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# Surfactant Tris(2,2′-bipyridine)ruthenium(II) Derivatives in Aqueous Micellar Solutions. Absorption and Emission Spectroscopy and Luminescence Quenching

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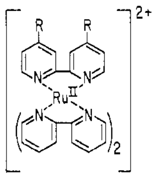
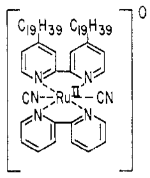
The surfactant ruthenium bipyridyl complexes $\{Ru^{II}(bpy)_2[bpy(COOC_{18}H_{37})_2]\}^{2+}$ (I), $\{Ru^{II}(bpy)_2[bpy(C_{19}H_{39})_2]\}^{2+}$ (II), $\{Ru^{II}(bpy)(CN)_2[bpy(C_{19}H_{39})_2]\}^0$ (III), and $\{Ru^{II}[bpy(COO^-)_2]_2[bpy(C_{19}H_{39})_2]\}^{2-}$ (IV) have been incorporated in anionic, cationic, and nonionic micellar solutions. The micellar environment perturbs the absorption and emission spectra of these complexes, relative to their solutions in organic solvents, in diverse ways; with the exception of the splitting of the absorption peak of I, these can be interpreted qualitatively on the basis of the polarity and charge of the micellar surface. A survey of luminescence quenching results for several of the systems by energy-transfer (e.g., $K_2Ni(CN)_4$) and electron-transfer (e.g., $CuCl_2$, methylviologen, *p*-anisidine) quenchers is presented. Suppression or enhancement of quenching due to Coulombic effects is noted; in addition, quenching of the luminescence of II and III in nonionic micelles by methylviologen is markedly suppressed. This may result from either the low effective dielectric constant at the micelle surface or a specific effect of the ethylene oxide chains of the surfactant in inhibiting approach by the charged quencher.

## Introduction

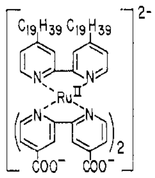
There is currently great interest in photochemistry in micellar systems because of the possibility of utilizing the phase boundary and charge effects which exist in such systems to control the progress of reactions.[1] At the same time, the photochemistry of the tris(2,2′-bipyridine)ruthenium(II) cation, $Ru(bpy)_3{}^{2+}$, has been the subject of intense study, both for its intrinsic interest and because of possible promise for solar energy conversion processes.[2] Several reports have now appeared concerned with the photochemistry of the water-soluble $Ru(bpy)_3{}^{2+}$ or its surfactant derivatives in micellar systems.[3-8] Recent work in this laboratory[9,10] has included the synthesis of several water-insoluble derivatives of $Ru(bpy)_3{}^{2+}$, I–IV. These surfactant compounds can be dispersed readily in aqueous solutions of a variety of anionic, cationic, and nonionic detergents. In this report, a survey of some photophysical and elementary photochemical processes which these solutions undergo is presented.



I, R = $-COOC_{18}H_{37}$
II, R = $-C_{19}H_{39}$



III



IV

## Experimental Section

Synthesis and characterization of the ruthenium complexes have been reported previously.[9,10] The supporting surfactants used were sodium dodecyl sulfate (SDS) (Fluka, puriss.), dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) (both Eastman, recrystallized from acetone), and Igepal CO-630 (nonylphenol–nonakis(ethyleneoxy)ethanol, GAF Corp.). Literature values of critical micelle concentration (cmc) and micelle aggregation numbers ($\bar{n}$) are (for solutions in 0.2 M NaCl) as follows: SDS, $9 \times 10^{-4}$ M, $\bar{n} = 100$;[11] DTAB, $5 \times 10^{-3}$ M, $\bar{n} = 70$;[12,13] CO-630, $6 \times 10^{-5}$ M, $\bar{n} = 225$.[14,15] These values have been used to estimate micelle concentrations; in all of the work reported [Ru] < [micelles]. Unless otherwise noted observations refer to $1.1 \times 10^{-2}$ M SDS, $1.2 \times 10^{-2}$ M DTAB, and $2.3 \times 10^{-2}$ M CO-630, all in 0.2 M NaCl, each of which corresponds to $10^{-4}$ M micelles. It was verified that these surfactant solutions showed no fluorescence, and their optical density (relative to water) was only that due to micellar scattering. Absorption spectra or surfactant solutions of the ruthenium complexes were in all cases measured against the corresponding chromophore-free surfactant solution. In the case of the diester complex I, $10^{-4}$ M HCl was also added to prevent hydrolysis.

**Table I.** Absorption and Emission Peak Wavelengths of Ruthenium Bipyridyl Complexes in Micellar and Nonmicellar Solutions

| | | $\lambda_p$, nm | |
|---|---|---|---|
| compd | medium | absorpn | emissn |
| $Ru(bpy)_3Cl_2$ | $H_2O$ | 457 | 605 |
| I | $CHCl_3$ | 485 | 665 |
| | 50% aqueous THF | 425, 490 | |
| | SDS | 415, 505 | 695 |
| | CO-630, DTAB | 420, 497 | 705 |
| II | $CHCl_3$ | 457 | 620 |
| | SDS | 452 | 625 |
| | CO-630, DTAB | 461 | 625 |
| III | $CHCl_3$ | 502 | 655 |
| | 0.1 M DTAC + 0.1 M NaCl, 0.4% $CHCl_3$ | 460 | 635 |
| | CO-630 | 460 | 650 |
| IV | 20% aqueous THF, alkaline | 466 | 618 |
| | acid | 484 | 660 |
| | SDS, pH 8 | 468 | 633 |
| | pH 1 | 478 | 662 |
| | DTAB, pH 11.5 | 465 | 615 |
| | pH 1 | 475 | 660 |
| | CO-630, pH 11.5 | 465 | 620 |
| | pH 1 | 475 | 650 |

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(2) For recent reviews, see: Sutin, N.; Creutz, C. *Adv. Chem. Ser.*, **1978**, *No. 168*, 1. Balzani, V.; Bolletta, F.; Scandola, F.; Ballardini, R. *Pure Appl. Chem.* **1979**, *51*, 299.
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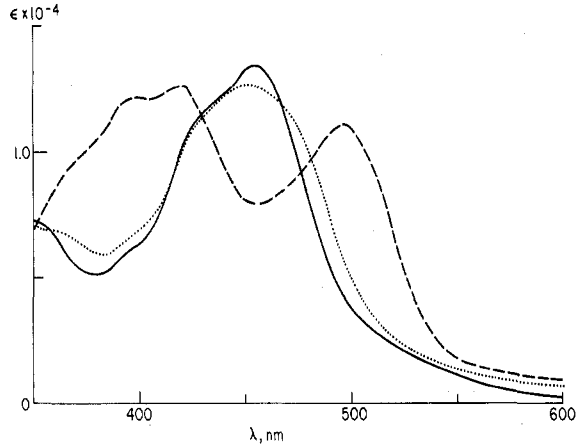

**Figure 1.** Typical absorption spectra of surfactant ruthenium bipyridyl complexes in micellar and nonmicellar solutions: (—) II in acetonitrile; (···) II in $1.1 \times 10^{-2}$ M SDS–0.2 M NaCl; (– – –) I in $2.3 \times 10^{-2}$ M Igepal CO-630–0.2 M NaCl + $10^{-4}$ M HCl.

In most cases, the ruthenium complexes dissolved readily in the surfactant solutions with agitation at room temperature. This procedure was not effective, however, for III in DTAB, DTAC, or CO-630; satisfactory solutions were obtained by adding a concentrated solution of III in chloroform to the DTAC solution and by adding neat CO-630 to the dry III and then diluting with 0.2 M NaCl.

All measurements were performed at room temperature in the same manner as previously described[16] except that no attempt was made to maintain constant ionic strength. Solutions were not deaerated, and emission spectra were not corrected for instrument sensitivity.[17] In measurements involving quenchers which were not colorless, the apparent emission intensities were corrected for quencher absorption by using measured optical densities of the solutions and the equation given by Demas and Adamson.[18]

Light scattering at a right angle could be observed conveniently in the fluorimeter; the 578-nm Hg line, at which wavelength all of the quencher-free solutions are transparent, was used. Since the solutions were not filtered, large transients presumably due to dust particles were frequently observed, and no attempt was made to make these observations quantitative.

## Results

**Absorption and Emission Spectra and Lifetimes.** Figure 1 depicts visible absorption spectra typical of the range of effects observed. The emission spectra at room temperature of all the micellar solutions examined are broad and featureless, resembling those of ruthenium polypyridyl complexes in nonmicellar solutions. The observed absorption and emission peak wavelengths are collected in Table I. Optical densities at the absorption peaks were generally 10–20% less than those observed in organic solvents, concomitant with the broader peaks in the micellar solutions. No changes were observed after storage of these solutions (in the dark) for periods of up to several weeks. In the case of II, no change in absorption and emission spectra was observed on varying surfactant concentration ([SDS] = $(1.1\text{–}7) \times 10^{-2}$ M; [DTAB] = $(1.2\text{–}8) \times 10^{-2}$ M; [CO-630] = $2.3 \times 10^{-2}$–0.2 M; these concentrations are all above the cmc).

Emission lifetimes of II were 0.50 μs in SDS, 0.43 μs in DTAB, and 0.31 μs in 9:1 $H_2O$–$CH_3CN$; the decays were strictly exponential.

The absorption and emission spectra of the nonsurfactant analogue of III, $Ru(bpy)_2(CN)_2$, were also recorded in some nonmicellar solutions. The absorption peak shifted from 430 nm in pure water to 456 nm in 50% dioxane–water; for intermediate mixtures, the peak wavelength varied linearly with the dielectric constant. The emission peak was at 608 nm in water and 632 nm in 50% dioxane–water. In polyethylene glycol 400 (J. T. Baker), the absorption maximum was at 482 nm and the emission peak at 650 nm. In chloroform (for which the absorption peak was found at 500 nm by Klassen[19]), the emission maximum was at 645 nm.

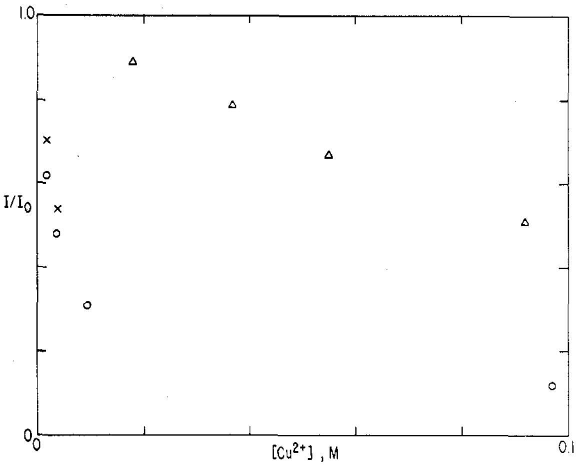

**Figure 2.** Quenching of luminescence of II ($1 \times 10^{-5}$ M) by $CuCl_2$ in micellar solutions: intensity (⊙) and lifetime (×) quenching in $1.1 \times 10^{-2}$ M SDS–0.2 M NaCl; intensity quenching (△) in $1.2 \times 10^{-2}$ M DTAB–0.2 M NaCl.

**Light Scattering.** As noted, no attempt at quantitative analysis of light-scattering measurements on these (unfiltered) solutions will be made. Some qualitative conclusions can be drawn, however. Incorporation of the ruthenium complexes did increase scattering moderately (up to approximately twofold) from the SDS and DTAB micellar solutions; scattering from CO-630 (whose larger micelles produce a much higher turbidity) was only very slightly increased. Larger effects were observed, however, with certain of the charged quenchers. Methylviologen additions to SDS solutions, for example, led to increases of scattered intensity up to severalfold. (At sufficiently high concentrations, the salt of methylviologen and dodecyl sulfate precipitates; thus a solution 0.1 M in SDS and 0.05 M in methylviologen yields a precipitate when cooled to ~5 °C, which redissolves on warming to room temperature.) Increased scattering was also observed in solutions containing 9-methylanthracene.

**Quenching by 9-Methylanthracene.** The luminescence quenching of DTAC and DTAB solutions of II by 9-methylanthracene, as a function of both quencher and surfactant concentration, was examined. While the results were qualitatively consistent with the observations of Turro and Yekta[20] —i.e., at constant [Q], the extent of quenching increased sharply as the concentration of surfactant was reduced toward the critical micelle concentration—quantitatively reproducible data were not obtained. Particularly at lower surfactant concentrations, the extent of quenching decreased with time, suggesting that this quencher aggregates in some way and does not remain uniformly dispersed in these micellar solutions.

**Quenching by Other Substances.** A variety of substances have been shown to function as quenchers of the excited state of ruthenium polypyridyl complexes by either energy-transfer or electron-transfer reactions,[2] and several of these were tested in micellar solutions. No quenching of emission intensity could

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(16) Gaines, G. L., Jr. *J. Phys. Chem.* **1979**, *83*, 3088.

(17) While emission spectra included in our previous publications[9,10] had been corrected for instrument sensitivity, we have subsequently discovered inadequacies in the calibration procedure used. Accordingly, while qualitative comparisons remain valid, exact quantitative analysis of peak positions or relative intensities is unwarranted.

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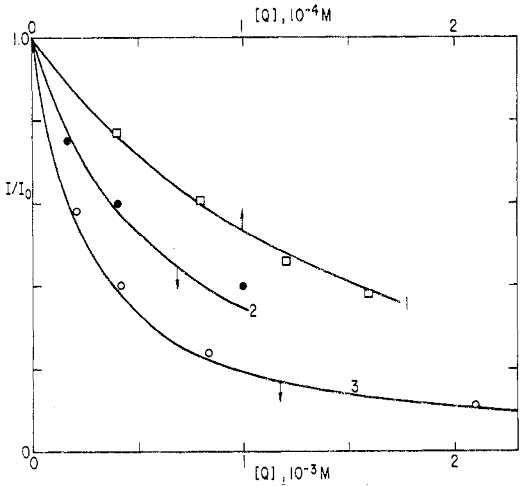

**Figure 3.** Quenching of luminescence of II in DTAB micelles by $K_2Ni(CN)_4$ (□) and *p*-anisidine (●) and in CO-630 micelles by $K_2Ni(CN)_4$ (○). Lines are calculated by eq 1, with $K$ = 2.0 (1), 0.2 (2) and 0.45 (3), by assuming [micelles] = $10^{-4}$ M in each case. [DTAB] = $1.2 \times 10^{-2}$ M; [CO-630] = $2.3 \times 10^{-2}$ M; [II] = $1 \times 10^{-5}$ M and 0.2 M NaCl in each case.

be detected in the following systems: II in DTAB with methylviologen ($[Q]_{max} = 10^{-2}$ M), II in SDS or DTAB with triethanolamine ($[Q]_{max} = 1.5 \times 10^{-2}$ M) or triethylamine ($[Q]_{max}$ = 0.14 M). With both II and III in CO-630, very slight quenching was obtained with methylviologen; for the former, a 10% decrease in emission was observed with $[MV^{2+}] = 2.4 \times 10^{-2}$ M, while the emission of the latter was reduced 7% at $[MV^{2+}] = 1.8 \times 10^{-2}$ M. Substantial quenching was obtained with several other substances. The results are summarized in Figures 2–4. (In the limited number of lifetime measurements with added quenchers, the decay was always observed to be exponential over ~2 lifetimes; no evidence for more than a single decay time was observed.)

## Discussion

**Effects of the Micellar Environment on Absorption and Emission.** The photophysical properties of each of the complexes I–IV are altered in somewhat different ways by the micellar environment. The smallest effects pertain to the complex with the least perturbation of ligand energetic symmetry, II. Analogously to the nonsurfactant complexes $Ru(bpy)_3^{2+}$ or $Ru(bpy)_2(bpy(CH_3)_2)^{2+}$, which exhibit only small spectral shifts in different solvent environments, the absorption and emission of II are only slightly red-shifted (as compared to its chloroform solution or to $Ru(bpy)_2(bpy(CH_3)_2)^{2+}$ in $H_2O$, which has the same peak positions) when it is incorporated in either nonionic or cationic micelles. In the anionic micelles of SDS, a small blue shift of the absorption spectrum is observed, while the emission remains slightly red-shifted. This result differs from the observations on $Ru(bpy)_3^{2+}$ in SDS micelles by Meisel et al.,[4] who found no shift in absorption and a larger (~20 nm) red shift of the emission peak. They interpreted this as resulting from the effect of the surfactant hydrocarbon chains on the $Ru(bpy)_3^{2+}$; in the present case, it must be noted that the hydrocarbon chains of the surfactant chromophore ($C_{19}$) are substantially longer than those of the supporting micelles ($C_{12}$). It may be that in our system, the chromophore resides in a more aqueous environment than in theirs; the blue shift in absorption is then to be ascribed to a Coulombic interaction.

The behavior of complex III parallels that of its nonsurfactant analogue, *cis*-$Ru(bpy)_2(CN)_2$,[19,21] which exhibits substantial shifts in both absorption and emission wavelengths with changes in solvent polarity. While the complexity of solvent polarity effects[22] precludes a detailed analysis, some qualitative comparisons are possible. Fernandez and Fromherz,[23] on the basis of titration data on indicator dyes incorporated in micelles, have concluded that the effective dielectric constant at the surface of nonionic micelles of the alkylphenoxy–ethylenoxy type, as well as charged micelles, is about 32. On the basis of present results with $Ru(bpy)_2(CN)_2$ in dioxane–water mixtures, a similar value would account for the absorption peak position of III in nonionic and cationic micelles. It also would appear reasonably consistent with the observed emission peak positions in both SDS and DTAC solutions (remembering that the latter may be slightly affected by the presence of a small amount of chloroform). The perturbation of the luminescent state in CO-630, on the other hand, appears to be different; the emission peak at 640 nm, however, is the same as that observed in nonaqueous polyethylene glycol, suggesting that in this case the luminescence is more affected by the specific environment of the polyethylene oxide chains. As for II, the blue shift of the absorption peak in SDS micelles may reflect a Coulombic interaction.

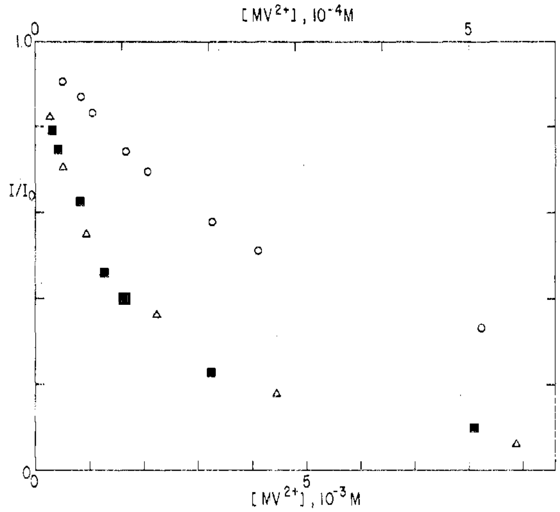

**Figure 4.** Luminescence quenching by methylviologen, $MV^{2+}$, in sodium dodecyl sulfate solutions. Points referred to concentration scale at top: II ($1 \times 10^{-5}$ M) (⊙) and III ($1 \times 10^{-5}$ M) (△) in $1.1 \times 10^{-2}$ M SDS–0.2 M NaCl. Points referred to scale at bottom: II ($5 \times 10^{-6}$ M) in $3.5 \times 10^{-2}$ M SDS–0.3 M NaCl (■).

The dioctadecyl ester, I, shows the greatest differences in spectra in micellar vs. organic solvent media of the complexes studied. The change from a broad absorption peak with a shoulder on the short wavelength side observed in chloroform or acetonitrile,[9] for example, to a spectrum with two well-resolved peaks, the one at longer wavelength being of lower intensity (Figure 1), is striking. The 30–40-nm red shift of the emission peak is also the largest observed. The splitting of the absorption peaks of this compound (as well as the corresponding diethyl ester in water) has been observed previously in monolayers and mixed aqueous solvents.[9,24] In view of the pronounced asymmetry introduced by the 4,4′ carboxy substituents, it would be tempting to rationalize this behavior as resulting from two separate charge-transfer transitions involving the dissimilar ligands. However, there is no evidence of splitting in the emission bands (the bands are of similar

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(22) For a review, see: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. A recent paper which indicates these complexities well is: Kamlet, M. J.; Kayser, E. G.; Jones, M. E.; Abboud, J. L.; Eastes, J. W.; Taft, R. W. *J. Phys. Chem.* **1978**, *82*, 2477.

(23) Fernandez, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 1755.

(24) Valenty, S. J.; Behnken, P. E. *Anal. Chem.* **1978**, *50*, 834.

breadth in all media which have been examined). It should also be noted that Crosby and Elfring[25] concluded that in mixed-ligand Ru(bpy)(phen) complexes, the properties of the excited state were of an average nature and did not reflect separable charge transfers involving the dissimilar ligands; the present case, of course, represents a much more extreme anisotropy of the ligand sphere. It would appear that more detailed photophysical studies will be required to permit interpretation of the spectral changes observed here.

In the case of the tetracarboxy complex IV, the predominant spectral shifts are those associated with protonation of the carboxyl groups, which are analogous to those observed with dicarboxy complexes.[9,24,26] There is no tendency for any of the absorption spectra observed with IV to split into separate peaks. The micellar environment seems to have little effect on the spectroscopic properties of this complex as compared with a medium of comparably low dielectric constant, 20% aqueous THF; only the emission of the ionized form in SDS at pH 8 exhibits any substantial shift. This may perhaps again be ascribed to a Coulombic effect, since the ground-state energy of the complex (which bears a 2− charge at this pH) may be raised slightly in the negative micelles.

**Light Scattering as an Indicator of Changes in Micellar Structure.** Although quantitative utility will depend on more elaborate experimental procedures to eliminate transient artifacts, the present limited observations do show that light scattering at wavelengths where the solutions are transparent can be used to detect changes in micellar structure or size. In particular, they give warning that the addition of quenchers—especially those which are incorporated into or can be bound by the micelles—may produce substantial alterations. In further studies, it will be essential to quantify these changes to permit detailed analysis of the luminescence quenching.

**Emission Quenching for the Measurement of Micelle Parameters.** Turro and Yekta[20] suggested that both the critical micelle concentration and the micelle aggregation number could be estimated from data on the quenching of a micelle-bound probe by a quencher which is also localized in the micelles.[27] The simplicity and versatility of this method makes it attractive. In principle, it is less subject to the uncertainties inherent in other "additive" methods for cmc measurement[14] because it effectively counts the number of micelles which do *not* contain quencher molecules, and the concentration of luminescent probe may be kept very small. As a probe, they used $Ru(bpy)_3^{2+}$, which is bound to SDS micelles but is not expected to be useful with cationic or nonionic micelles. The surfactant complexes should permit the extension of the technique to such systems. The present results imply, however, that other quenchers than the 9-methylanthracene which they used will be required to generalize the applicability of this method.

**Electron- and Energy-Transfer Quenching.** The fact that micelle charge can control the effectiveness of quenching by ionized species was noted by Meisel et al.,[4] who found >200-fold reduction of the efficiency of quenching of $Ru(bpy)_3^*$ by $K_3Fe(CN)_6$ in the presence of SDS. Two additional examples of electrostatic repulsion reducing electron-transfer quenching are noted here. The emission of II in DTAB is not quenched at all by methylviologen up to $[Q] = 10^{-2}$ M, whereas the dimethyl analogue of II had its luminescence reduced by 75% by this quencher at $10^{-2}$ M in 0.2 M aqueous NaCl.[16] In the case of $Cu^{2+}$ quenching of II* in DTAB, there is also a large reduction relative to nonmicellar solutions; according to the results of Hoselton et al.[30] in aqueous solutions, $Cu^{2+}$ at $1.8 \times 10^{-2}$ M would reduce the luminescence of a variety of ruthenium polypyridyl complexes by 38–93%, while in our system the decrease is only ~10% (Figure 2). (It should be noted, too, that in this case the corrections for trivial absorption by the quencher are large, so that the values reported are somewhat uncertain; no quenching could be detected at lower $[Cu^{2+}]$.)

More surprising is the large inhibition of quenching by methylviologen observed in nonionic micelles containing either II (10% quenched at $[MV^{2+}] = 2.4 \times 10^{-2}$ M) or III (7% quenched at $[MV^{2+}] = 1.8 \times 10^{-2}$ M); in the latter case, of course, the complex is uncharged, so the micelles should bear no electrostatic charge. Either the low dielectric constant or the specific nature of the ethylene oxide chains at the micellar surface, as already suggested, may effectively prevent the approach of the charged quencher to the excited complex.

Quenching by $Ni(CN)_4^{2-}$ is much less affected by the micelle environment; while directly comparable data in nonmicellar media are not available, Demas and Addington[31] observed ~70% decrease in the luminescence of $Ru(bpy)_3^{2+}$ on addition of $1.5 \times 10^{-4}$ M $K_2Ni(CN)_4$, which may be compared with ~60% decreases at $4.2 \times 10^{-4}$ M $K_2Ni(CN)_4$ for II in CO-630 micelles or at $1.6 \times 10^{-4}$ M $K_2Ni(CN)_4$ for II in DTAB micelles. The same workers concluded that quenching by $Ni(CN)_4^{2-}$ is via energy transfer; this may provide the rationale for these observations, since this mechanism may not demand the close approach required for electron-transfer quenching.

The possibility of electron-transfer quenching by neutral amines is of some interest because many of these compounds have been shown to quench ruthenium polypyridyl complexes reductively;[32] under certain circumstances, this process has been found to be nearly irreversible.[33-35] If such a reaction occurred with a ruthenium complex bound in a positively charged micelle, electrostatic repulsion of the oxidized quencher cation might also inhibit back-reaction. The present results do not comment on this point—no permanent spectral changes were observed nor would they be expected in aerated solutions. The quenching (or lack of it) which was observed, however, parallels the behavior of the amines examined with other ruthenium complexes in homogeneous solution. At concentrations similar to those used with II in SDS or DTAB solutions, $Ru(bpy)_3^*$ is not significantly quenched by triethylamine (in acetonitrile)[34] or by triethanolamine (in water).[36] On the other hand, *p*-anisidine, which causes a 60% reduction in the emission of II in DTAB micelles at the $10^{-3}$ M level, reduces the emission of $Ru(bpy)_3^{2+}$ in acetonitrile by ~35% at this concentration.[32]

**Concentration Dependence.** Henglein and Scheerer[28] have considered the concentration dependence of quenching in micellar systems. Their analysis leads to eq 1 where [Q] and [M] are the concentrations of quencher and micelles, re-

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(25) Crosby, G. A.; Elfring, W. H., Jr. *J. Phys. Chem.* **1976**, *80*, 2206.
(26) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187.
(27) The same method for estimating micelle size and critical concentration was also suggested independently by Henglein and Scheerer.[28] Infelta and Grätzel[29] have pointed out, however, that the use of Poisson statistics on which the method is based implies that interactions between quencher molecules in the same micelle must not be such as to perturb their rate of entry or exit.
(28) Henglein, A.; Scheerer, R. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1107.
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(34) DeLaive, P. J.; Lee, J. T.; Abruña, H.; Sprintschnik, H. W.; Meyer, T. J.; Whitten, D. G. *Adv. Chem. Ser.* **1978**, *No. 168*, 28.
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$$\frac{I}{I_0} = e^{-[Q]/[M]} \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{[Q]}{[M]} \right)^m \frac{1}{1 + Km} \qquad (1)$$

spectively, and $K$ is the ratio of the rate constant for quenching in micelles occupied by a single quencher molecule to the rate constant for light emission in the absence of quencher. In a few of the systems examined here, eq 1 can be used to fit the data (cf. Figure 3). Especially in the case of quenching by $Ni(CN)_4^{2-}$, good fits are obtained with $K = 2.0$ in DTAB and 0.45 in CO-630. It may be that this model, which assumes that the mass action law can be applied to micelles containing more than one quencher molecule, is most appropriate when quenching is by energy transfer. The lower value of $K$ for the larger nonionic surfactant micelles also seems reasonable on this basis.

As is apparent from Figure 3, the fit is less satisfactory for *p*-anisidine, although semiquantitative agreement is obtained. The other results reported do not exhibit conformity to eq 1; in view of our light scattering observations, this may result from changes in micelle size, which would invalidate the assumptions of the model.

In a study reported after the work described here was completed,[37] more extensive measurements of the quenching of luminescence of the octadecyl analogue of II by methylviologen in SDS and cetyltrimethylammonium micelles have been carried out. As found here, quenching was strongly inhibited in the positively charged micelles and enhanced in SDS. On the basis of their emission lifetime measurements (which showed only single logarithmic decays and lifetime quenching paralleling intensity quenching), Schmehl and Whitten concluded that quenching in the SDS micellar solutions is dynamic, with the residence time of the bound methylviologen cations on the micelles being short compared to the lifetime of the ruthenium complex excited state. This conclusion, however, is contrary to that reached by Rodgers et al.,[38] who interpreted their results on the reaction of hydrated electrons with methylviologen in SDS solutions as indicating irreversible binding of the viologen cations to the micelles. It would appear that further study is needed before a definitive model for methylviologen quenching in anionic micelles can be proposed.

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# Photosensitization of Oxygen-Bridged Dicobalt(III) Cations by the Tris(2,2′-bipyridine)ruthenium(II) Excited State. Luminescence Quenching and Product Quantum Yields

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Mechanisms of quenching of the excited state of $Ru(bpy)_3^{2+}$ by superoxo-bridged dinuclear cobalt(III) complexes are investigated by using luminescence quenching studies and by product quantum yield analysis. Bimolecular quenching constants are of the order of $10^9$ $M^{-1}$ $s^{-1}$, which is somewhat higher than the value expected on formal charge basis. Formation of $Ru(bpy)_3^{3+}$ and the cobaltous ion as products of photosensitization although in low yields is explained to occur in an energy-transfer pathway. The energy-transfer pathway accounts for about 10% of the quenching events whereas the excited-state electron-transfer process accounts for 90% of the quenching. The dark redox reaction which follows the energy-transfer pathway leads to the products formed in steady photolysis studies.

The role of dioxygen species in redox reactions has been of interest for a long time as important reactions in chemical and biological systems are known to involve the superoxo and peroxo species.[1] Both the superoxo and the peroxo radicals are unstable in solution, offering limited opportunities to study the properties of these systems either by using pulse radiolysis methods or indirect means. The stability of dioxygen species increases when coordinated to metal ions. The dioxygen complexes of cobalt(III) are known as model systems for biological oxygen carriers.[2] In these complexes the oxygen bridges exist either in superoxo or in peroxo forms as evidenced by EPR and X-ray crystallographic measurements.[3,4] The oxidation state of the metal center is known to be trivalent, and the oxygen bridge could be in the peroxo form ($O_2^{2-}$) or in the superoxo form ($O_2^-$). Sykes and co-workers among others[5] have investigated the redox reactions of the peroxo- and superoxo-bridged cobalt(III) dimers with one-electron reducing agents. Excited-state electron-transfer reactions of the superoxo-bridged complexes with the excited state of

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