solution. X-band ESR spectra were obtained with a Varian E-4 spectrometer equipped with a variable-temperature accessory. Temperatures quoted in this paper were read from the uncalibrated temperature controller and are thus of qualitative significance only. The microwave frequency was measured with a Systron Donner 6054A frequency counter. The magnetic-field calibration of the E-4 spectrometer was checked with a proton resonance gaussmeter. Q-band ESR spectra were obtained by Dr. Ira Goldberg, Rockwell Science Center, Thousands Oaks, CA, with a Varian TE$_{011}$ cavity, Varian V-4561 Q-band microwave bridge, a modified Varian V-4502 spectrometer, and a Magnion 15-in. magnet.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Research Committee of the New Zealand Universities Grants Committee for financial support.

**Registry No.** $C_6H_5CCo_3(CO)_9^-$, 61024-80-4.

## References and Notes

(1) Part 5: P. Dawson, B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, submitted for publication in *Inorg. Chem.*

(2) T. W. Matheson, B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *J. Chem. Soc., Chem. Commun.*, 894 (1973); B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 405 (1977).

(3) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

(4) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

(5) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

(6) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(7) P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, **44**, 169 (1966).

(8) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, 1972, p 201.

(9) W. B. Lewis and L. O. Morgan, *Transition Met. Chem.*, **4**, 33 (1968).

(10) Reference 8, p 154.

(11) N. M. Atherton, "Electron Spin Resonance", Ellis Harwood, Chichester, England, 1973, p 222.

(12) The negative signs assumed for $\langle a \rangle$, $a_\parallel$, and $a_\perp$ are based on theory and analogy with similar radicals. See ref 13.

(13) C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, **47**, 93 (1969).

(14) D. C. Miller and T. B. Brill, *Inorg. Chem.*, **17**, 240 (1978).

(15) Using the experimental quadrupole coupling constant, $P = 2.66$ MHz,[14] and the theoretical quadrupolar line-width contribution for radicals with a single nucleus (ref 11, p 350), one can estimate a line-width contribution on the order of 0.0003 mT when $\tau_R = 6 \times 10^{-11}$ s. Although this is quite negligible, the contribution might be significantly larger when three equivalent nuclei are taken into account.

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# Photochemical Pathways of the Dimeric, Mixed Dimer, and Monomeric Sulfophthalocyanines of Cobalt(III) and Iron(II)

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*Received July 27, 1978*

The photochemical reactivity of the dimeric, mixed dimer, and monomeric sulfophthalocyanines of cobalt(III) and iron(II) was investigated by steady-state and flash irradiations. The dimeric species photodissociated into sulfophthalocyanine radicals which were coordinated to either Co(III) or Fe(II) metal centers. Reactions of such intermediates were investigated by interception with alcohols and $O_2$. Also, photoredox reactions were detected with monomeric acidocobalt(III) sulfophthalocyanines. These processes produce the oxidation of the acido ligands ($Cl^-$, $Br^-$, $N_3^-$, $I^-$) and the reduction of the metal center. The photoredox dissociation was also investigated by using mixed dimers of the cobalt sulfophthalocyanines with $Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$. The photogeneration of sulfophthalocyanine radicals was observed as a general reaction which was produced by excitation of either the $Cr(bpy)_3^{3+}$ or $Ru(bpy)_3^{2+}$ units in the mixed dimer. The nature of the reactive excited states involved in the various photochemical reactions of the sulfophthalocyanines of Co(II), Co(III), Cu(II), and Fe(II) is discussed.

## Introduction

The photochemistry of the dimeric and monomeric sulfophthalocyanines of copper(II) and cobalt(II) have been recently investigated.[1,2] Such a study has demonstrated that dimeric species are photodissociated by irradiation of the ultraviolet bands. Copper(II)–ligand radicals and sulfophthalocyanines with cobalt(I) and cobalt(III) metal centers are the primary products of these reactions. In addition, photoredox processes of the monomeric cobalt(II) and copper(II) sulfophthalocyanines were observed when these species were irradiated in the presence of hydrogen donors. These photochemical properties of the dimeric and monomeric complexes were related to the population of a ligand-centered excited state which is probably an $n\pi^*$ state of the ligand. In this regard, it seems that there is some parallelism between the photochemistries of the sulfophthalocyanines and porphyrins.[3,4] In fact, it has been reported that population of $n\pi^*$ excited states of the porphyrins induces their reduction by tertiary amines.

Also, a photoredox process has been briefly reported for a methylcobalt(III) sulfophthalocyanine by Day et al.[5] This reaction can probably be described as the same homolytic photodissociation of the metal–carbon bond which is observed with other methylcobalt(III) macrocyclic complexes.[6-8] Nevertheless, the behavior of the methylcobalt(III) sulfophthalocyanine contrasts with the photochemistries of the sulfophthalocyanines of copper(II) and cobalt(II). These differences suggest that a low-energy charge-transfer ligand-to-metal, CTTM, excited state is the photoactive state of the methyl complex.[9] In this regard, one may expect that the photochemistry of some sulfophthalocyanines should have the combined features of the reactions which are originated in either charge-transfer or ligand-centered states.[9] In such a case, the nature of the ligands attached to the metal center in axial positions will have a large influence on the nature of the photochemical process.

The study of the photochemistry of the sulfophthalocyanines of the transition-metal ions has been continued in this work by use of complexes with $d^6$ metal centers, Fe(II) and Co(III).[2] The results, obtained with monomeric and dimeric species, are compared with those of the copper(II) and cobalt(II) complexes.

## Experimental Section

**Photochemical Procedures.** Steady-state irradiations were carried out with an experimental setup that was previously described in some detail.[1] A 300-W xenon Varian lamp, combined with collimating filters, lenses, and a high intensity Bausch and Lomb monochromator, was used for ultraviolet–visible photolyses. The entrance and exit slits of the monochromator were adjusted until the light output corresponded to a Gaussian distribution of the intensity with a half-bandwidth equal to or smaller than 10 nm. Low-pressure mercury lamps, a Rayonet RPR 2537 Å and a GE G4T4.1, were used for 254-nm photolyses. The light intensities used in the determination of the quantum yields were measured by ferrioxalate actinometry.[11] In addition, the constancy of the light intensity was frequently tested with $Co(NH_3)_5Br^{2+}$.[12]

Flash photolysis experiments were carried out in the same apparatus which was described elsewhere.[13] Nevertheless, some of the more significant details are explained below. Values of the stored electrical energy between 250 and 40 J/flash were obtained by charging a 5-$\mu$F capacitor at preselected voltages between 4 and 10 kV. The flash output and the amount of transient produced per pulse were proportional to the stored energy. The phototube output was displayed on a 564 Tektronix storage oscilloscope. Pretrigger values of the phototube voltage were measured with ±2 mV accuracy in a dc digital voltmeter with an internal resistance of 10 MΩ. Solutions in the reaction cell were protected from unnecessary exposure to the light of the monitoring beam. A shutter, used for such a purpose, was opened a few seconds in advance of the flash. Furthermore, cutoff filters were placed between the cell and the monitor source in order to prevent the ultraviolet irradiation ($\lambda \leq 380$ nm) of the solution.

Solutions used for either continuous-wave or flash-photolysis experiments were deaerated with streams of argon or nitrogen which were scrubbed in towers filled with chromous solutions. The liquids, liberated of oxygen, were handled in a gastight apparatus.

Acido complexes[2] of cobalt(III), e.g., $Co(PTS)(OH_2)_{2-n}(X)_n^{(4+n)-}$ with $n = 1$ or 2 and $X^- = Cl^-, Br^-, N_3^-$ etc., were photochemically transformed into products when their solutions were exposed to the laboratory light. These reactions were noticeable, in particular, when dilute solutions of the substrates had to be deaerated for long periods of time. Nevertheless, the problem was circumvented by working in a room illuminated with a red safety light.

Solutions of the $Fe(PTS)^{4-}$ were handled in a nitrogen or argon atmosphere because of the reactivity of the iron(II) complex with oxygen; see above and ref 14. Although the oxidation by oxygen seems to be a slow process, these solutions were made by the addition of solid samples of the complex to deaerated solvents.

**Electrochemical Procedures.** Electrolysis of the $Fe^{II}(PTS)^{4-}$ and $Co^{II}(PTS)^{4-}$ complexes was carried out with a DC Hewlett-Packard 6216A power supply. Voltages were measured with a dc Digiec voltmeter accurate to ±0.002 V. Current intensities were determined with a Fairchild digital panel meter, DC 53, which was modified for the measurements of intensities larger than 1 mA.

Deaerated solutions of the complexes, prepared as indicated above (see photolysis procedures), were electrolyzed over platinum electrodes in a gastight cell. The liquids were stirred with both a magnetic bar and streams of nitrogen before and during the reaction. Moreover, these electrochemical processes were normally carried out at current densities smaller than 1.6 mA/cm$^2$. The transformation into products was followed by means of the absorption spectrum of the solution and silver coulometry.

**Analysis of the Reaction Products.** The photochemical formation of the cobalt(II) sulfophthalocyanine, produced in continuous-wave photolyses of the various cobalt(III) sulfophthalocyanines, was investigated by means of the UV-vis absorption spectra of irradiated samples. These spectra were obtained under anaerobic conditions in cells with either 1-cm or 1-mm optical path. Calibation curves, absorbance vs. $Co(PTS)^{4-}$ concentration, were constructed for wavelengths where the sulfophthalocyanines of Co(II) and Co(III) had a significant difference of absorptivities, e.g., at $\lambda \sim 320$ nm and $\lambda \sim 620$ or 660 nm. Solutions with known concentrations of the cobalt(II) and -(III) sulfophthalocyanines were used for the preparation of the calibration curves under the experimental conditions which were used in photochemical experiments.

The formation of aquated metal ions, $Co^{2+}(aq)$, $Fe^{2+}(aq)$, and $Fe^{3+}(aq)$, was investigated with procedures reported in the literature.[15] The nitroso-R salt was used for the investigation of $Co^{2+}(aq)$. Ferrous ions were analyzed with 1,10-phenanthroline. Ferric ions were reduced with ascorbic acid, and the amount of $Fe^{2+}(aq)$, formed in this reaction, was determined as it is indicated above.

The formation of $Fe(PTS)^{5-}$ in photolyses of iron(II) sulfophthalocyanine was followed by means of the absorption spectra of the irradiated solutions. The absorption spectrum of $Fe(PTS)^{5-}$ in various media was determined by electrochemical reduction of the iron(II) sulfophthalocyanine; see Electrochemical Procedures.

Gas products were investigated by chromatographic and mass spectrometric procedures that were reported elsewhere.[16]

Formaldehyde was determined with chromotropic acid.[17]

**Materials.** Cobalt(II), cobalt(III), and copper(II) sulfophthalocyanines were available from a previous work.[1]

The aquohydroxocobalt(III) sulfophthalocyanine was anated in solutions, where sodium salts of the halides and pseudohalides, $Cl^-$, $Br^-$, and $NCS^-$, were added in a large excess (a 10:1 molar ratio with respect to the complex). The concentration of hydrogen ion was adjusted to $10^{-2}$ M with perchloric acid. Crystallization from warm solutions produced solids with the stoichiometry expected for trans diacido complexes. Results on the stoichiometry of these compounds and on the nature of other species which are also formed in aqueous solutions are reported elsewhere in the text.

Iron(II) sulfophthalocyanine was prepared by the procedure of Weber and Busch.[14] The solid compound was stored and handled under a nitrogen atmosphere. Spectroscopic properties of the complex agreed well with literature reports.

$[Cr(bpy)_3](ClO_4)_3$ was obtained by published procedures.[18] This compound and $[Ru(bpy)_3]Cl_3$, purchased from G. F. Smith, were recrystallized from warm aqueous solutions by addition of sodium perchlorate.

Alcohols, 2-propanol and methanol, were spectroquality AR and used without further purification. Other materials were reagent grade.

## Results

**(A) The Nature of the Species in Aqueous Solutions.** The association of the cobalt(III) and iron(II) sulfophthalocyanines was investigated in aqueous solutions by means of the distinct absorptions at 600–700 nm.[19-21] The association of the complexes is affected by various medium conditions, namely, the ionic strength, the nature of the anions (see below), and the concentration of hydrogen ion. Indeed, the dependence of the aquocobalt(III) sulfophthalocyanine spectrum on the concentration of the acid is shown in Figure 1a.[22] An equilibrium constant, $K \approx 10^{-7}$, was estimated from these results for the dissociation equilibrium, eq 1. The same

$$[Co(PTS)(OH_2)_2]_2^{6-} \rightleftharpoons 2[Co(PTS)(OH_2)_2]^{3-} \qquad (1)$$

tendency toward association was exhibited by iron(II) sulfophthalocyanine in aqueous solutions.

The association equilibrium 1 can be displaced by halides, $Cl^-$, $Br^-$, and $I^-$, or pseudohalides, $NCS^-$ or $N_3^-$. It was observed that, in general, these anions produce changes of the absorption spectrum of the complex in the region of 600–700 nm. Such modifications show that the proportion of the monomeric species increases with the concentration of halides or pseudohalides. This behavior, dissociation of the dimeric species, is attributed to an anation equilibria, eq 2, where $n = 1$ or 2.[23]

$$[Co(PTS)(OH_2)_2]^{3-} + nX^- \rightleftharpoons [Co(PTS)(OH_2)_{2-n}(X)_n]^{(3+n)-} \qquad (2)$$

The existence of the anation equilibria is also supported by the distinct photochemistry exhibited by anated species and the isolation of some acidocobalt(III) sulfophthalocyanines. The stoichiometric relationships for these compounds are shown in Table I.[22]

The association of the cobalt(II) sulfophthalocyanine and aquocobalt(III) sulfophthalocyanine with cationic complexes, e.g., $Ru(bpy)_3^{2+}$, $Cr(bpy)_3^{3+}$, or Cu(tet a)$^{2+}$, produces changes in the absorption spectra of the sulfophthalocyanines, e.g., in the 600–700 nm region, Figure 1b,[22] which show an increase in the dissociation of the dimeric species. These transformations may be explained if equilibrium 1 is perturbed by the association of the cationic complexes, indicated above, with aquocobalt(III) sulfophthalocyanine. This process is described in eq 3, where M is Cr ($z = 3$) or Ru ($z = 2$). An equilibrium

$$[Co(PTS)(OH_2)_2]^{3-} + M(bpy)_3^{z+} \rightleftharpoons [Co(PTS)(OH_2)_2{}^{3-}, M(bpy)_3{}^{z+}] \qquad (3)$$

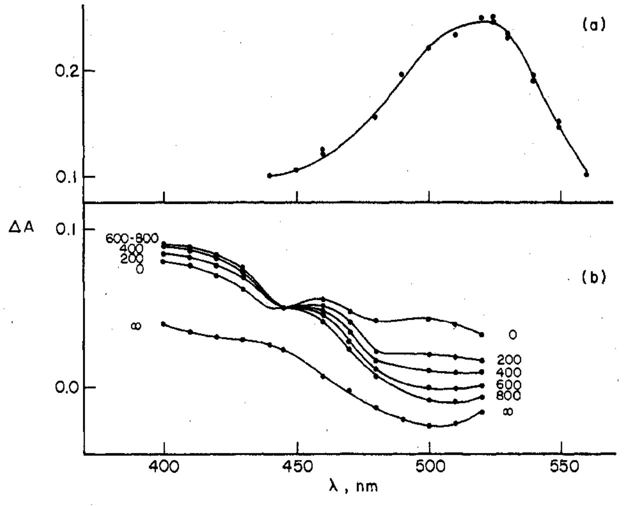


**Figure 2.** Transient spectra generated in flash photolyses of sulfophthalocyanines. (a) Spectrum obtained in photolyses of deaerated acidic ($10^{-1}$ M $HClO_4$) solutions of $[Co(PTS)(OH_2)_2]_2^{6-}$. Points determined 50 μs after 250 J/flash pulses. (b) Time-resolved spectrum generated in flash irradiations of a deaerated, acidic ($10^{-1}$ M $HClO_4$) solution of $[Fe(PTS)(OH_2)_2]_2^{6-}$. Points determined at 0, 200, 400, 600, and 800 μs and 10 ms (∞) after 250 J/flash pulses.

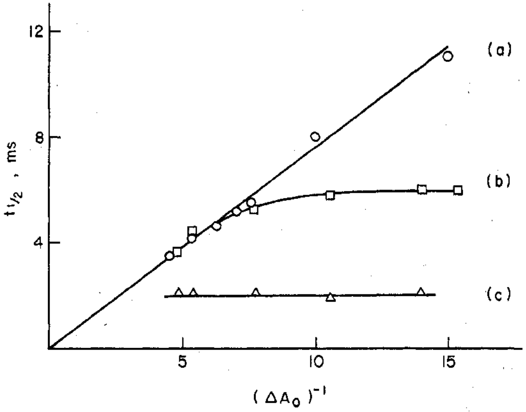


**Figure 3.** Flash photolysis of $[Co(PTS)(OH_2)_2]^{6-}$. Dependence of the half-lifetime, $t_{1/2}$, for the decay of the 520-nm absorbance upon the reciprocal of the transient absorbance, $\Delta A_0$, in (a) deaerated solutions, (b) $4.8 \times 10^4$ M $O_2$, and (c) $1.6 \times 10^{-3}$ M $O_2$.

constant, $K = 5 \times 10^6$, was estimated for the association of the aquocobalt(III) sulfophthalocyanine and $Ru(bpy)_3^{2+}$.

**(B) Photochemistry of the Dimeric Species.** The photochemical reactions of $[Co(PTS)(OH_2)_2]_2^{6-}$ and $[Fe(PTS)(OH_2)_2]_2^{8-}$ were studied by continuous-wave and flash irradiations. Although these complexes present several photochemical features which are largely related, the results obtained with each of them are presented in separate subsections.

**(1) Flash Photolysis of $[Co(PTS)(OH_2)_2]_2^{6-}$.** Deaerated, acidic ($10^{-1}$–$10^{-3}$ M $HClO_4$) solutions of $[Co(PTS)(OH_2)_2]_2^{6-}$ (concentrations $\geq 10^{-5}$ M) were photolyzed at wavelengths larger than 220 nm. A transient spectrum, observed under those conditions, had a maximum absorption, $\lambda_{max}$ ~520 nm, Figure 2a, which is expected for sulfophthalocyanine radicals $Co^{III}(P\dot{T}S)^{4-}$ and $Co^{III}(P\dot{T}S)^{2-}$.[1,23,24] The absorbance, produced with the life of the flash, disappears by a second-order reaction; see curve a in Figure 3. A ratio of the second-order rate constant to the extinction coefficient $k/\epsilon = 2.7 \times 10^4$ cm s$^{-1}$ was obtained at $\lambda_{max}$ 520 nm. Flash irradiations of $[Co(PTS)(OH_2)_2]_2^{6-}$ (concentrations $\geq 10^{-5}$ M) in acidic solutions ($10^{-1}$ M $HClO_4$) which were saturated with air under a pressure of 1 atm, $[O_2] \simeq 4.8 \times 10^{-4}$ M, also produce transient absorbances. The decay of these absorbances no longer obeys a second-order rate law as shown in curve b of Figure 3. In addition, the disappearance of this transient takes place by a first-order process in solutions saturated with oxygen under a pressure of 1 atm ($[O_2] \simeq 1.6 \times 10^{-3}$ M; curve c in Figure 3). This deviation from a second-order rate law was attributed to a reaction of the intermediate $Co^{III}(P\dot{T}S)^{4-}$ with oxygen as it was already observed with a copper(II) sulfophthalocyanine radical, $Cu^{II}(P\dot{T}S)^{5-}$.[1,24,25] A second-order rate constant, $k = 1.7 \times 10^5$ M$^{-1}$ s$^{-1}$ for the reaction of the intermediate with oxygen, was estimated from the results which were reported above.

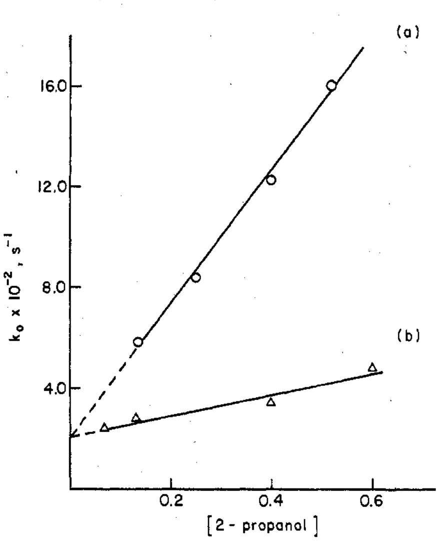


**Figure 4.** Interception of the intermediates produced in flash irradiations of acidic ($10^{-1}$ M $HClO_4$) solutions of $[Co(PTS)(OH_2)_2]_2^{6-}$. Dependence of the rate constant for the decay of the 480-nm transient absorbance upon 2-propanol concentration in (a) deaerated solutions and (b) $4.8 \times 10^{-4}$ M $O_2$ solutions.

Also, the radical nature of the intermediates was investigated by intercepting these transients with alcohols. These reactions were studied in deaerated acidic ($10^{-1}$ M $HClO_4$) solutions of $[Co(PTS)(OH_2)_2]_2^{6-}$, which has 2-propanol in various concentrations, 0.1 M $\leq$ [2-propanol] $\leq$ 0.6 M. The rate of the absorbance decay, followed at $\lambda_{max} \simeq 480$ nm, exhibited a first-order dependence in alcohol concentration; see Figure 4. The slope of the curve in Figure 4 corresponds to a second-order rate constant, $k = 2.6 \times 10^3$ M$^{-1}$ s$^{-1}$, for the reaction of the transient $Co(P\dot{T}S)^{2-}$ with 2-propanol. Furthermore, the value of the rate constant, $k^\circ_{obsd}$, obtained by extrapolating to zero the 2-propanol concentration in Figure 4, is equivalent to a reaction half-life, $t_{1/2} = 3.3 \times 10^{-3}$ s, for an initial transient absorbance, $A_0 = 0.220$. These values were in good agreement with a $t_{1/2} = 3.7 \times 10^{-3}$ s, which was determined by direct measurements; see above and curve a in Figure 3.

A stable product, characterized as cobalt(II) sulfophthalocyanine by means of the absorption spectrum (see below), was formed by interception of the intermediate $Co(P\dot{T}S)^{2-}$ with 2-propanol. The formation of the reaction product was investigated in deaerated, dilute solutions of the aquocobalt(III) sulfophthalocyanine complex (~$5.7 \times 10^{-3}$ M in 0.1 M $HClO_4$) at $\lambda \geq 540$ nm. The recovery of the bleached absorbance, due to the transformation of the reduced ligand radical $Co(P\dot{T}S)^{4-}$ into cobalt(II) sulfophthalocyanine, obeys a first-order rate law with $k \simeq 1.8 \times 10^2$ s$^{-1}$.

The reactivity of the transient was also investigated by a competitive interception with 2-propanol and oxygen. These experiments were carried out with acidic ($10^{-1}$ M $HClO_4$) solutions of $[Co(PTS)(OH_2)_2]_2^{6-}$ in 0.05–1.0 M 2-propanol saturated with air at 1 atm. The dependence of the reaction half-life on 2-propanol concentration, less marked in aerated than in deaerated solutions, Figure 4, shows that oxygen and 2-propanol react with two distinct intermediates.

**(2) Flash Photolysis of $[Fe(PTS)(OH_2)_2]_2^{8-}$.** Acidic solutions ($10^{-1}$–$10^{-3}$ M $HClO_4$) of the dimeric iron(II) complex were irradiated at wavelengths larger than 220 nm. The spectrum, generated in the life of the flash, decays by forming new transient absorptions which can be followed at $\lambda \leq 445$ nm, Figure 2b. The growth of the absorbance at 410 nm and the decay at 460 nm take place by first-order reactions (rate constants $k_{410} = k_{460} = (6.3 \pm 0.5) \times 10^3\ s^{-1}$), which are attributed to a transformation of a primary ligand radical species, $Fe(P\dot{T}S)^{5-}$, into iron(I) sulfophthalocyanine. Moreover, the slow disappearance of the absorbance, detected at 460 nm for reaction times larger than 1 ms, Figure 2b, obeys a second-order rate law with a ratio of the rate constant to the molar extinction at 460 nm of $k/\epsilon = 6.7 \times 10^2\ cm\ s^{-1}$. The final transformations of the absorption spectrum, bleach of the absorbance at $\lambda \geq 450$ nm and increments at $\lambda < 450$ nm, indicated for $t = \infty$ in Figure 2b, are also produced when iron(I) sulfophthalocyanine is generated by electrochemical reduction[26] or continuous-wave photolysis (see below) of the iron(II) sulfophthalocyanine.

The radical character of the intermediates that were primarily generated in flash photolysis was investigated by scavenging with alcohols. Flash irradiation ($\lambda_{excit} \geq 220$ nm) of acidic ($10^{-2}$ M $HClO_4$) solutions of $[Fe(PTS)(OH_2)_2]_2^{8-}$ in either $10^{-1}$–$5 \times 10^{-3}$ M 2-propanol or $10^{-1}$–$10^{-2}$ M methanol produced iron(I) sulfophthalocyanine. The formation of this product, followed at 410 nm, obeys a first-order rate law with a rate constant $k = 6.9 \times 10^3\ s^{-1}$. This value and one obtained in the absence of scavengers (see above) are in good agreement. In addition, the rate of the disappearance of the absorbance with $\lambda_{max} \sim 460$ nm (see Figure 2b) increases with 2-propanol concentration. Such a behavior indicates that the maximum absorbance at 460 nm (see Figure 2b) must be assigned as an iron(II) ligand radical, $Fe(P\dot{T}S)^{3-}$; see above and Discussion.

**(3) Continuous-Wave Irradiations of $[Co(PTS)(OH_2)_2]_2^{6-}$.** The irradiation of $[Co(PTS)(OH_2)_2]_2^{6-}$ in oxygen-free $10^{-1}$–$10^{-4}$ M $HClO_4$ was carried out at wavelengths of the Soret band ($\sim$30 000 $cm^{-1}$) and bands placed at larger energies. Products, $Co^{2+}(aq)$ and cobalt(II) sulfophthalocyanine, were not detected in samples irradiated for short periods, e.g., less than 30 min with $I_0 \approx 10^{-4}$ einstein/(L min) at 254 nm under the conditions stated above. However, extended irradiations, e.g., 3–4 h with $I_0 \approx 8 \times 10^{-4}$ einstein/(L min) at 254 nm, produced small changes of the absorption spectrum. A limit yield, $\phi \leq 7 \times 10^{-6}$, was estimated for the formation of $Co^{2+}(aq)$ or cobalt(II) sulfophthalocyanine in ultraviolet irradiations, namely, $\lambda_{excit} \leq 400$ nm.[27]

Also, the photochemical reactions of the dimeric cobalt(III) sulfophthalocyanine were investigated in acidic ($10^{-1}$–$10^{-4}$ M $HClO_4$) solutions containing 3.0–0.1 M 2-propanol. The spectra of irradiated samples and blanks exhibited differences, e.g., increase of the absorbance at 650 nm and decrease at 320 nm, which indicate that cobalt(II) sulfophthalocyanine is formed by photolysis under the conditions stated above. Yields of this product, $Co(PTS)^{4-}$, are markedly dependent on the wavelength of the excitation, as it is shown in Table II.

**(4) Continuous-Wave Irradiations of $[Fe(PTS)(OH_2)_2]_2^{8-}$.** Photolyses of $[Fe(PTS)(OH_2)_2]_2^{8-}$ were carried out in neutral or acidic ($10^{-1}$ M $HClO_4$) solutions. Excitation at 254 or 225 nm produces a gradual decrease of the absorbances at 550–700 and 260–400 nm; see Figure 5a. Moreover, $Fe^{3+}(aq)$ was detected as a reaction product in irradiated samples. These observations suggest some degradation of the ligand, e.g., opening of the phthalocyanine ring, in reactions which follow the photochemical formation of iron(II)–ligand radicals. The yields of $Fe^{3+}(aq)$ were estimated to be $\phi = (3.0 \pm 0.3) \times 10^{-3}$ for excitations at 254 nm ($I_0 = 8.0 \times 10^{-4}$ einstein/(L min)) and $\phi = 0.030$ for excitations at 225 nm ($I_0 = 5.0 \times 10^{-5}$ einstein/(L min)).

**Table II.** Quantum Yields for Photolyses of Sulfophthalocyanine Complexes of Cobalt(III) and Iron(II)

| $\lambda_{excit}$, nm | $I_0$, einstein/(L min) | $10^3\phi_{redox}$[a] | [2-propanol],[b] M |
|---|---|---|---|
| | (a) $[Co(PTS)(OH_2)_2]_2^{6-}$[d] | | |
| 345 | $6.4 \times 10^{-5}$ | $<6 \times 10^{-4}$[c] | 10.6 |
| 280 | $5.8 \times 10^{-5}$ | $2.5 \pm 0.2$ (3) | 10.6 |
| 254 | $2.2 \times 10^{-4}$ | $0.63 \pm 0.03$ (3) | 0.27 |
| 254 | $2.2 \times 10^{-4}$ | $0.44 \pm 0.05$ (4) | 0.81 |
| 254 | $2.2 \times 10^{-4}$ | $1.51 \pm 0.07$ (3) | 1.33 |
| 254 | $2.2 \times 10^{-4}$ | $3.3 \pm 0.1$ (2) | 4.0 |
| 254 | $2.2 \times 10^{-4}$ | $5.0 \pm 0.1$ (5) | 8.0 |
| 254 | $2.2 \times 10^{-4}$ | $7.5 \pm 0.2$ (5) | 10.6 |
| 225 | $3.0 \times 10^{-5}$ | $0.05 \pm 0.03$ (10) | 10.6 |
| | (b) $[Co(PTS)(OH_2)_{2-n}(I^-)_n]^{(3+n)-}$ ($n = 1, 2$)[d,e] | | |
| 460 | $8.0 \times 10^{-5}$ | $12 \pm 3$ (3) | |
| 430 | $8.2 \times 10^{-5}$ | $10 \pm 3$ (4) | |
| 345 | $6.4 \times 10^{-5}$ | $13 \pm 2$ (3) | |
| 280 | $5.8 \times 10^{-5}$ | $12 \pm 3$ (3) | |
| | (c) $[Fe(PTS)(OH_2)_2]_2^{8-}$ ($3.0 \times 10^{-4}$ M) | | |
| 345 | $6.4 \times 10^{-5}$ | $<10^{-4}$[c] | 3.3 |
| 280 | $5.8 \times 10^{-5}$ | $4.8 \pm 0.3$ (3) | 3.3 |
| 254 | $8.0 \times 10^{-4}$ | $25 \pm 4$ (5) | 3.3 |
| 254 | $8.0 \times 10^{-4}$ | $24 \pm 5$ (3) | 3.3[f] |
| 225 | $3.0 \times 10^{-5}$ | $32 \pm 5$ (2) | 3.3 |

[a] Yields of cobalt(II) sulfophthalocyanine, $Co(PTS)^{4-}$, and iron(I) sulfophthalocyanine, $Fe(PTS)(OH_2)_2^{5-}$, which are formed under the conditions stated above. Number of determinations in parentheses. [b] Solutions deaerated with nitrogen streams. [c] Upper detection limits. [d] Yields measured in 0.1 M $HClO_4$. [e] Yields measured in 0.1 M $I^-$. [f] $[[Fe(PTS)(OH_2)]_2^{8-}] = 0.8 \times 10^{-4}$ M.

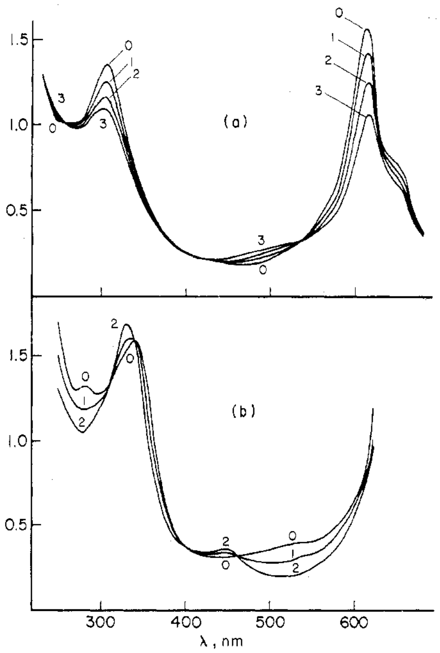


**Figure 5.** Changes in the absorption spectrum of $[Fe(PTS)(OH_2)]_2^{8-}$ solutions irradiated by various periods at 254 nm ($I_0 \approx 3 \times 10^{-5}$ einstein/(L min)): (a) solutions in $10^{-1}$ M $HClO_4$ photolyzed (0) zero min, (1) 15 min, (2) 30 min, and (3) 45 min; (b) solutions with 1.3 M 2-propanol and $10^{-1}$ M $HClO_4$ photolyzed (0) zero min, (1) 2.7 min, and (2) 5.4 min.

The photochemical reactivity of $[Fe(PTS)(OH_2)_2]_2^{8-}$ was also investigated with 1.0–0.1 M 2-propanol; see flash photolysis section. The spectra of irradiated samples and blanks exhibited differences, e.g., new absorptions at 330, 450, and

**Table III.** Rate of the Formation and the Decay of $[Co^{III}(PTS)(OH_2)_{2-n}(Cl)]^{(3+n)-}$ during Flash Photolysis of $[Co^{III}(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-}$ in Aqueous Acidic Solutions[c]

| $k_{obsd}$,[b] $s^{-1}$ | $\Delta A_{max}$ | conditions[a] |
|---|---|---|
| | (a) Formation of the 550-nm Transient Absorption | |
| 6.7 | 0.102 | 0.1 M HCl, 203 J/flash |
| 6.0 | 0.092 | 0.1 M HCl, 160 J/flash |
| 6.3 | 0.075 | 0.1 M HCl, 122 J/flash |
| 6.3 | 0.062 | 0.1 M HCl, 90 J/flash |
| 5.8 | 0.038 | 0.1 M HCl, 63 J/flash |
| 6.3 | 0.023 | 0.1 M HCl, 40 J/flash |
| 6.6 | 0.102 | 0.1 M NaCl, 0.01 M HCl, 203 J/flash |
| 6.7 | 0.102 | 0.1 M NaCl, 0.005 M HCl, 203 J/flash |
| 13.8 | 0.130 | 0.1 M HCl, 203 J/flash, $[Co(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-} = 4.0 \times 10^{-5}$ M |
| 26.3 | 0.140 | 0.1 M HCl, 203 J/flash, $[Co(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-} = 8.0 \times 10^{-5}$ M |
| | (b) Decay of the 500-nm Transient Absorption | |
| 8.1 | 0.113 | 0.02 M HCl, 0.1 M NaCl; 203 J/flash |
| 8.4 | 0.095 | 0.02 M HCl, 0.1 M NaCl; 160 J/flash |
| 8.2 | 0.084 | 0.02 M HCl, 0.1 M NaCl; 122 J/flash |
| 8.2 | 0.065 | 0.02 M HCl, 0.1 M NaCl; 90 J/flash |
| 8.0 | 0.044 | 0.02 M HCl, 0.1 M NaCl; 63 J/flash |
| 13.8 | 0.113 | 0.10 M HCl, 0.1 M NaCl; 203 J/flash |
| 6.9 | 0.114 | 0.06 M HCl, 0.14 M NaCl; 203 J/flash |
| 5.6 | 0.110 | 0.02 M HCl, 0.18 M NaCl; 203 J/flash |
| 4.3 | 0.115 | $10^{-3}$ M HCl, 0.20 M NaCl; 203 J/flash |

[a] Irradiations with $\lambda > 260$ nm in solutions deaerated with Ar streams. The concentration of $[Co(PTS)(OH_{2-n}(Cl)_n]^{(3+n)-}$ was $2.0 \times 10^{-5}$ M for these experiments unless specially stated. [b] Average of 3-7 determinations. [c] Values for $k_{obsd}$ for (a) are $\times 10^3$ and for (b) are $\times 10$.

700 nm and a decrease of the absorbance at other wavelengths, Figure 5b, which indicated that iron(I) sulfophthalocyanine is the reaction product. Moreover, the difference in the values of the molar extinctions of iron(I) and iron(II) sulfophthalocyanines at 450 nm, $\epsilon$ $7.8 \times 10^3$ $M^{-1}$ $cm^{-1}$ for $Fe^I(PTS)^{5-}$ and $\epsilon$ $4.6 \times 10^3$ $M^{-1}$ $cm^{-1}$ for $[Fe(PTS)(OH_2)_2]_2^{8-}$, were used for the evaluation of the product yields; see Table II. These efficiencies were obtained by use of 1–2% conversions into products since secondary processes became otherwise noticeable.

**(C) Photochemical Properties of Cobalt(III)–Acido and Mixed Dimer Species. (1) Photolysis of Acidocobalt(III) Sulfophthalocyanines.** Flash photolyses of the acidocobalt(III) sulfophthalocyanines $Co^{III}(PTS)(H_2O)_{2-n}(X)_n^{(3+n)-}$ ($n = 1, 2$; $X = Cl^-, I^-, SCN^-$) were carried out in deaerated, acidic ($10^{-1}$ M $HClO_4$) solutions, where the ionic strength was adjusted with both the corresponding sodium halide and sodium perchlorate ($[NaClO_4] + [NaX] = 1.0$ M). A cutoff filter, 100% transmission at $\lambda \geq 350$ nm, was used in order to prevent the irradiation of the nonanated species at wavelengths shorter than 350 nm, where they present a large photosensitivity; see section B and ref 1 and 5.

Flash photolyses of $Co(PTS)(H_2O)_{2-n}(Cl)_n^{(3+n)-}$ in solutions equilibrated with 1.0 M NaCl (see above) produce transient absorptions with a maximum absorption at $\lambda_{max} \sim 500$ nm, Figure 6a. The growth and the decay of the absorbance, Figure 6b, are first-order reactions independent of the flash energy; see Table III and the Appendix. However, the rate of growth also has a first-order dependence on the concentration of the complex as is discussed in the Appendix. The disappearance of the absorbance is, in addition, dependent on the concentration of hydrogen ions, as indicated in Table III, the Appendix, and eq 4.

$$k_{obsd} = \left(45 + 0.5\frac{1}{[H^+]}\right) s^{-1} \qquad (4)$$

Transient bleach of the absorbance at 420–540 nm and transient absorbances at 420–540 nm were observed when $Co(PTS)(H_2O)_{2-n}(SCN)_n^{(3+n)-}$ ($n = 1, 2$) was flash photolyzed in 1.0–0.1 M $NCS^-$. These transformations of the spectrum indicate that $Co^{II}(PTS)^{4-}$ is formed during the life of the flash. The amount of the absorbance change, measured at 420 and 580 nm, shows that the amount of the cobalt(II) sulfophthalocyanine, $6.4 \times 10^{-9}$ M $J^{-1}$ for flash energies $E \leq 250$ J/pulse, has a linear dependence on flash energy. Moreover, the recovery of the 420–540-nm absorbance obeys a second-order rate law with a rate constant $k = 2.5 \times 10^8$ $M^{-1}$ $s^{-1}$. Such a value of the rate constant was obtained from the half-life of the reaction and the concentration of cobalt(II)

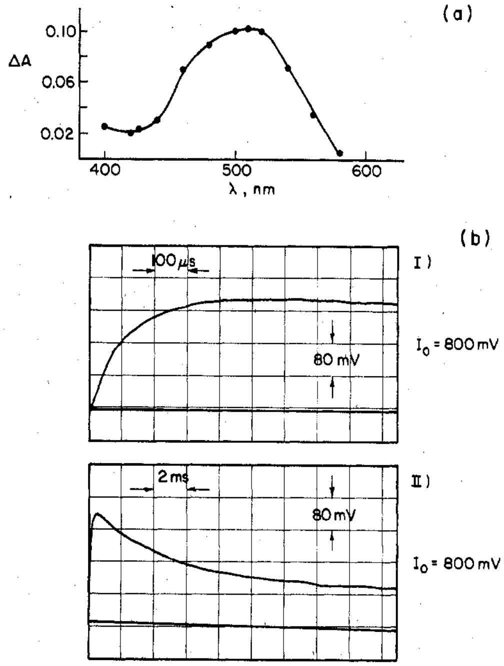


**Figure 6.** (a) Transient spectrum obtained 600 μs after the pulse in flash photolyses of $[Co(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-}$ (conditions: 1 M HCl and $2.0 \times 10^{-5}$ $[Co(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-}$; deaerated solutions). (b) Oscillographic traces showing (I) the growth and (II) the decay of the 500-nm transient absorbance.

sulfophthalocyanine produced during the life of the flash.

Both species, the radical $I_2^-$ and $Co(PTS)^{4-}$, were generated during the life of the pulse in flash irradiations of $Co(PTS)(H_2O)_{2-n}(I)_n^{(3+n)-}$ ($n$ = 1, 2) in 0.1 M NaI. The iodine radical $I_2^-$, detected from its absorptions at $\lambda \leq 420$ nm, disappears in a second-order reaction, rate constant $k = 6.7 \times 10^9\ M^{-1}\ s^{-1}$, by producing $I_3^-$. It was estimated from the absorbance change that $Co^{II}(PTS)^{4-}$ and $I_2^-$ were produced in a 1:1 stoichiometric relationship as indicated in eq 5, where $\beta = (2.7 \pm 0.3) \times 10^9\ M\ J^{-1}$.

$$[I_2^-]_0 = [Co^{II}(PTS)_4^-]_0 = \beta \times \text{flash energy} \qquad (5)$$

Continuous-wave photolyses of $Co(PTS)(H_2O)_{2-n}(I)_n^{(3+n)-}$ ($n$ = 1, 2) were carried in deaerated, acidic ($10^{-1}$ M $HClO_4$) solutions containing 0.1 M NaI. The irradiation produces spectral transformations (see above) which indicate that the product of the reaction is $Co^{II}(PTS)^{4-}$. Quantum yields for excitations at various wavelengths, Table II, show that this process is produced with an energy threshold, $E_{th} \leq 64$ kcal/mol, which is placed at a photonic energy smaller than the threshold for the photoredox dissociation of the dimeric $[Co(PTS)(OH_2)_2]_2^{6-}$, $E_{th} \approx 100$ kcal/mol; see Table II.

The species anated with $SCN^-$ or $N_3^-$ also show photoredox reactions for excitations at wavelengths larger than 300 nm. Indeed, photolyses ($\lambda_{excit}$ 400 nm; $I_0 = 7.5 \times 10^{-5}$ einstein/(L min)) of $Co(PTS)(H_2O)_{2-n}(N_3)_n^{(3+n)-}$ in solutions with $10^{-2}$ M $NaN_3$ produce nitrogen ($\phi$ = 0.11) and $Co^{II}(PTS)^{4-}$ ($\phi$ = 0.10).

**(2) Photolysis of Mixed Dimer Species.** Flash photolyses of the mixed dimer $[Co^{III}(PTS)(OH_2)_2^{3-},Ru(bpy)_3^{2+}]$ were carried out at wavelengths larger than 420 nm, where no photochemical transformations were observed with either monomeric or dimeric cobalt(III) sulfophthalocyanines; see above. Concentrations of $Ru(bpy)_3^{2+}$ ($10^{-2}$–$5 \times 10^{-3}$ M) were adjusted in order to associate 99.9% of the $Co(PTS)(OH_2)_2^{3-}$ ($10^{-6}$–$5 \times 10^{-6}$ M). The photochemical reaction was followed at 520 nm, where large absorptions have been reported for various reduced sulfophthalocyanine radicals coordinated to metal ions; see section B(1) and ref 1, 24, and 25. A transient, detected under these experimental conditions, can be assigned as a cobalt(III) reduced ligand radical, $Co(P\dot{T}S)(OH_2)_2^{4-}$, which is also produced in the photoredox dissociation of $[Co(PTS)(OH_2)_2]_2^{6-}$; see section B(1). This metastable species, $\lambda_{max} \sim 530$ nm, transforms into $Co^{II}(PTS)^{4-}$ by a first-order reaction with $k = 1.6 \times 10^2\ s^{-1}$. This transformation was also followed at wavelengths where the absorptivities of the cobalt(III) sulfophthalocyanine were the largest of all the species, e.g., at $\lambda \geq 580$ nm. The absorbance, bleached during the life of the flash, recovers by two successive stages. The first has a first-order rate constant, $k = 1.7 \times 10^2\ s^{-1}$, which is the same as the transformation of $Co^{III}(P\dot{T}S)(OH_2)_2^{4-}$ into $Co(PTS)^{4-}$; see above. Moreover, the half-life is dependent on the initial amount of the bleached absorbance for the second stage. Such a stage was assigned as a reoxidation of the $Co^{II}(PTS)^{4-}$ by $Ru(bpy)_3^{3+}$. The ratio of the second-order rate constant to the extinction coefficient, $k/\epsilon = 2.7 \times 10^4$ cm $s^{-1}$, was measured at 580 nm. The rate constant $k = 4.5 \times 10^7\ M^{-1}\ s^{-1}$ was obtained from such a ratio by use of the difference in the molar extinctions, $\Delta\epsilon \sim 1.7 \times 10^3\ M^{-1}\ cm^{-1}$, of the cobalt(III) and cobalt(II) sulfophthalocyanines.

Photochemical reactions of the mixed dimer $[Co^{II}(PTS)^{4-},Cr(bpy)_3^{3+}]$ were investigated in solutions ($10^{-6} \geq [Co^{II}(PTS)^{4-}]$ and $10^{-2} \geq [Cr(bpy)_3^{3+}] \geq 5.0 \times 10^{-3}$ M) where more than 90.0% of the complex was associated with $Cr(bpy)_3^{3+}$.[28] Appropriate cutoff filters were used in order to prevent irradiation at wavelengths shorter than 420 nm. This reaction, followed at 560 nm, shows that the absorbance—bleached during the life of the flash—is recovered by two successive stages; see Figure 7a. Also, transient absorbances were observed after the decay of the $^2E$ $Cr(bpy)_3^{3+}$ at 500–520 nm. The same half-life ($t_{1/2} = (1.9 \pm 0.2) \times 10^{-3}$ s), independent of the flash energy, was obtained for the short-lived stages of the absorbance decay at 500 nm and the recovery at 560 nm. Furthermore, the transient absorbances at 450–620 nm indicate that both $Cr(bpy)_3^{3+}$ and an oxidized ligand radical, $Co^{II}(P\dot{T}S)^{3-}$, are primarily formed in this reaction. Therefore, the short-lived stage was assigned as a transformation of the coordinated radical $Co^{II}(P\dot{T}S)^{3-}$ into the stable cobalt(III) sulfophthalocyanine. The long-lived stage, followed either at 500 or 560 nm, Figure 7b, obeys a second-order reaction attributed to the reduction of the cobalt(III) sulfophthalocyanine by $Cr(bpy)_3^{2+}$; see above. The ratio of the second-order rate constant to the extinction coefficient, $k/\epsilon = 1.9 \times 10^5$ cm $s^{-1}$ at 560 nm, gave a rate constant, $k = 8.2 \times 10^8\ M^{-1}\ s^{-1}$, for this reaction.

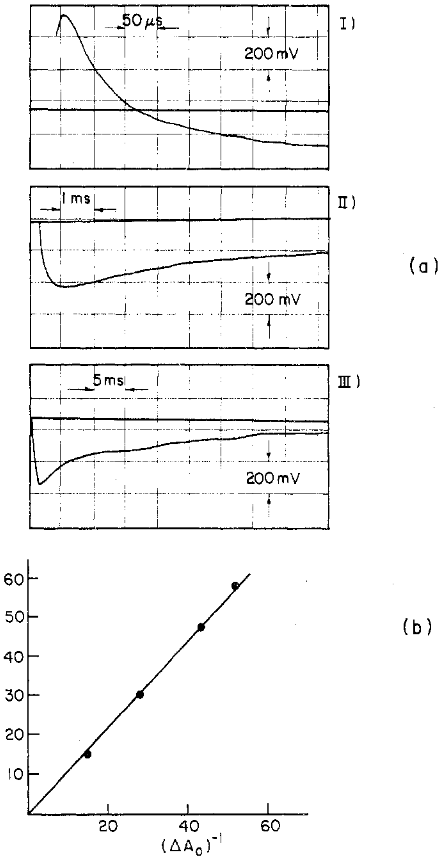


Figure 7. (a) Oscillographic traces obtained in flash photolysis of the mixed dimer $[Co(PTS)^{4-}{\cdot}Cr(bpy)_3^{3+}]$ (conditions: $Co(PTS)^{4-}$, $1.1 \times 10^{-6}$ M; $Cr(bpy)_3^{3+}$, $5.0 \times 10^{-4}$ M in deaerated $10^{-2}$ M $HClO_4$; 250 J/pulse). Reaction was followed at 560 nm showing the $^2E$ $Cr(bpy)_3^{3+}$ (trace I) and the first stage (trace II) and the second stage (trace III) of the recovery of the bleached absorbance. (b) Dependence of the half-lifetime for the second stage upon the reciprocal of the amount of the absorbance bleached 1 ms after the flash, $\Delta A_0$.

Also, the photodissociation of the mixed dimer $[Co(PTS)^{4-},Ru(bpy)_3^{2+}]$ was investigated by use of deaerated, acidic ($10^{-1}$–$10^{-3}$ M HCl) solutions with excess $Ru(bpy)_3^{2+}$ ($10^{-2}$–$10^{-3}$ M). Flash irradiations ($\lambda_{excit} \geq 420$ nm) produced a transient spectrum with a maximum absorbance at 520 nm. This absorbance disappears in two successive steps. The shortest lived stage, followed at 520 nm, has a half-lifetime independent of the flash energy ($t_{1/2}$ = 600 μs for $E \leq 250$ J/flash). This step was assigned as a transformation of a primarily formed radical, $Co^{II}(P\dot{T}S)^{5-}$, into $Co^{I}(PTS)^{5-}$ with a rate constant $k = (1.2 \pm 0.3) \times 10^3\ s^{-1}$. In addition, the cobalt(I) species, $Co^{I}(PTS)^{5-}$, is reoxidized by $Ru(bpy)_3^{3+}$ in the longest lived decay of the transient absorbance. A second-order rate constant $k = 2.9 \times 10^8$ $M^{-1}$ $s^{-1}$ was estimated for such a reaction.

## Discussion

The results, reported above, show that the photochemistry of the cobalt(III) and iron(II) sulfophthalocyanines can be easily influenced by various experimental conditions. Indeed, the association and the nature of the monomeric species, controlled by various media conditions, determine the kind of processes which will be induced by the absorption of light. Some aspects of these processes are discussed next.

The primary species, observed in flash photolysis of the dimeric cobalt(III) and iron(II) sulfophthalocyanines, do not have the spectra expected for complexes with reduced and oxidized metal centers. Furthermore, such species exhibit a chemical reactivity toward oxygen and alcohols which is expected for ligand radicals of the transition-metal sulfophthalocyanines.[1] In this regard, the photochemistry of the dimeric cobalt(III) and iron(II) species exhibited features that were previously reported for photolysis of the dimeric copper(II) sulfophthalocyanine. This photochemical reactivity is represented in a general form by eq 6–9, where M = Co(III)

$$[\mathrm{M(PTS)(OH_2)}_n]_2^{2(6-z)-} + h\nu \rightarrow \text{(excited state)} \quad (6)$$

$$\text{(excited state)} \rightsquigarrow [\mathrm{M(PTS)(OH_2)}_n]_2^{2(6-z)-} \quad (7)$$

$$\text{(excited state)} \rightarrow \mathrm{M(P\dot{T}S)(OH_2)}_n^{(5-z)-} + \mathrm{M(P\dot{T}S)(OH_2)}_n^{(7-z)-} \quad (8)$$

$$\mathrm{M(P\dot{T}S)(OH_2)}_n^{(5-z)-} + \mathrm{M(P\dot{T}S)(OH_2)}_n^{(7-z)-} \rightarrow [\mathrm{M(PTS)(OH_2)}_n]_2^{2(6-z)-} \quad (9)$$

($z$ = 3), Fe(II) ($z$ = 2), or Cu(II) ($z$ = 2) and $n$ = 0, 1, or 2. Recombination of the coordinated radicals, eq 9, returns the photodissociated dimers to their initial condition.

The common features, exhibited by the photochemistries of the dimeric Co(III), Cu(II), and Fe(II) sulfophthalocyanines, show that they must be originated in similar excited states. The nature of this state, charge transfer between units of the dimer or a ligand-centered state, was briefly discussed elsewhere for cobalt(II) and copper(II) sulfophthalocyanines.[1] Moreover, a comparison of the threshold energies for the photoredox dissociation for these complexes (see Table II and ref 1) demonstrates that such energies are almost the same, $E_{\mathrm{th}} \approx 100$ kcal/mol. This independence of the metal ion suggests that the photoreactions are produced in an excited state, where the participation of the metal orbitals must be at a minimum. Such a ligand-centered excited state, e.g., an $n\pi^*$ state of the sulfophthalocyanine, may be mainly localized in one unit of the dimer which will oxidize the ligand or the metal center of the other. This electron-transfer process, between one unit in an excited state and the other in the ground state, does not have to produce primary species, eq 8, with the same nature as that of the products generated by electrochemical means.[23,25] However, one may expect the transformation of the photochemically generated species into more stable redox products by secondary thermal reactions. This seems to be the case of the iron(II) sulfophthalocyanine, where the reduced ligand radical $\mathrm{Fe(P\dot{T}S)(OH_2)_2}^{5-}$, formed in reaction 5, was observed to transform into iron(I) sulfophthalocyanine in a slow process, eq 10.

$$\mathrm{Fe^{II}(P\dot{T}S)(OH_2)_2}^{5-} \rightarrow \mathrm{Fe^{I}(PTS)(OH_2)_2}^{5-} \quad (10)$$

The yields of the photoredox dissociation for cobalt(III), copper(II), and iron(II) sulfophthalocyanines increases with photonic energy. However, 225-nm photolysis of the dimeric cobalt(III) sulfophthalocyanine induces the redox dissociation but with a low yield (see Table II). This behavior is attributed to a competitive population of a new excited state. Indeed, the photochemistries of the acidocobalt(III) sulfophthalocyanines (see below) suggest that states with charge-transfer character, from axially coordinated ligands to Co(III), can be competitively populated for photonic energies larger than 100 kcal/mol. Indeed, the results on the photochemistry of the monomeric acidocobalt(III) sulfophthalocyanines, $[\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{X})_n]^{(3+n)-}$ with $n$ = 1 or 2 and $\mathrm{X}^-$ = $\mathrm{Cl}^-$, $\mathrm{Br}^-$, $\mathrm{I}^-$, $\mathrm{SCN}^-$, or $\mathrm{N_3}^-$, show that they present a significant amount of photoredox chemistry which involves axially coordinated ligands. The photochemical processes can be described by eq 11–15, where CTTM stands for a reactive charge-transfer ligand-to-metal state; see below. Products of reaction 13 can be regarded as ion–radical pairs with the same nature as that of the species which are obtained in the photoredox processes of the acidopentaamminocobalt(III) complexes.[12,30-32]

$$[\mathrm{Co^{III}(PTS)(OH_2)}_{2-n}(\mathrm{X})_n]^{(3+n)-} + h\nu \rightarrow \mathrm{CTTM} \quad (11)$$

$$\mathrm{CTTM} \rightarrow [\mathrm{Co^{III}(PTS)(OH_2)}_{2-n}(\mathrm{X})_n]^{(3+n)-} \quad (12)$$

$$\mathrm{CTTM} \rightarrow \{[\mathrm{Co^{II}(PTS)(OH_2)}_{2-n}(\mathrm{X})_{n-1}]^{(3+n)-},\mathrm{X}\cdot\} \quad (13)$$

$$\{[\mathrm{Co^{II}(PTS)(OH_2)}_{2-n}(\mathrm{X})_{n-1}]^{(3+n)-},\mathrm{X}\cdot\} \rightarrow [\mathrm{Co^{III}(PTS)(OH_2)}_{2-n}(\mathrm{X})_n]^{(3+n)-} \quad (14)$$

$$\{[\mathrm{Co^{II}(PTS)(OH_2)}_{2-n}(\mathrm{X})_{n-1}]^{(3+n)-},\mathrm{X}\cdot\} \rightarrow \mathrm{Co^{II}(PTS)}^{4-} + (n-1)\mathrm{X}^- + \mathrm{X}\cdot \quad (15)$$

Reactions 11–15 are followed by secondary reactions. Radical complexation and disproportionation are processes which dominate the decay of the radicals generated with iodide and thiocyanate complexes.[33,34] Reactions of $\mathrm{I_2}^-$ or $\mathrm{(SCN)_2}^-$ with acidocobalt(III) sulfophthalocyanine complexes were not detected. However, a metastable species, assigned as a cobalt(III) sulfophthalocyanine radical, $[\mathrm{Co(P\dot{T}S)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-}$, was observed in photolysis of the chloride-anated complex $[\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(3+n)-}$. Species with a similar radical nature have been obtained by chemical oxidation of a nonsulfonated phthalocyanine of cobalt(III) in nonaqueous solvents.[35] Moreover, the radical $[\mathrm{Co(P\dot{T}S)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-}$ is closely related to the oxidized product of the reaction 8. The formation of the oxidized radical can be attributed to the oxidation of the $[\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(3+n)-}$ complex by chlorine radicals as is indicated in eq 11–17. The disappearance of $[\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-}$ is a base-assisted process; see eq 4 and the Appendix. Such behavior agrees with reports on the reactivity of a similar sulfophthalocyanine radical coordinated to copper(II).[1,23,24] In this regard, the decay of the intermediate can be represented by an acid–base equilibrium which involves the oxidized ligand, eq 18, followed by degradative reactions of the conjugated forms, eq 19 and 20; see also the Appendix.

$$\mathrm{Cl}\cdot + \mathrm{Cl}^- \rightleftharpoons \mathrm{Cl_2}^- \quad (16)$$

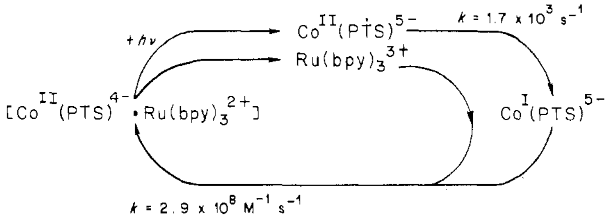
$$\mathrm{Cl_2}^- + [\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(3+n)-} \rightarrow \mathrm{Cl}^- + [\mathrm{Co(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-} \quad (17)$$

$$[\mathrm{Co^{III}(PTS)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-} + \mathrm{H_2O} \rightleftarrows [\mathrm{Co^{III}(\{P\dot{T}S\}OH)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(3+n)-} + \mathrm{H}^+ \quad (18)$$

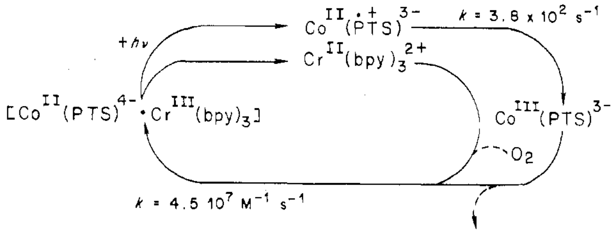
$$[\mathrm{Co^{III}(P\dot{T}S)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(2+n)-} \rightarrow \mathrm{Co^{2+}(aq)} + \text{ligand degradation products} \quad (19)$$

$$[\mathrm{Co^{III}(\{P\dot{T}S\}OH)(OH_2)}_{2-n}(\mathrm{Cl})_n]^{(3+n)-} \rightarrow \mathrm{Co^{2+}(aq)} + \text{ligand degradation products} \quad (20)$$

The photochemical reactivities of the acidocobalt(III) sulfophthalocyanines show that ligand-to-metal charge-transfer states are underlying the ligand-centered states. Therefore, Scheme I



Scheme II



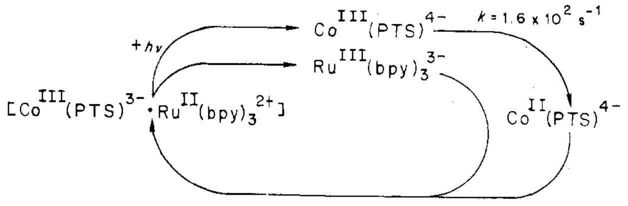
the less significant role of the charge-transfer states in the photochemistry of the dimeric cobalt(III) sulfophthalocyanine can be attributed to a very unfavorable position, namely, above the energy of the photoactive ligand-centered state. This inversion is expected upon consideration of the distinct energies that are associated with the oxidation of the axial ligands, $H_2O$ or $I^-$, in the charge-transfer process.[31,32] It is feasible that similar arguments would be valid in the case of the monomeric sulfophthalocyanines of copper(II) and cobalt(II), where the observed photochemistry is largely related to the population of the ligand-centered states.[1]

The primary photochemical formation of cobalt(I) and cobalt(III) sulfophthalocyanines in the photoredox dissociation of the dimeric cobalt(II) sulfophthalocyanine was reported previously; see ref 1. The photochemical behavior of the Co(II) complex cannot be explained by assuming that such a reactivity is originated in a pure ligand-centered state. Indeed, it is clear, by comparison with sulfophthalocyanines of Co(III), Fe(II), and Cu(II), that the cobalt(II) complex is abnormal for both photochemical[1] and electrochemical processes.[22] One can attribute these departures from the behavior of the other sulfophthalocyanines to large electronic interactions between metal centers of the dimeric cobalt(II) species.[29] Such a possibility was tested by use of mixed dimers which contain sulfophthalocyanines associated with $Ru(bpy)_3^{2+}$ or $Cr(bpy)_3^{3+}$. Negligible or extremely weak interactions between metal centers are expected for these dimers.

The general feature of the electron-transfer processes is the formation of oxidized or reduced sulfophthalocyanine radicals. The intramolecular oxidation or reduction of the metal center in the radical species is observed as a slow secondary process. Indeed, the formation of a stable reducing radical coordinated to an oxidizing metal center, Scheme III, and vice versa, Scheme II, suggests that the overlap between the electronic clouds of the metal center and the sulfophthalocyanine ligand must be weak in these intermediates.

The formation of ligand radicals in the primary electron-transfer process of the cobalt(II) sulfophthalocyanine mixed dimers, Schemes I and II, contrasts markedly with the photoredox reaction which involves both cobalt(II) centers in the dimeric cobalt(II) sulfophthalocyanine.[1] The distinct photochemical behavior exhibited by these species may be attributed to different interactions between metal centers as it is indicated above. In this regard, this argues in favor of the participation of the cobalt(II) orbitals with a larger proportion than in the case of other metal sulfophthalocyanines, e.g., cobalt(III), copper(II), and iron(II), in the description of the excited state.

Scheme III



## Appendix

The formation and decay of the intermediate, generated in flash photolyses of $[Co(PTS)(OH_2)_{2-n}(Cl)_n]^{(3+n)-}$, can be represented by eq 21–23 for a more simple mathematical

$$A + h\nu \rightarrow I + X \tag{21}$$

$$X + A \xrightarrow{k_1} T \tag{22}$$

$$T \xrightarrow{k_0} \text{products} \tag{23}$$

treatment of the problem. The formation of the precursor X (notice X = $Cl_2^-$), eq 21, is regarded as a process faster than reactions 22 and 23. In addition, the intermediate T is equivalent to the observed transient species $[Co(P\dot{T}S)(OH_2)_{2-n}(Cl)_n]^{(2+n)-}$; see (7) in the Discussion. The rate law for this intermediate is shown in eq 24. Conventional methods

$$d[T]/dt = k_1[A][X] - k_0[T] \tag{24}$$

gave the integrated expression of the rate, eq 25, where $[X]_0$

$$[T] = [X]_0\left[\frac{k_1[A]}{k_0 - k_1[A]}\right][e^{-k_1}[A]t - e^{-k_0t}] \tag{25}$$

is the concentration of X generated in the life of the flash. The growth and decay of T (see Figure 6) gives a maximum concentration $[T]_m$, eq 26, at a reaction time $\tau$, eq 27. Values

$$[T]_m = [X]_0\left[\frac{k_1[A]}{k_0}\right] - \frac{k_1[A]}{k_1[A] - k_0} \tag{26}$$

$$\tau = \frac{1}{k_1[A] - k_0} \ln \frac{k_1[A]}{k_0} \tag{27}$$

of the rate constants were obtained from direct measurements at various concentrations of $[Co(PTS)(OH_2)_{2-n}(X)_n]^{(3+n)-}$, $[A] \leq 2 \times 10^{-5}$ M, and flash energies, 250–40 J/flash. In one of these experiments with $[A] = 2.0 \times 10^{-5}$ M (see also Table III and Figure 6) the values of the rate constants were $k_1 = 3.3 \times 10^8$ $M^{-1}$ $s^{-1}$ and $k_0 = 1.2 \times 10^2$ $s^{-1}$. Substitution of $k_1$ and $k_2$ in eq 24 gave $\tau = 625 \times 10^{-6}$ s which is in good agreement with an experimental value $\tau = (650 \pm 50) \times 10^{-6}$ s.

The base-assisted decay of $[Co(P\dot{T}S)(OH_2)_{2-n}(Cl)_n]^{(2+n)-}$ was represented by eq 18–20, where the acid–base equilibrium 18 is expected to be very fast. Therefore, the conjugate species can be regarded as being in equilibrium throughout the reaction. Such an assumption yields eq 28 for the expression

$$k_0 = k_{19} + \left[\frac{k_{20} - k_{19}}{[H^+] + K}\right]K \tag{28}$$

of $k_0$, where $K$ is the dissociation constant of equilibrium 18 and $k_{19}$ and $k_{20}$ are the rate constants for the conjugate species. Values of $k_0$, obtained with various concentrations of acid, were used in conjunction with eq 28. The values obtained were $k_{18} \simeq 4.5 \times 10$ $s^{-1}$, $k_{20} \simeq 1.4 \times 10^2$ $s^{-1}$, and $K \approx 5.9 \times 10^3$.

**Acknowledgment.** The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1890

from the Notre Dame Radiation Laboratory.

**Registry No.** $Fe^{II}(PTS)^{4-}$, 69087-62-3; $Co^{II}(PTS)^{4-}$, 67462-30-0; $Co^{III}(PTS)^{3-}$, 69087-63-4; $Co^{III}(PTS)(H_2O)Cl^{4-}$, 69028-14-4; $Co^{III}(PTS)Cl_2{}^{5-}$, 69028-15-5; $Co^{III}(PTS)(H_2O)I^{4-}$, 69056-52-6; $Co^{III}(PTS)I_2{}^{5-}$, 69028-16-6; $Co(PTS)(H_2O)(SCN)^{4-}$, 69028-17-7; $Co(PTS)(SCN)_2{}^{5-}$, 69042-79-1; $Co(PTS)(H_2O)(N_3)^{4-}$, 69028-18-8; $Co(PTS)(N_3)_2{}^{5-}$, 69028-19-9; $Fe(PTS)(OH_2)_2{}^{5-}$, 69028-20-2; $[Co(PTS)(OH_2)_2{}^{3-},Cr(bpy)_3{}^{3+}]$, 69028-25-7; $[Co(PTS)(OH_2)_2{}^{3-},Ru(bpy)_3{}^{2+}]^-$, 69028-26-8; $[Co(PTS)(OH_2)_2{}^{4-},Cr(bpy)_3{}^{3+}]^-$, 69028-28-0; $[Co(PTS)(Cl)_2]Na_5$, 69028-21-3; $[Co(PTS)(Br)_2]Na_5$, 69028-22-4; $[Co(PTS)(NCS)_2]Na_5$, 69028-23-5; $[Co^{II}(PTS)^{4-},Ru(bpy)_3{}^{2+}]^{2-}$, 69028-30-4.

**Supplementary Material Available:** Figure 1 showing transformations in the absorption spectrum of cobalt(III) and cobalt(II) sulfophthalocyanines and Table I with analytical data for acidocobalt(III) sulfophthalocyanines (3 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) G. Ferraudi and E. Srisankar, *Inorg. Chem.*, **17**, 3164 (1978).
(2) Ligand abbreviations: $(PTS)^{6-}$, phthalocyaninetetrasulfonate hexaanion; $(\dot{P}TS)^{5-}$, one-electron-oxidized radical; $(P\dot{T}S)^{7-}$, one-electron-reduced radical; $(PTSH)^{5-}$, hydrogenated derivative with the same oxidation state as $(PTS)^{6-}$.
(3) Y. Harel and J. Manassen, *J. Am. Chem. Soc.*, **99**, 5817 (1977).
(4) Y. Harel, J. Manassen, and H. Lavanon, *Photochem. Photobiol.*, **23**, 337 (1976).
(5) P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc. A*, 90 (1968).
(6) G. Ferraudi and J. F. Endicott, *J. Am. Chem. Soc.*, **99**, 243 (1977).
(7) C. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, **99**, 1276 (1977), and references therein.
(8) R. T. Taylor, L. Smucker, M. L. Hanna, and J. Gill, *Arch. Biochem. Biophys.*, **156**, 521 (1973).
(9) Although it is accepted that $\pi-\pi^*$ transitions make the main contribution to the absorption spectrum of the phthalocyanines, the authors do not agree on the order of the excited states which are populated in these transitions; e.g., see ref 10. Moreover, charge-transfer transitions with a metal-to-ligand character have been assigned for various iron(II) sulfophthalocyanine complexes and cobalt(I) sulfophthalocyanine; see for example: M. Whalley, *J. Chem. Soc.*, 866 (1964); B. W. Dale, *J. Chem. Soc.*, 331 (1968); ref 5.
(10) A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 65 (1965).
(11) C. A. Parker and G. E. Hatchard, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1965).
(12) G. Ferraudi, J. F. Endicott, and J. Barber, Jr., *J. Am. Chem. Soc.*, **97**, 6406 (1975).
(13) G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).
(14) J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).
(15) J. Fries, "Trace Analyses", E. Merk, Darmstadt, 1971.
(16) G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).
(17) W. Wolfrom, *Methods Carbohydr. Chem.*, **1** (1962).
(18) B. R. Baker and B. D. Mehta, *Inorg. Chem.*, **4**, 848 (1965).
(19) K. Bernaver and S. Fallab, *Helv. Chim. Acta*, **44**, 1728 (1961).
(20) A. R. Monahan, J. A. Brado, and A. F. DeLuca, *J. Phys. Chem.*, **76**, 446 (1972).
(21) A very intense absorption, $\epsilon \sim 10^5\ M^{-1}\ cm^{-1}$, is observed at $\lambda_{max} \sim 680$ nm in the absorption spectra of the monomeric sulfophthalocyanines.[19] This is a very noticeable difference with the absorption spectrum of the dimeric species.[19,20] Moreover, both the differences in the absorption spectra of the monomeric and dimeric species and the dependence of the association equilibrium in medium conditions[20] suggest that a large component of the dimer may be due to ligand–ligand interactions. This will compensate the Coulombic repulsion of the sulfonate groups.
(22) Supplementary material.
(23) Anation equilibria have been observed in related systems. See for example: J. J. Watkins and A. Balch, *Inorg. Chem.*, **14**, 2720 (1965); D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, **96**, 2733 (1974); E. B. Fleischer, S. Jacobs, and L. Mestichelli, *ibid.*, **90**, 2527 (1968); R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 886 (1975).
(24) L. D. Rollman and R. T. Imamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).
(25) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **73**, 2847 (1951).
(26) C.-Y. Li and D.-H. Chin, *Anal. Lett.*, **8**, 291 (1975).
(27) Failures in the deaeration of the solution gave values of the product yields which were larger than the limit reported above.
(28) The long life of $^2E\ Cr(bpy)_3{}^{3+}$ allows a dynamic quenching of this species by bulk sulfophthalocyanine. However, this process makes a very small contribution to the overall reaction under the experimental conditions indicated above.
(29) See ref 10, ESR spectra, p 78–80.
(30) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
(31) J. F. Endicott, *Concepts Inorg. Photochem.*, 104–134 (1975).
(32) G. J. Ferraudi and J. F. Endicott, *J. Phys. Chem.*, **80**, 949 (1976).
(33) Complexation and disproportionation of iodine radicals: $I^- + I\cdot \rightleftharpoons I_2{}^-$, $k = 1.1 \times 10^5$; $I\cdot + I\cdot \rightarrow I_2$, $k = 10 \times 10^9\ M^{-1}\ s^{-1}$; $I_2{}^- + I_2{}^- \rightarrow I_3{}^-$, $k = 9 \times 10^9\ M^{-1}\ s^{-1}$ [J. K. Thomas, *Adv. Radiat. Chem.*, **1**, 103 (1969); I. M. Grossweiner and M. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957)].
(34) Complexation and disproportionation of thiocyanate radicals: $SCN\cdot + SCN^- \rightleftharpoons (SCN)_2{}^-$, $k = 2.0 \times 10^5$; $SCN\cdot + SCN\cdot \rightarrow (SCN)_2$, $k = 5.0 \times 10^9$; $(SCN)_2{}^- + (SCN)_2{}^- \rightarrow (SCN)_2 + 2SCN^-$, $k = 2.1 \times 10^9$ [M. Schoneshofer and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **74**, 393 (1970); J. H. Baxendale and D. A. Stott, *Proc. Chem. Soc., London*, 699 (1967); J. A. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968)].
(35) J. F. Myers, G. W. Rayner Canham, and A. B. P. Lever, *Inorg. Chem.*, **14**, 461 (1975).

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# Ligand Field Parameters and Photochemistry from Charge-Transfer Excited States of Bis[*o*-phenylenebis(dimethylarsine)]iron(III) Halides

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*Received July 20, 1978*

The charge-transfer spectroscopy and photochemistry of the title compounds $Fe(das)_2XY^+$ ($X^-$, $Y^-$ = $Cl^-$, $Br^-$, $I^-$) are reported. The d-orbital energies are determined from the arsine-to-iron charge-transfer spectra. Ligand field and angular overlap parameters are calculated from the charge-transfer spectra and compared to those of other first-row transition-metal(III) compounds. $Fe(das)_2Cl_2{}^+$ reacts photochemically in the presence of organoiodides to produce $Fe(das)_2ClI^+$ with quantum yields on the order of $10^{-3}$.

The electronic spectroscopy and photochemistry of metal complexes containing ligands having low optical electronegativity are not well understood. Accurate determination of the ligands' spectrochemical properties is frequently prevented by low-energy ligand-to-metal charge-transfer absorption bands which obscure the ligand field transitions. Photoreactions from charge-transfer states include photoredox reactions and reactions of coordinated ligands for which detailed understanding is lacking. Recent spectroscopic and photochemical studies of charge-transfer excited states suggest that the photoreactions can be interpreted in terms of a formally reduced metal center in ligand-to-metal charge-transfer (LTMCT) excited states[1-4] and a formally oxidized metal in metal-to-ligand charge-transfer (MTLCT) excited states.[5,6] However, many CT states transfer energy via intersystem crossing to lower lying ligand field states, and many are photoinactive.[1,7-9]

During spectroscopic and photochemical studies in this laboratory of metal complexes of bis[*o*-phenylenebis(dimethylarsine)], das, it was observed that the slightly photoactive *trans*-dihaloiron(III) complexes contained four well-resolved charge-transfer absorptions in addition to much

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