$$\frac{I}{I_0} = e^{-[Q]/[M]} \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{[Q]}{[M]} \right)^m \frac{1}{1 + Km} \qquad (1)$$

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.

Registry No. I, 59520-37-5; II, 70281-14-0; III, 70281-17-3; IV, 70288-41-4.

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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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Table I. Direct-Photolysis Quantum Yields[a]

complex	$\phi(Co^{II})$	complex	$\phi(Co^{II})$
$[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+}$	0.005[b]	$[(bpy)_2Co(\mu\text{-}NH_2,O_2)Co(bpy)_3]^{4+}$	0.017
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$	0.070	$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2]^{4+}$	0.002
$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$	0.002		

[a] [HCl] = 1.0 M; irradiation wavelength = 450 nm; temperature = 31 ± 0.5 °C. [b] Quantum yield for the decomposition of the complex:
$$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+} \xrightarrow[H^+]{h\nu} Co^{2+} + [Co(NH_3)_5H_2O]^{3+} + O_2 + 5NH_4^+$$

$Ru(bpy)_3^{2+}$ are reported in a preliminary communication recently,[11] and this paper gives an account on the luminescence quenching studies and photosensitized decomposition reactions of the quenchers **1–5**. It is also attempted in this study to

$[(NH_3)_5Co\text{---}O_2\text{---}Co(NH_3)_5](NO_3)_5$

1

$[(NH_3)_4Co \overset{O_2}{\underset{NH_2}{\diagdown\diagup}} Co(NH_3)_4](NO_3)_4$

2

$[L_2Co \overset{O_2}{\underset{NH_2}{\diagdown\diagup}} CoL_2(ClO_4)_4]$

3, L = ethylenediamine
4, L = 2,2'-bipyridine
5, L = 1,10-phenanthroline
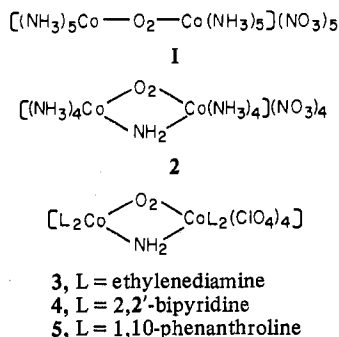
understand the nature of the excited states of cobalt(III) complexes. Although, cobalt(III) complexes show a variety of photochemical reactions,[6,7] identification of the photoreactive excited state has been difficult inspite of investigations using photosensitization methods,[8] flash spectroscopy,[9] and mixed-solvent systems.[10]

Experimental Section

Preparation of the Complexes. $[Ru(bpy)_3]Cl_2$ was prepared from $RuCl_3$ and 2,2'-bipyridine as described.[12] $Ru(bpy)_3^{3+}$ was prepared by oxidizing $[Ru(bpy)_3]Cl_2$ with PbO_2 in solution. $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_4]Cl_5$ was prepared by the literature method.[13] The unstable chloride salt was converted to the stable nitrate salt by treating it with concentrated nitric acid until the precipitation was complete. The precipitation was repeated twice to obtain the pure material. The μ-amido-μ-superoxo dibridged complexes were prepared as described in the literature.[13,14] UV–vis absorption spectra were obtained in a Carl-Zeiss Specord spectrophotometer. Emission spectral measurements were carried out by using a Aminco-Bowman spectrophotofluorometer.

Emission Quenching Studies. Solutions containing the $Ru(bpy)_3^{2+}$ ion and the quencher were irradiated by using 450-nm light at 25 °C. Quenching studies were carried out in hydrochloric acid solutions unless otherwise indicated as the complexes were not very highly soluble either in H_2SO_4 or in $HClO_4$ solutions. The solutions were deaerated by purging with purified nitrogen. The exciting light of the fluorometer $(4 \times 10^{-10}$ einstein/s) did not cause any decomposition of the quencher or $Ru(bpy)_3^{2+}$ during the time of measurement. The relative emission intensities were corrected[15] for light absorption by the quencher.
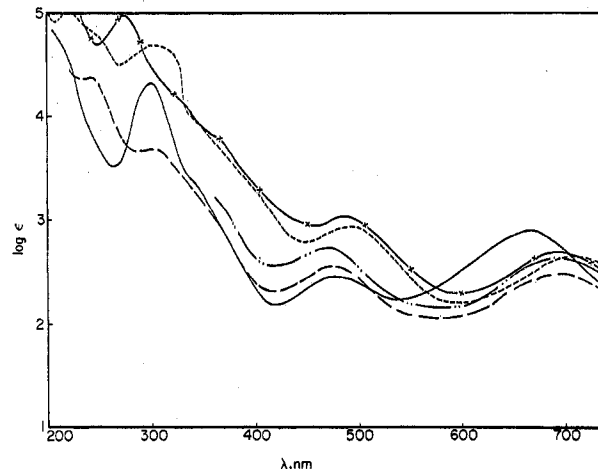
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Figure 1. Spectra of the superoxo-bridged dicobalt(III) complexes: **1** (—), **2** (- -), **3** (-··-), **4** (- - -), **5** (-×-).

Intensities of the light emitted by $*Ru(bpy)_3^{2+}$ in the presence (I) of and in the absence (I_0) of the quencher were related to the quencher concentration according to the Stern–Volmer relationship (eq 1), where

$$I_0/I = 1 + K_{sv}[Q] \qquad K_{sv} = k_q\tau \qquad (1)$$

k_q is the bimolecular quenching constant and τ is the radiative lifetime of $*Ru(bpy)_3^{2+}$ at 25 °C which was measured to be 0.5 μs. Ionic strengths of the solutions were adjusted by adding NaCl in HCl solutions or by adding $NaClO_4$ in $HClO_4$ solutions.

Photosensitization Reactions. The photosensitization studies were carried out at 30 ± 1 °C by using a 250-W high-pressure mercury-vapor lamp (Applied Photophysics), and the setup was fitted with cells containing filter solutions and glass filters to obtain monochromatic light. Concentrations of the $Ru(bpy)_3^{2+}$ ion in solution were adjusted such that >95% of the light from the irradiating beam was absorbed by the sensitizer. After the irradiation, the solution was mixed well and the absorbance of the solution was measured. The change in absorbance at 450 nm was followed as a function of time which corresponded to a first-order process. The first-order growth of absorbance was attributed to the reduction of $Ru(bpy)_3^{3+}$ formed in the primary photochemical reaction. $Ru(bpy)_3^{3+}$ concentration immediately after irradiation was calculated from the extrapolation of the first-order plot to "zero" time. $Ru(bpy)_3^{3+}$ decay during irradiation was found to be less than 5–10% of the total $Ru(bpy)_3^{3+}$ formed in the photosensitization reaction.

The cobaltous ion produced in the photosensitization reactions was determined by the ammonium thiocyanate method.[16] Cobalt(II) formation due to direct photolysis of the quenchers was found to be much less than 1% of the total cobalt(II) formed in the sensitization reaction. Quantum yields for the products of photosensitization reactions were determined in the presence of added $Ru(bpy)_3^{3+}$ by using freshly prepared solutions of the complex.

Results

Visible absorption spectra of the superoxo dinuclear cobalt(III) complexes used in this investigation are shown in Figure 1.

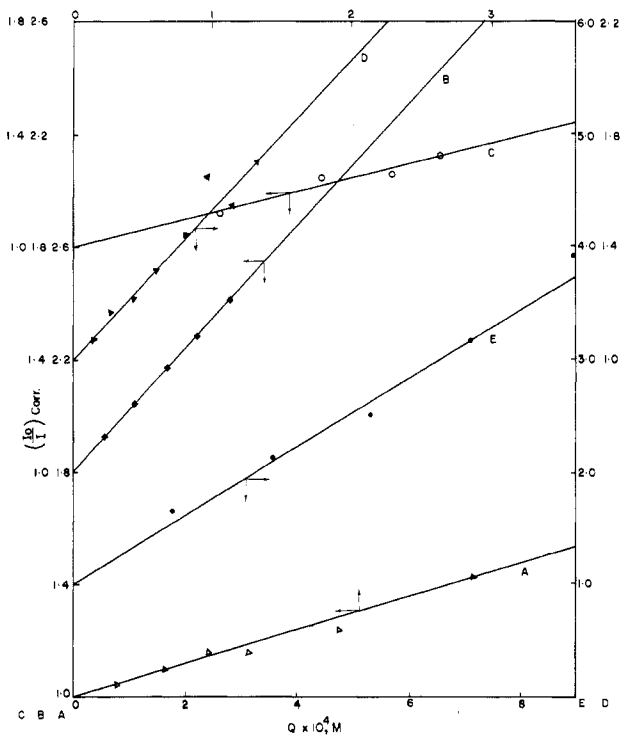In acid solutions, $[H^+] \simeq 10^{-2}$ M, all the complexes are stable to either substitution or redox reactions. The direct-

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Table II. *Ru(bpy)$_3$$^{2+}$ Quenching Constants for the Dinuclear Cobalt(III) Complexes

complex	[HCl], M	[HClO$_4$], M	[H$_2$SO$_4$], M	μ_i, M	K_{sv}	$10^{-9}k_q$, M^{-1} s^{-1}
[(NH$_3$)$_5$Co(μ-O$_2$)Co(NH$_3$)$_5$]$^{5+}$	1.0			1.0	956	1.91
	0.1			0.1	368	0.74
		1.0		1.0	2154	4.30
		0.1		0.1	1110	2.22
		0.02		0.02	640	1.28
		0.02		0.42	2241	4.48
			0.5	1.50	2307	4.62
[(NH$_3$)$_4$Co(μ-NH$_2$,O$_2$)Co(NH$_3$)$_4$]$^{4+}$	1.0			1.0	2000	4.00
					(2058)^a	(4.12)^a
	0.1			0.1	1045	2.09
	0.01			0.01	500	1.00
	0.01			1.33	2178	4.36
	0.01			0.54	1375	2.75
		1.0		1.0	4421	8.84
		0.1		0.1	534	1.07
		0.01		0.21	1474	2.95
		0.01		0.81	1750	3.50
[(en)$_2$Co(μ-NH$_2$,O$_2$)Co(en)$_2$]$^{4+}$	1.0			1.0	1600	3.20
					(1750)^a	(3.50)^a
	0.1			0.1	2182	4.36
	0.01			0.01	348	0.70
	0.01			0.51	1800	3.60
[(bpy)$_2$Co(μ-NH$_2$,O$_2$)Co(bpy)$_2$]$^{4+}$	0.81			0.81	2237	4.47
	0.11			0.11	2105	4.21
	0.01			0.01	1500	3.00
[(phen)$_2$Co(μ-NH$_2$,O$_2$)Co(phen)$_2$]$^{4+}$	1.0			1.00	4048	8.10

^{a} Values calculated from lifetime quenching studies.

Figure 2. Stern–Volmer plots for luminescence quenching of the *Ru(bpy)$_3$$^{2+}$ by the superoxo cobalt(III) complexes: **1**, ■ (μ_i = 1.0 M); **2**, ○ (μ_i = 0.10 M); **3**, ▲ (μ_i = 0.10 M); **4**, △ (μ_i = 0.01 M); **5**, ● (μ_i = 1.0 M).

photolysis quantum yield data for the complexes investigated are given in Table I.

Results of the emission quenching studies in the form of Stern–Volmer plots are shown in Figure 2, and the bimolecular quenching constants and Stern–Volmer constants (K_{sv}) are given in Table II.

Steady irradiation of an aqueous acidic solution containing Ru(bpy)$_3$$^{2+}$ and the cobalt(III) dimer produces the cobaltous ion and Ru(bpy)$_3$$^{3+}$. Results of the quantum yields for the formation of Ru(bpy)$_3$$^{3+}$ and the cobaltous ion for different

Table III. Determination of Stern–Volmer Constants from $1/\phi$ vs. $1/[Q]$ Plots

complex	intercept	slope × 10^3	intercept/slope	K_{sv}
[(NH$_3$)$_5$Co(μ-O$_2$)Co(NH$_3$)$_5$]$^{5+}$	12	6.35	1890	1914
[(NH$_3$)$_4$Co(μ-NH$_2$,O$_2$)Co(NH$_3$)$_4$]$^{4+}$	13	54	241^a	3909
[(en)$_2$Co(μ-NH$_2$,O$_2$)Co(en)$_2$]$^{4+}$	33	135	244^a	3200
[(bpy)$_2$Co(μ-NH$_2$,O$_2$)Co(bpy)$_2$]$^{4+}$	52	10.4	5000	4473

^{a} Values could not be determined accurately due to the nonlinearity of the plot as a result of complications from secondary reactions.

Table IV. Effect of Added Ru(bpy)$_3$$^{3+}$ on Photosensitization Quantum Yields^a

complex (concn)	10^5[Ru(bpy)$_3$$^{3+}$], M	$10^2\phi$ (Co^{II})	$10^2\phi$ (Ru(bpy)$_3$$^{3+}$)
[(NH$_3$)$_5$Co(μ-O$_2$)Co(NH$_3$)$_5$]$^{5+}$ (3.325 × 10^{-4} M)^b	1.18	2.04	2.4
	2.36	1.87	1.91
	5.06	2.10	2.40
	12.32	2.3	2.09
[(NH$_3$)$_4$Co(μ-NH$_2$,O$_2$)Co(NH$_3$)$_5$]$^{4+}$ (1.095 × 10^{-3} M)	0.290	5.42	4.5
	1.1	4.17	3.9
	1.8	3.00	3.9
	3.3	3.10	3.9
[(en)$_2$Co(μ-NH$_2$,O$_2$)Co(en)$_2$]$^{4+}$ (4.48 × 10^{-4} M)	0.7	1.2	8.8
	1.06	1.2	6.62
	1.80	1.23	7.413
[(bpy)$_2$Co(μ-NH$_2$,O$_2$)Co(bpy)$_2$]$^{4+}$ (5.3 × 10^{-4} M)	0.47	3.0	1.57
	1.4	3.1	1.5
	2.4	3.1	1.2

^{a} [Ru(bpy)$_3$$^{2+}$] = 3.65 × 10^{-4} M; [HCl] = 1.0 M; I_0 = 5.00 × 10^{-6} einstein/min. ^{b} [Ru(bpy)$_3$$^{2+}$] = 2.65 × 10^{-4} M.

quenchers are presented as plots of $1/\phi$ vs. $1/[$quencher$]$ in Figure 3. The intercept/slope values calculated from these plots are given in Table III.

Quantum yields for the products of photosensitization reactions determined in the presence of added Ru(bpy)$_3$$^{3+}$ are presented in Table IV for a given concentration of the quencher. The data determine the effect of added Ru(bpy)$_3$$^{3+}$, which is a product of the photosensitization reaction, on the
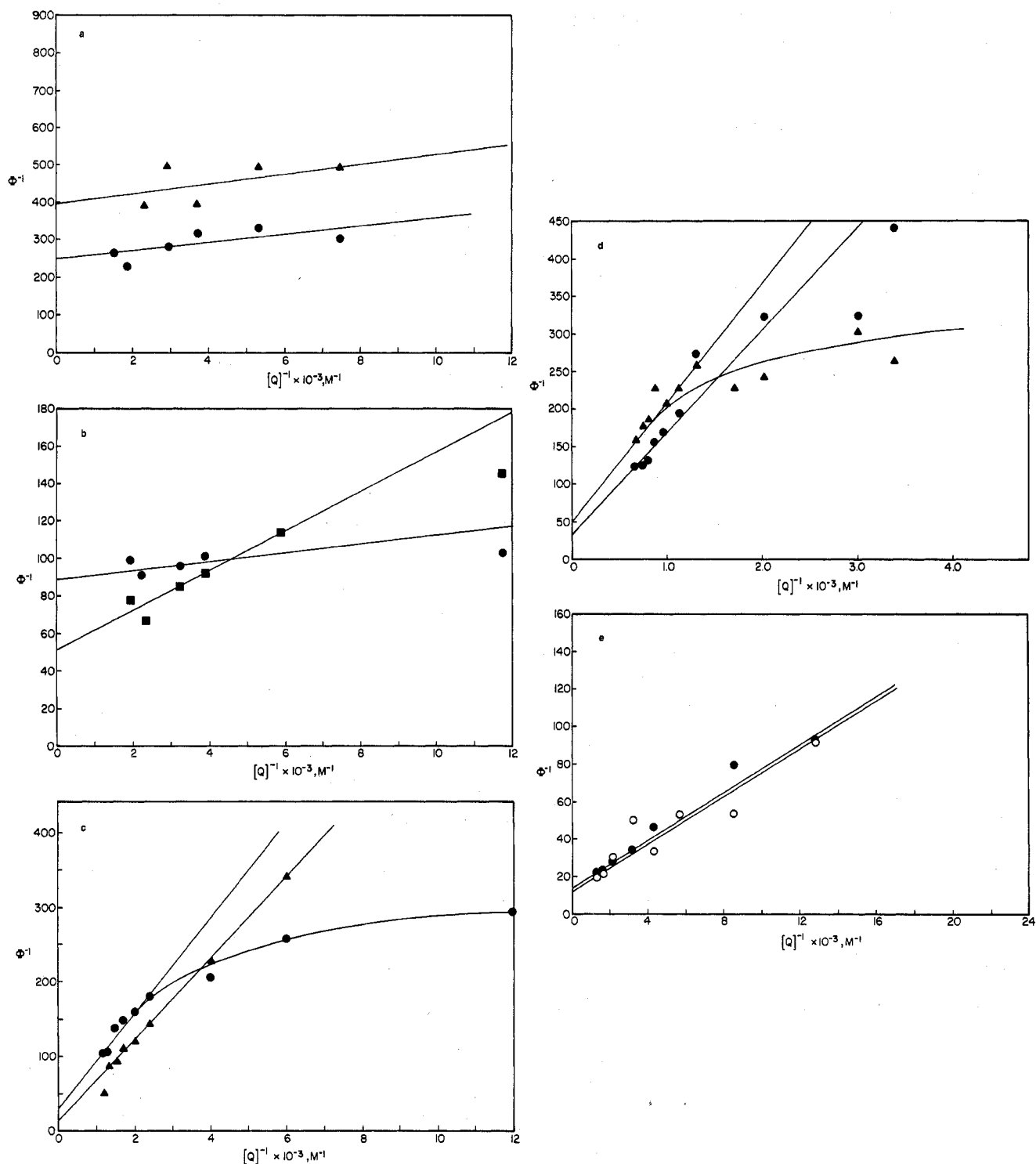
Figure 3. Variation of quantum yield for $Ru(bpy)_3^{3+}$ and Co^{2+} formation as a function of quencher concentration in 1.0 M HCl; e, c, d, b, and a correspond to the cases for the quenchers **1**, **2**, **3**, **4**, and **5**, respectively. Limiting quantum yields for Co(II) are about twice that of $Ru(bpy)_3^{3+}$ for **2**, **3**, **4**, and **5**.

quantum yield for cobaltous ion.

Flash-photolysis investigations have indicated[11] that the redox products resulting from the primary photosensitization reaction get accumulated before reacting again to give the starting materials as reported earlier. Our attempts to determine the steady-state concentrations of the primary photoproducts failed to give reliable values because the corrections involved were large. The approximate steady-state concentrations of the photoproducts were in the range of 15% of $Ru(bpy)_3^{2+}$ used for the sensitization studies. However, absorption by these products was negligible to contribute to the

products formed in steady photolysis.

Discussion

The sensitizer $*Ru(bpy)_3^{2+}$ is a well-characterized species and is formed on exciting the complex $Ru(bpy)_3^{2+}$ in the intense visible absorption band. The excited state is assigned a charge-transfer[17] character in accordance with the high intensity of the absorption band ($\epsilon(450\ nm) = 1.41 \times 10^4$ L $mol^{-1}\ cm^{-1}$). $*Ru(bpy)_3^{2+}$ is known to be a powerful reducing

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agent[18] ($E°$ for Ru(bpy)$_3$$^{3+}$/*Ru(bpy)$_3$$^{2+}$ is –0.82 V) and a mild oxidizing agent as well.[19] *Ru(bpy)$_3$$^{2+}$ transfers the excitation energy to suitable acceptors,[20] and recently photoelectron production from this excited state has been attributed to a biphotonic absorption process.[21]

The absorption spectra of the dinuclear cobalt(III) complexes are complicated due to the fact that the intensities of the transitions in the visible region are fairly high to assign them as pure ligand field transitions. While earlier reports[22,23] assign the low-energy bands due to d–d transitions, recent studies indicate that the bands are predominantly charge transfer in character.[24,25]

As far as the thermal reactions of the quenchers are concerned, all the complexes are substitution inert and stable for days in aqueous acidic solutions. The superoxo-bridged dicobalt(III) complexes are reduced by one-electron reducing agents in aqueous medium, producing the corresponding peroxo complexes.[26] The single-bridged peroxo complex decomposes further to give the fragments [Co(NH$_3$)$_5$]$^{2+}$ and [Co(NH$_3$)$_5$O$_2$]$^{2+}$ which decomposes subsequently to give aqueous cobaltous ion (eq 2). [Co(NH$_3$)$_5$O$_2$]$^{2+}$ has been

$$[(NH_3)_5Co-O_2-Co(NH_3)_5]^{5+} + e^- \xrightarrow{H^+}$$
$$2Co^{2+} + O_2 + 10NH_4^+ \quad (2)$$

observed in the reduction of the dinuclear superoxocobalt(III) complex by the chromous ion.[27] The reduction of **3** by various one-electron reducing agents has been investigated in detail,[28] and the studies show that the superoxo group is reduced directly and is not reduced through the cobalt(III) center.[29] The peroxo complex readily protonates at the peroxo bridge and the protonation equilibria lead to different isomers of the peroxo complex as in eq 3, where K_1 = 0.141 M^{-1} and K_2 = 1.1. One-electron-reduction products of **3**, **4**, and **5** are stable in solution and have been isolated in solid form.[30]

(eq 3)

Direct irradiation of the superoxo-bridged complexes produces the cobaltous ion, in low quantum yields,[14] as one of the photolysis products. None of the quenchers used in the present study is very photosensitive at 450 nm where photosensitization studies were carried out.

Mechanism of the Quenching of *Ru(bpy)$_3$$^{2+}$. Bimolecular

Figure 4. Schematic diagram of the reaction mechanism.

quenching constants observed for all the quenchers shown in Table II are higher than the diffusion-controlled rate constants predicted by Debye's equation.[31] The quenchers carry high positive charge and are of large size which predict somewhat lower diffusional limiting rate constants. However, it may also be noted that the charge is distributed all over the molecule and the net charge at a given point may be much lower. In fact the superoxo bridge carries a negative charge, and the large quenching rate constant may be indicative of the predominant quenching by the superoxo group. The predominant mode of quenching by the dinuclear complexes is by the excited-state electron transfer from *Ru(bpy)$_3$$^{2+}$ to the quencher. In the sensitization experiment using flash spectroscopy, bleaching of the Ru(bpy)$_3$$^{2+}$ absorption at 450 nm and the subsequent reappearance of Ru(bpy)$_3$$^{2+}$ due to reaction 4 have already been demonstrated.[11]

Ru(bpy)$_3$$^{3+}$ + peroxo complex ⇌
    Ru(bpy)$_3$$^{2+}$ + superoxo complex (4)

The bimolecular rate constant for this thermal back-reaction is about two orders of magnitude lower than that for the photoreaction. Our estimates show that 80 ± 10% of the quenching process proceeds through this excited-state electron-transfer process.[32] As shown earlier,[11] lifetime measurements show identical results as the luminescent quenching measurements, and the quenching process occurs by a dynamic quenching mechanism.

Photosensitized Formation of Cobaltous and Ru(bpy)$_3$$^{3+}$ Ions. While the predominant process described above is the one anticipated on thermodynamic grounds and the mechanism is well understood for this process, formation of the cobaltous ion and Ru(bpy)$_3$$^{3+}$ through this pathway does not seem feasible. Thermal back-reaction converts most of the primary photochemical products arising from the excited-state electron-transfer process to the starting materials. Direct-photolysis studies show that the superoxo complexes are not highly photosensitive at 450 nm and the decomposition of the complex observed during sensitization is not due to direct photolysis since the light absorbed by the quencher is less than 5% of the incident light. The formation of cobaltous ion in the photosensitization reaction could also arise due to the decomposition of the peroxo complex formed in the excited-state electron-transfer process in competition with the thermal back-reaction or other sensitization processes. However, the peroxo complexes do not give rise to cobaltous ions as shown for the dibridged complexes.[33] The formation of the observed

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(32) Electron-transfer efficiency from the excited state is determined by using Lin and Sutin's procedure: C. T. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976).
(33) Single-bridged peroxo complexes decompose in acid solution to give rise to cobalt(II); the reaction is too slow[34] to compete with the electron-transfer back-reaction.
(34) J. Simplicio and R. G. Wilkins, *J. Am. Chem. Soc.*, **91**, 1325 (1969).

products is not possible from this pathway, and to account for the decomposition reaction some other mechanism has to be proposed. The emitting state of $Ru(bpy)_3^{2+}$ can also be deactivated by transferring the excited-state energy to the quencher provided the excited state of the quencher lies below that of $Ru(bpy)_3^{2+}$. Indeed such low-lying states are available in principle as the absorption spectra of cobalt(III) complexes show. Energy transfer to the superoxo dicobalt(III) complex could lead to the decomposition of the complex from the states which are active in direct photolysis. The presence of $Ru(bpy)_3^{3+}$ in addition to cobaltous ion as a product of the sensitization rules out this process also.

The pathway in which net products of photosensitization are observed is different from the excited-state electron-transfer pathway discussed earlier and is elucidated from the results obtained for the μ-amido-μ-superoxo complexes. In the case of the ethylenediamine dibridged complex and $Ru(bpy)_3^{2+}$, the excited-state electron-transfer process produces the peroxo dibridged complex and $Ru(bpy)_3^{3+}$ (see eq 5). Thermal

back-reaction between the photoproducts is fast, and there is little accumulation of the peroxo complex or $Ru(bpy)_3^{3+}$ in the medium. Since the μ-amido-μ-peroxo ethylenediamine complex itself does not decompose in the acidic medium to give the cobaltous ion, the predominant excited-state electron-transfer pathway is not the one which causes formation of the cobaltous ion. Again excited-state electron transfer directly

to the metal center is also ruled out considering the fact that one-electron transfer by various reducing agents in thermal reaction involves the dioxygen bridge only and does not involve the metal center.[35] Thus the net products of the photosensitive reaction are to be attributed to an independent pathway, and the following mechanism in Figure 4 is proposed to account for the products.

$Ru(bpy)_3^{3+}$ externally added to the steady photolysis system does not change the photosensitization quantum yields for $Ru(bpy)_3^{3+}$ production as well as dicobalt(III) complex decomposition as shown in Table IV. These results indicate that $Ru(bpy)_3^{3+}$ production is also not coupled with the primary electron-transfer reaction observed in flash photolysis. It is proposed that formation of $Ru(bpy)_3^{3+}$ is due to the oxidation of $Ru(bpy)_3^{2+}$ ion by the excited state of the dicobalt(III) cation. In this process the cobalt complex decomposes to give the cobaltous ion as one of the products. $Ru(bpy)_3^{3+}$, which remains in solution, slowly decays to $Ru(bpy)_3^{2+}$ with a half-life of more than 1 h, probably reacting with the species present in the medium. On the basis of the above mechanism, the quantum yield for net product formation was related to the quencher concentration by eq 6.

$$\frac{2}{\phi(Co^{2+})} = \frac{1}{\phi(Ru(bpy)_3^{3+})} = \frac{1}{k_s\tau[Q]} + \frac{k_q + k_s}{k_s} \quad (6)$$

The intercept vs. the slope in the $1/\phi$ vs. $1/[Q]$ plot gives a measure of the Stern–Volmer constant, and the values of K_{sv} calculated from the plots are given in Table III. Good agreement is seen in cases where secondary reactions do not complicate the measurement of quantum yields. Complications seen for the dibridged ammine complexes are due to the secondary reaction described in Figure 4.

Registry No. 1, 12139-91-2; **2**, 12139-90-1; **3**, 73199-19-6; **4**, 12578-75-5; **5**, 12580-23-3; $[(NH_3)_5Co(\mu-O_2)Co(NH_3)_5]^{5+}$, 12259-09-5; $[(NH_3)_4Co(\mu-NH_2,O_2)Co(NH_3)_4]^{4+}$, 12381-36-1; $[(en)_2Co(\mu-NH_2,O_2)Co(en)_2]^{4+}$, 12387-59-6; $[(bpy)_2Co(\mu-NH_2,O_2)Co(bpy)_2]^{4+}$, 11059-95-3; $[(phen)_2Co(\mu-NH_2,O_2)Co(phen)_2]^{4+}$, 11060-43-8; $Ru(bpy)_3^{2+}$, 15878-95-2; $Ru(bpy)_3^{3+}$, 19052-39-2; Co^{2+}, 22541-53-3.

(35) Recent pulse-radiolysis experiments confirm that reduction by strong organic radicals, unstable metal ions, and hydrated electrons reduces the dioxygen bridge to give the analogous peroxo complexes.[36]
(36) P. Natarajan and N. V. Raghavan, *J. Chem. Soc., Chem. Commun.*, 268 (1980).

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Organophosphazenes. 12. He I Photoelectron Spectra of Selected Phenyl- and [p-(Dimethylamino)phenyl]fluorocyclotriphosphazenes[1]

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He I photoelectron spectra are presented for $P_3N_3F_{6-n}(C_6H_5)_n$ ($n = 1,2,4$) and $P_3N_3F_5C_6H_4N(CH_3)_2$. Ionization energies are discussed in terms of perturbations of molecular orbitals of the parent aryl and phosphazene functions. The data confirm the strong electron-withdrawing effect of the $P_3N_3F_5$ moiety and show a dramatic decrease in this effect as fluorine atoms are replaced by phenyl groups. One also observes a significant destabilization of the phosphazene out-of-plane π molecular orbital as the fluorine atoms are replaced by phenyl groups. The ionizations from the phenyl π_{a_2} and π_{b_1} orbitals are unresolved in phenylphosphazenes, thus demonstrating the lack of significant phosphazene–aryl group mesomeric interactions. The electronic effect of the electron-donating dimethylamino substituent on the phenyl unit is transmitted to the phosphazene through the σ-bond system.

Introduction

The nature of the electronic interaction between aromatic hydrocarbon groups and directly bonded second-row atoms such as silicon and phosphorus continues to attract considerable

attention. Various spectroscopic probes have been applied to these systems in order to evaluate the relative importance of conjugative, hyperconjugative, and inductive effects.[3-5] Aryl-substituted cyclophosphazenes have been examined by

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