₆ S ^e	0.83	0.14	0.053	22	-590
	C ₈ OS	120	120	—	14	-380
phen	C ₁₀ OS	29	16	9	18	-490
	C ₁₂ OS	8.3	1.1	0.8	22	-590
	C ₁₀ OS	29	13	7	17	-470
Me ₂ bpy ^d	C ₁₀ OS	8.3	1.0	0.45	19	-520
	C ₁₀ OS	29	9.0	5	18	-470
	C ₁₂ OS	8.3	1.5	0.45	22	-570

^aWith respect to values in the absence of surfactant. ^bC_nS and C_nOS denote the alkylsulfonate and alkylsulfate, respectively, with hydrocarbon chain CH₂(CH₂)_{n-1}. ^cCmc's in water measured by pyrene fluorescence probed method. ^dThe Ru(II) complex with this ligand showed large blue-shifted emission band in intermediated concentration region of surfactants (see, Figure 3). ^eMeasured at 50°C.

intermediate surfactant concentration range. Ru(phen)₃²⁺ in SDeS solution showed similar trend, but to much less extent. For all Ru(II) complexes examined, the resolubilized solutions at high surfactant concentration showed red-shifted emission. The variations of the emission maxima of the centrifuged solutions with SDS and SDeS concentrations are presented in Figure 2.

As can be seen from Figure 2, the red-shift of emission maxima was observed above the critical concentration of the surfactant. The magnitude of the emission shift leveled to constant values at high surfactant concentration. In Table 2, we summarized the critical concentrations of the surfactants for the emission shift and the maximum magnitude of the shift.

To correlate the luminescent properties of the RuL₃²⁺ in surfactant solutions to the chemical species present in the solutions, we have plotted the emission maxima (λ_{max}^B), absorbance values (Abs) and emission intensities (I_E) of the cen-

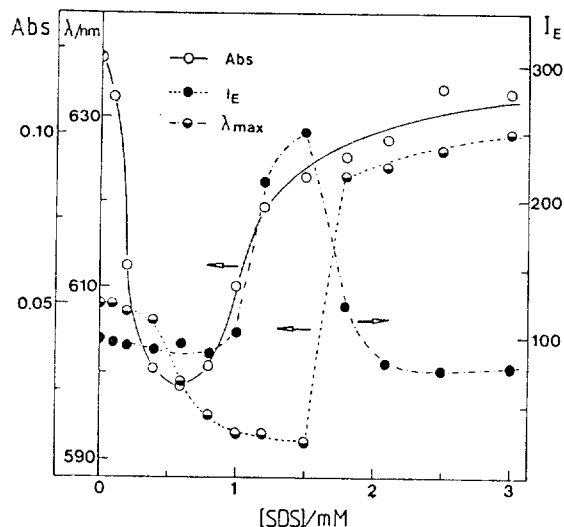


Figure 3. Variations of absorbance, emission intensity, and wavelength of emission maxima of the centrifuged $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ by the addition of sodium dodecylsulfate. The initial concentration of the complex was $8.6 \times 10^{-6}\text{M}$.

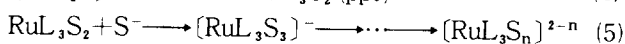
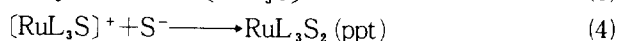
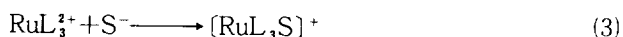
trifuged $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ solutions against [SDS] in Figure 3. The I_E values were expressed in terms of relative intensity per unit concentration of the dissolved lumiphore and corrected for the difference in the incident light intensity due to absorption.

$$I_E = (I_{\text{obsd}} / \text{Abs}) \times 10^{\text{Abs}} \quad (2)$$

Though the boundaries are not distinct, the overall SDS concentration range can be divided into three regions based on the dependencies of λ_{max}^E , Abs and I_E on [SDS]. The first region is $[\text{SDS}] < 0.4 \text{ mM}$ in which Abs decreases as [SDS] increases. This indicates that the more $\text{Ru}(\text{Me}_2\text{bpy})_3 \cdot (\text{C}_{12}\text{OS})_2$ precipitate is formed as [SDS] is higher. The luminescent properties of the centrifuged solutions are not significantly modified by the presence of the surfactant. The SDS concentration range of about 0.5-1.5 mM belongs to the second region. In this region the precipitate is redissolved by the addition of SDS, and the emission maxima shift to shorter wavelength region and the emission intensity is greatly enhanced. The third region is $[\text{SDS}] > 1.5 \text{ mM}$. The onset of marked emission quenching and red-shift of the emission band is observed at about 1.5 mM SDS.

$\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ in SDeS solutions also showed similar trend as can be noticed by comparing Figures 1 and 2. But the boundary between region 1 and 2 was less clear: the absorbance decreased up to 7 mM SDeS, while the blue-shifted enhanced emission was observed in 3-9 mM range. $\text{Ru}(\text{bpy})_3^{2+}$ in both SDeS and SDS and $\text{Ru}(\text{phen})_3^{2+}$ in SDS solutions did not show the enhanced blue-shifted emission band. However, in all cases, the resolubilization of the precipitates was detected at lower surfactant concentration than that at which the onset of the emission quenching and red shift of emission band was observed.

The association of surfactant anion with RuL_3^{2+} can be described as the following successive reactions.



The sum of reactions 3 and 4 is the precipitation reaction forming 1:2 salts (eq 1). Reaction 5 stands for successive accretion of the surfactant anions to form water-soluble surfactant-rich anions containing Ru(II) complex. These anions might aggregate with themselves or with S^- and possibly with RuL_3^{2+} , to produce large clusters.

Obviously, the reactions 3 and 4 are the major reactions in the lowest surfactant concentration region. The independency of the apparent K_{sp} of $\text{Ru}(\text{bpy})_3\text{S}_2$ on the surfactant concentration implies that the concentration of water soluble surfactant-associated $\text{Ru}(\text{bpy})_3^{2+}$ species is insignificant in the region. On the other hand, the increase of the K_{sp} for $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ as the surfactant concentration is increased can be taken as an evidence of the presence of the species. They would be $[\text{RuL}_3\text{S}]^+$ and $[\text{RuL}_3\text{S}_n]^{2-n}$ ($n > 2$). At this point we are not able to estimate the concentrations of these species. However, it seems clear that formation of the species in low surfactant concentration is favored by hydrophobic interaction.

The resolubilization of RuL_3S_2 salts manifested as absorbance increase in the region 2 is due to reaction 5. Thus, the major emitting species in the region are the anionic $[\text{RuL}_3\text{S}_n]^{2-n}$ ($n > 2$). The luminescent characteristics of the anions for $\text{L} = \text{bpy}$ and phen appeared to be the same as the free RuL_3^{2+} . The different emitting behavior of $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ in the region 2 from other RuL_3^{2+} complexes is quite interesting. The enhanced and blue-shifted emission band of $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ in the region 2 is reminiscent of that observed for the aforementioned $\text{Ru}(\text{bpy})_3\text{S}_2$ suspended solutions,⁹ $\text{Ru}(\text{bpy})_3^{2+}$ in poly(methacrylic acid) solutions^{18,22} and in rigid matrices.²³⁻²⁶ Delocalization of charge on reduced ligand by the restricted rotational mobility of the ligand was accounted for the observation in rigid media.^{25,26} If this is held, only $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ among Ru(II) complexes studied experiences the effect when it associates with more than two surfactant anions. The presence of methyl group in the ligand might be responsible for that.

The onset of quenching of RuL_3^{2+} emission and the red shift of the emission in the region 3 indicates formation of large clusters containing several Ru(II) complexes per cluster.^{2,6,10} Thus the major reaction in the region would be aggregation of $[\text{RuL}_3\text{S}_n]^{2-n}$ anions. The sharpness of the transition from region 2 to 3 evidenced by the emission shift in Figure 3 suggests that the aggregation is a cooperative process. This is similar to micellization of surfactant molecules. With the exception in octylsulfate and octylsulfonate solutions, this reaction is observed below the cmc's of the surfactants (Table 2).

We could not observe any drastic change in spectral properties of RuL_3^{2+} above the critical concentration of surfactants for the emission red shift. This leads to a conclusion that the RuL_3 -surfactant clusters do not undergo a major structural transition by further addition of surfactant. Therefore the structure of the clusters might be similar to that adopted at higher surfactant concentration, above cmc of the surfactant. The structure was suggested as normal micelle-like one in which Ru(II) complexes reside in the Stern layer of the micelle.¹⁶ In this situation, the structure of the surfactant rich $[\text{RuL}_3\text{S}_n]^{2-n}$ anions, which are present in the region 2 and show quite different spectral behaviors from the clusters for $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$, must be different from the normal micelle-like structure. The inverted micelle-like

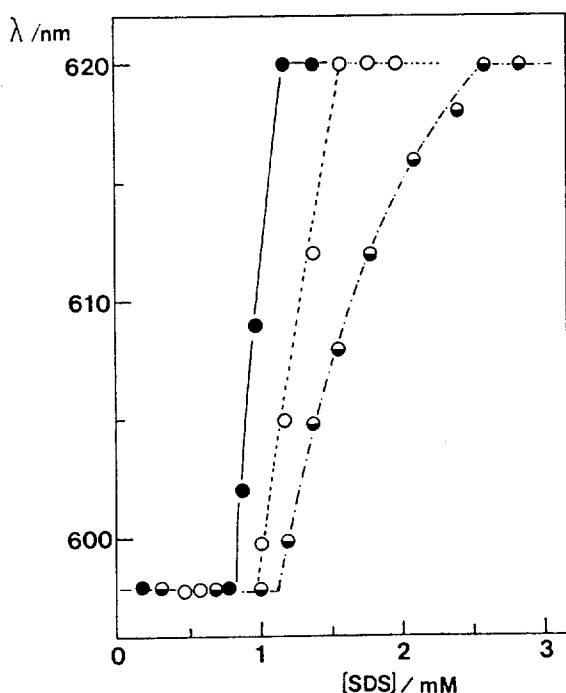


Figure 4. Variations of the wavelength of emission maxima of the centrifuged $\text{Ru}(\text{bpy})_3^{2+}$ solutions with concentration of sodium dodecylsulfate. The concentrations of NaCl in the solutions were 0 (●), 0.05 (○) and 0.10 M (●).

structure of which exterior is composed of hydrocarbon chain and 2,2'-diimine ligand can be suggested for it.²⁷ The close contact of hydrocarbon chain of surfactant with the ligands in the structure may cause the aforementioned restricted rotational mobility of ligand and thus the observed blue shift of emission band for $[\text{Ru}(\text{Me}_2\text{bpy})_3\text{S}_n]^{2-n}$ ($n > 2$).

The red-shift of emission band of RuL_3^{2+} in anionic surfactant solutions at room temperature was ascribed to the energy stabilization of thermally equilibrated emitting metal-to-ligand charge-transfer (MLCT) state, relative to the initially formed excited state.¹⁶ The energy is in the range of $380\text{--}600\text{ cm}^{-1}$, with respect to that in water (Table 2). For the given Ru(II) complex, the stabilization of the energy is slightly greater as the alkyl length of the surfactant is longer. This is parallel to the observation in alkyl alcohols^{2,16}, and suggests that the hydrophobic interaction also contributes to the stabilization of the emitting state.

Effects of Ionic Strength. As expected from the charges on the interacting species of RuL_3^{2+} -surfactant associations, ionic strength of medium exerts large effects on the overall processes. The precipitation of RuL_3S_2 was greatly inhibited by the addition of NaCl. In fact, we could not observe significant decrease in absorbance after centrifugation of $1 \times 10^{-5}\text{ M}$ Ru(II) complex solutions in all SDS concentration range in the presence of 0.1 M NaCl. This suggests that, though the hydrophobic interaction between RuL_3^{2+} and the surfactant anions facilitates the precipitation, the major driving force for the precipitation reaction is electrostatic attraction between the oppositely charged species.

In contrast to the precipitation, the red-shift of emission band was observed at lower surfactant concentration as the NaCl concentration is increased. This was shown in Figure 4 for $\text{Ru}(\text{bpy})_3^{2+}$ -SDS system. We have determined the critical

concentration of surfactants for red-shift of the emission band in 0.1 M NaCl and they are included in Table 2. Below the critical concentration of the surfactants, we could not observe any noticeable change in spectral properties of RuL_3^{2+} solutions: even the enhanced blue-shifted emission of $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$ solutions appeared in the absence of NaCl was not detected in the presence of 0.1 M NaCl. This indicates that the band is indeed from $[\text{Ru}(\text{Me}_2\text{bpy})_3\text{S}_n]^{2-n}$ ($n > 2$) anions, of which concentration is insignificant in the high ionic strength solutions due to self-association of the anions to form clusters.

Conclusions

The spectroscopic studies on RuL_3^{2+} ($\text{L} = \text{bpy}$, phen, Me_2bpy) in pre-micellar alkylsulfate and sulfonates solutions lead to the following conclusions.

(1) At low surfactant concentration, the Ru(II) complexes form 1:2 salt-like precipitates with surfactant anions (S^-). The apparent solubility product of the precipitate is constant over wide range of surfactant concentration for $\text{L} = \text{bpy}$. But they increase with $[\text{S}]$ for $\text{L} = \text{phen}$ and Me_2bpy . The latter is due to the presence of $[\text{RuL}_3\text{S}]^+$ ion pair, of which formation is favored by hydrophobic interaction.

(2) Accretion of S^- to the precipitate redissolves the precipitate to form $[\text{RuL}_3\text{S}_n]^{2-n}$ ($n > 2$) anions. The anions with $\text{L} = \text{Me}_2\text{bpy}$ show enhanced blue-shifted emission. However the anions with $\text{L} = \text{bpy}$ and phen exhibit the same spectral behaviors as the free RuL_3^{2+} .

(3) The $[\text{RuL}_3\text{S}_n]^{2-n}$ anions aggregate at critical concentration of surfactant to produce large clusters. The emission band of the clusters is red-shifted and the emission is greatly quenched with respect to that of the free RuL_3^{2+} . The critical concentration of surfactant for the formation of the clusters is lower and the shift of emission bands is greater as the surfactant is more hydrophobic.

(4) The structures of the $[\text{RuL}_3\text{S}_n]^{2-n}$ anions and clusters are best described as inverted micelle-like and normal micelle-like ones, respectively.

(5) Increased ionic strength of media prevents precipitation, but it facilitates the cluster formation.

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References

1. For reviews, see: (a) D. G. Whitten, *Acc. Chem. Res.*, **13**, 83 (1983); (b) J. H. Fendler, in "Membrane Mimetic Chemistry", John Wiley, N. Y. 1983, pp. 492-505; (c) E. A. Seddon and K. R. Seddon, in "The Chemistry of Ruthenium", Elsevier, N. Y. 1984, pp. 1173-1260; (d) K. Kalayanasundaram, in "Photochemistry in Microheterogeneous Systems", Academic Press, N. Y. 1987.
2. U. Lachish, M. Ottolenghi and J. Rabani, *J. Am. Chem. Soc.*, **99**, 8062 (1977).
3. D. Meisel, M. S. Matheson and J. Rabani, *J. Am. Chem. Soc.*, **100**, 117 (1978).
4. R. H. Schmehl and D. G. Whitten, *J. Am. Chem. Soc.*, **102**, 1938 (1980).
5. M. A. J. Rodgers and J. C. Becker, *J. Phys. Chem.*, **84**,

- 2762 (1980).
6. J. H. Baxendale and M. A. J. Rodgers, *Chem. Phys. Lett.*, **72**, 424 (1980).
 7. T. K. Foreman, W. M. Sobol and D. G. Whitten, *J. Am. Chem. Soc.*, **103**, 5333 (1981).
 8. K. Mandel and J. N. Demas, *Chem. Phys. Lett.*, **84**, 410 (1981).
 9. H. Sato, M. Kawasaki, K. Kasatani and T. Ban, *Chem. Lett. (Jpn.)*, 139 (1982).
 10. J. H. Baxendale and M. A. J. Rodgers, *J. Phys. Chem.*, **86**, 4906 (1982).
 11. T. Miyashita, T. Murakata and M. Matsuda, *J. Phys. Chem.*, **87**, 4529 (1983).
 12. B. L. Hauenstein, Jr., W. J. Dressick, S. L. Buell, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, **105**, 4251 (1983).
 13. W. J. Dressick, B. L. Hauenstein, Jr., J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, **23**, 1107 (1984).
 14. T. Miyashita, T. Murakata, Y. Yamaguchi and M. Matsuda, *J. Phys. Chem.*, **89**, 497 (1985).
 15. K. Takagi, K. Aoshima, Y. Sawaki and H. Iwamura, *J. Am. Chem. Soc.*, **107**, 47 (1985).
 16. W. J. Dressick, J. Cline, III, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, **108**, 7567 (1986).
 17. (a) Y. Kusumoto and H. Sato, *Chem. Phys. Lett.*, **68**, 13 (1979); (b) H. Sato, M. Kawasaki and K. Kasatani, *J. Photochem.*, **17**, 243 (1981); (c) H. Sato, Y. Kusumoto, N. Nakashima and K. Yoshihara, *Chem. Phys. Lett.*, **71**, 326 (1980); (d) H. Sato, M. Kawasaki and K. Kasatani, *J. Phys. Chem.*, **87**, 3579 (1983).
 18. J. W. Park and Y. H. Paik, *Bull. Korean Chem. Soc.*, **7**, 137 (1986).
 19. B. L. Hauenstein, Jr., K. Mandal, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, **23**, 1101 (1984).
 20. C-T. Lin, W. Böttcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6536 (1976).
 21. J. W. Park and H. Chung, *Bull. Korean Chem. Soc.*, **7**, 113 (1986).
 22. D. Y. Chu and J. K. Thomas, *J. Phys. Chem.*, **89**, 4065 (1985).
 23. J. Wheeler and J. K. Thomas, *J. Phys. Chem.*, **86**, 4540 (1982).
 24. W. Shi, S. Wolfgang, J. C. Streckas and H. D. Gafney, *J. Phys. Chem.*, **89**, 974 (1985).
 25. J. Ferguson, E. Krausz and M. Maedar, *J. Phys. Chem.*, **89**, 1852 (1985).
 26. J. Ferguson and E. Krausz, *Inorg. Chem.*, **25**, 3333 (1986).
 27. This structure was suggested for Ru(bpy)₃²⁺-dodecyl-sulfate clusters, not for the anions, by Baxendale and Rodgers.¹⁰

Selective Reduction of Oximes to N-Monosubstituted Hydroxylamines with Lithium Borohydride

Byung Tae Cho* and See Yearl Seong

Department of Chemistry, Hallym University, Chunchon, 200-010. Received July 1, 1988

Selective reduction of aldoximes and ketoximes with lithium borohydride in tetrahydrofuran was investigated. Thus, aldoximes and cyclic ketoximes such as hexanaloxime, heptanaloxime, cyclopentanone oxime and cyclohexanone oxime were reduced smoothly to the corresponding N-monosubstituted hydroxylamines at room temperature in 65-93% yield. The reduction of alicyclic ketoxime was very slow, requiring somewhat high reaction temperature (65 °C) for the complete reduction to give the hydroxylamines. The reduction of aromatic oximes such as benzaldoxime and acetophenone oxime was very sluggish, giving a mixture of the corresponding hydroxylamines and amines at 65 °C.

Introduction

Lithium borohydride is a mild reducing agent which reduces only aldehyde, ketone and acyl chloride.¹ Recently, much efforts have devoted to selective reduction of organic functional groups with this hydride,² since it is soluble in organic solvent(diethyl ether or tetrahydrofuran) and simply prepared from the reaction of sodium borohydride and lithium chloride.³

There are many reports for the reduction of oximes with several kind of metal hydrides.⁴⁻¹⁶ Of these reagents, only mild reducing agents such as borane,⁴⁻⁵ pyridine-borane⁸⁻⁹ and sodium cyanoborohydride¹⁰⁻¹² could accomplish the reduction of oximes **1** to give the corresponding N-monosubstituted hydroxylamines **3**. However, the reduction with borane required the restricted reaction condition to obtain



the desired hydroxylamines without over reduction. In the case of pyridine-borane, the reaction should be performed with excess reagent under strong acidic condition. On the other hand, cyanoborohydride could smoothly reduce oximes to the hydroxylamines, but the reduction of aldoximes is extremely pH-dependent.¹⁷ To overcome these difficulties, therefore, we decided to investigate the reduction of oximes with lithium borohydride in tetrahydrofuran.

Results and Discussion

Procedure for Approximate Rate and Stoichiometry