transition between A_{1u}' and A_{1g}' is symmetry forbidden. Due to electron-phonon coupling, however, there may be relatively weak vibronic transitions from the vibrationally nonexcited A_{1u}' state to excited vibrational levels of the A_{1g} state, namely, an $\vec{E}\perp c$ transition for an e_g vibration and an $\vec{E}\parallel c$ transition for an a_{2g} vibration.

At low temperatures ($T \approx 1.9$ K) the sole $\vec{E}\perp c$ emitting state is the relatively long-lived A_{1u}'. With increasing temperature E_u' becomes thermally repopulated and begins to dominate the $\vec{E}\perp c$ emission, accompanied by a blue shift in the order of the vibrational energy e_g and an increase of the intensity. This is the explanation of the observed behavior of the $\vec{E}\perp c$ emission between $T = 1.9$ and 10 K (Figures 3 and 4).

The right side of Figure 10 presents the energy level diagram of a $[Pt(CN)_4]^{2-}$ ion in a homogeneous magnetic field, $\vec{H}\perp c$. The magnetic field lowers the local symmetry to C_{2h}' and the E_u' state splits into B_u' and A_u'. An important consequence of the symmetry lowering is the magnetic field induced interaction of $A_u'(E_u')$ and $A_u'(A_{1u}')$. This mixing opens up a new radiative channel from the lowest A_u state to the vibronic A_g' ground state. This explains the large, magnetically induced blue shift of the $\vec{E}\perp c$ emission and its saturation behavior at $T = 4.2$ K when the emission from A_u' dominates. The observed value of 220 cm^{-1} is smaller than the molecular e_g vibrational wavenumber (318 cm^{-1}) because the emission from the E_u' state cannot be totally neglected at $T = 4.2$ K.

Conclusion

With enH_2CP for the first time a tetracyanoplatinate(II) complex with an organic cation has been studied by spectroscopic methods. The optical properties (polarized absorption and emission) of enH_2CP single crystals measured under variation of temperature (1.9 K $\leq T \leq$ 295 K), hydrostatic pressure (1 atm $\leq P \lesssim$ 32 kbar), and magnetic fields ($0 \leq H \leq 5$ T) behave just like those found for tetracyanoplatinates(II) with alkali or alkaline-earth cations. There we see a further strong indication that the role of the cations seems to be restricted to the adjustment of the intrachain Pt-Pt distance R.

With decreasing temperature down to $T \approx 50$ K the absorption energy is shifted to the red. Below this temperature it remains constant. A corresponding behavior has been observed for the polarized emission between room temperature and $T \approx 10$ K. Following the R^{-3} law, which correlates the optical frequencies of quasi-one-dimensional tetracyanoplatinates(II) with the intrachain Pt-Pt distance R, the observed temperature dependence expresses a thermal contraction, which is completed at $T \approx 50$ K. The polarized emission of enH_2CP single crystals shows a drastic pressure-induced red shift of ~360 cm^{-1}·kbar^{-1}, corresponding to a linear compressibility of ~5.3×10^{-3} kbar^{-1}. Above 10.5 kbar the crystals seem to undergo a phase transition.

In the low-temperature range between T = 1.9 K and $T \approx 10$ K at least two excited states take part in the $\vec{E}\perp c$ emission. Below $T \approx 5$ K the upper one is frozen out. Increasing the temperature and raising the magnetic field strength $\vec{H}\perp c$ yields a blue shift of ~220 cm^{-1}, which is traced back to a vibrational quantum of the crystal-bound $[Pt(CN)_4]^{2-}$ ion.

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Photochemistry of Transition-Metal Phthalocyanines. Analysis of the Photochemical and Photophysical Properties of the Acido(phthalocyaninato)rhodium(III) Complexes

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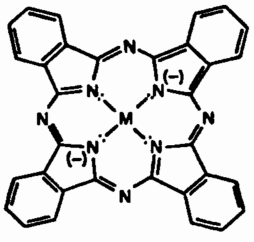
The ultraviolet photochemistry of the rhodium(III) phthalocyanines $Rh(ph)(CH_3OH)X$ with X = Cl^-, Br^-, and I^- was investigated at different wavelengths. The same action spectrum for the photoinduced hydrogen abstraction was obtained for the three compounds. The photonic energy of the excitation is degraded in part by emission at short wavelengths, e.g. $\lambda_{max} \approx 420$ nm. Such a violet emission, observed with phthalocyanines of Al(III), Rh(III), Co(III), and Ru(II), has been attributed to the relaxation of an upper $^3\pi\pi^*$ excited state. The emission spectra at 77 K exhibited vibronic components with a separation between successive peaks $\Delta\nu \approx 1.3 \times 10^3$ cm^{-1}. A comparison between the excitation and action spectra shows the difference in the paths that populate the reactive $n\pi^*$ and upper emissive $\pi\pi^*$ states. An investigation of the time dependence of the upper $^3\pi\pi^*$ emission and lowest $^3\pi\pi^*$ absorptions reveals the participation of triplet sublevels in the degradation of the excitation energy. The relationship between photoemissive and photoreactive states is discussed.

Introduction



I

The ultraviolet photochemistry of several monomeric and dimeric transition-metal phthalocyanines (I) has been investigated in recent years.[1-6] Most of these compounds undergo photoinduced reductions by abstraction of hydrogen from the solvent (eq 1). Such a photochemical reactivity has been

$$\begin{gathered} M(pc) \underset{\leftarrow\cdots}{\xrightarrow{h\nu}} n\pi^* \xrightarrow{SH} M(\dot{p}c\text{-}H) + S\cdot \\ (\text{e.g., } M = Cu(II), Co(II), Rh(III)) \end{gathered} \tag{1}$$

associated with the population of reactive $n\pi^*$ excited states,

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(1) G. Ferraudi and E. V. Srisankar, *Inorg. Chem.*, **17**, 3164 (1978).
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(3) K. Schmatz, S. Muralidharan, K. Madden, R. Fessenden, and G. Ferraudi, *Inorg. Chim. Acta*, **64**, L23 (1981).
(4) R. Prasad and G. Ferraudi, *Inorg. Chim. Acta*, **54**, L231 (1981).
(5) R. Prasad and G. Ferraudi, *Inorg. Chem.*, **21**, 2967 (1982).
(6) K. Schmatz, S. Muralidharan, and G. Ferraudi, *Inorg. Chem.*, **21**, 2961 (1982).

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namely, states that involve the nonbonding orbitals of the bridging nitrogens of the phthalocyanine ligand. The rhodium(III) phthalocyanines, $Rh(pc)(CH_3OH)X$ with X = Cl^-, Br^-, or I^-, exhibited this type of photochemistry.[3,6] The overall photoprocess can be described as a redox-induced substitution of the axial ligand, namely, one that forms the terminal $Rh(pc)(solvent)_2^+$ and X^- products.[3,6] Such a photochemistry departs from the photochemical behavior of the isoelectronic cobalt(III) phthalocyanines. Such complexes exhibited a photochemistry that is a characteristic of the acido to cobalt(III) charge-transfer states, $CT_{X\rightarrow Co}$ (eq 2).[2]

$$Co^{III}(pc)X \overset{h\nu}{\rightleftarrows} CT_{X\rightarrow Co} \rightarrow Co^{II}(pc) + X\cdot \qquad (2)$$

The excitation of transition-metal phthalocyanines and phthalocyanines with closed-shell ions, e.g., Mg(II) or Al(III), at wavelengths of the near-infrared band does not produce any chemical transformation of the complexes. However, lowest lying $^3\pi\pi^*$ excited states, lifetimes between 30 ns and 10 μs, are produced in the near-infrared excitations.[5,7-11] Such states behave as oxidants capable of reductive quenching (eq 3).[9,12-15]

$$M(pc) \overset{h\nu}{\rightleftarrows} {}^3\pi\pi^* \xrightarrow{D} M(\dot{p}c)^+ + D^-\cdot \qquad (3)$$

The singlet state is much shorter lived than the triplet states but can also be quenched by some of the triplet-state quenchers.[9] These low-lying singlet and triplet states undergo competitive nonradiative and radiative relaxations with the emissions placed in the near-infrared region, $\lambda_{em} > 600$ nm.[8,9] We have previously observed that the population of the low-lying $\pi\pi^*$ takes place to some degree by relaxation from upper states, namely, states populated by irradiation at wavelengths of the B, N, L, and C bands in the UV regions.[5,16] However, it is clear that some upper states can trap some of the excitation energy and emit light. We have investigated in this work the participation of the upper states in the degradation of the excitation energy and their relationship with the reactive $n\pi^*$ state.

Experimental Section

Laser Flash Photolysis. Laser flash photolysis experiments were carried out in an apparatus that was described elsewhere.[6,19] A Quanta Ray neodymium yag pumped dye laser with a DCM dye was used as a source of 10-ns pulses of 640-nm light. The collimated light of the high-pressure xenon lamp was used for monitoring the species formed in laser excitation. The xenon lamp was pulsed several orders of magnitude above the steady-state power in order to enhance the sensitivity of the detection system. The phototube output was digitized and processed by a PDP-11 computer. These experiments were performed with deaerated solutions that were refreshed after each irradiation.

Emission Experiments. Time-resolved luminescence experiments for emissions in the ultraviolet or visible regions were carried out with a Photochemical Research Associates apparatus provided with excitation and emission monochromators. The output, stored in a Terak microprocessor, was finally processed by a Digital PDP-11 computer.

The emission and excitation spectra were determined in a spectrofluorimeter equipped with single-photon counting and programmed correction of instrument response. In this regard the spectra reported in this work have been corrected for instrument response and determined under conditions where experimental artifacts, e.g., self-absorption, could be ignored.[20] Calibrations with quinine sulfate in 1 M H_2SO_4 were used for the determination of emission yields.

Experiments carried out at temperatures lower than room temperature were carried out with the sample cell inserted in a Dewar flask. Appropriate thermostatic baths of given temperatures or liquid nitrogen were used for stabilizing the temperature of the sample.

Quantum Yields. Continuous-wave irradiations at 254 nm were carried out with low-pressure mercury lamps. A Rayonet lamp, placed in a Merry-Go-Round minireactor, or a U-shaped GE 4T4 lamp were used for 254-nm photolyses under different geometrical configurations and intensities. A high-pressure xenon lamp, VIX 300 W UV Eimac Illuminator, coupled with a high-intensity monochromator and collimating lenses was used for quasi-monochromatic visible and ultraviolet irradiations. Values of the light intensity were measured with tris(oxalato)ferrate(III).[21] Routine checks of the intensity at wavelengths shorter than 300 nm were carried out with $Co(NH_3)_5Br^{2+}$ or with a thermopile-microvoltmeter apparatus. The concentrations of the photolytes were adjusted in order to absorb more than 99.99% of the incident light. Quantum yields were from the slope of concentation vs. irradiation extrapolated to zero time.

Chloride, bromide, and iodide ions were analyzed with ion-selective electrodes.[6] Irradiated solutions and blanks were diluted with a $NaNO_3$ solution in order to adjust the ionic strength to 0.1 M. A differential procedure was used whenever the analysis demanded to measure ion concentrations in regions where the electrodes exhibit a low sensitivity. A known concentration of the halide was added to the blank and irradiated solutions in order to bring an appropriate sensitivity to the electrodes. The difference in the redox potentials of the solutions, prepared with the sample and the blank, was associated with the additional concentration of halide produced during photolyses.

Materials. The rhodium(III) complexes, $Rh(ph)(CH_3OH)X$ with X = Cl^-, Br^-, and I^-, were prepared according to procedures reported elsewhere.[6] The ruthenium(II) phthalocyanine $Ru(ph)(py)_2$ was available from a previous work.[15] Aluminum phthalocyanine, Al(ph)Cl, was obtained from Eastman and was purified by recrystallization. The purity of each compound was tested by means of the elemental analysis, the extinction coefficients of the absorption bands in the UV-vis region, and the photochemical and photophysical response to the irradiation in the Q and N bands.

Acetonitrile, Aldrich Gold Label, was distilled in an all-glass apparatus provided with a 40-theoretical-plate fractionating column. The distillate was dried over molecular sieves. Solutions were prepared with freshly distilled solvent. Other chemicals were analytical grade and used without further purification.

Results

Emission and Excitation Spectra. During our study of the photochemistry of rhodium(III) phthalocyanines we observed that the ultraviolet excitation of these compounds, $\lambda_{excit} \leq 370$ nm, induced a broad violet emission with $\lambda_{max} \approx 420$ nm (Figure 1). The emission is not characteristic of the rhodium(III) complexes alone, and it has also been observed with phthalocyanines containing open-shell diamagnetic ions, e.g., Co(III) and Ru(II), and closed-shell ions, e.g., Al(III). Emission with an extremely low intensity was observed with copper(II) phthalocyanine (see below). The emission spectra

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(7) P. S. Vincett, E. A. Voigt, and R. E. Riechkoff, *J. Chem. Phys.*, **55**, 4131 (1971).

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(10) E. R. Menzel, K. E. Rieckhoff, and E. M. Voigt, *Chem. Phys. Lett.*, **13**, 604 (1972).

(11) The properties of the lowest lying triplet state of rhodium(III) phthalocyanines were previously investigated by E. R. Menzel, K. E. Rieckhoff, and E. M. Voigt, *J. Chem. Phys.*, **58**, 5726 (1973). Although the structure of the compounds used by these authors is bound to some uncertainties (see the ninth line from the bottom in the second column of p 5726), we found quite good agreement on experimental details where there is overlap between works.

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(15) D. R. Prasad and G. Ferraudi, *J. Phys. Chem.*, **86**, 4037 (1982).

(16) The absorption bands at $\lambda_{max} \approx$ 650, 320, 275, 245, and 200 nm are ligand-centered $\pi \rightarrow \pi^*$ transitions commonly labeled as Q, B, N, L, and C bands.[17,18]

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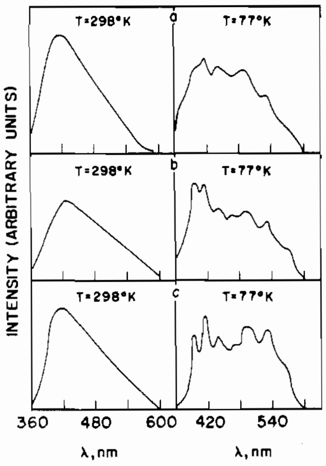

Figure 1. Emission spectra of the rhodium(III) phthalocyanines, Rh(pc)(CH_3OH)X, with (a) X = Cl^-, (b) X = Br^-, and (c) X = I^- in deaerated CH_3CN (T = 298 K) or 9:1 ethanol–methanol (T = 77 K).

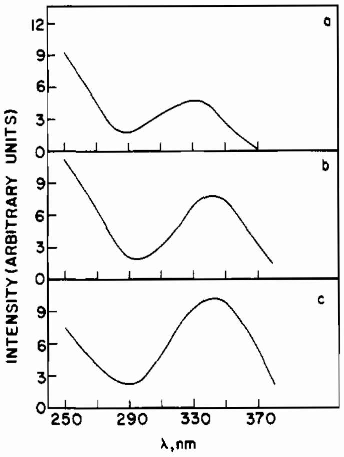

Figure 2. Excitation spectra of Rh(pc)(CH_3OH)X with (a) X = Cl^-, (b) X = Br^-, and (c) X = I^- in deaerated CH_3CN at 298 K. The intensity of the emission was investigated at 420 nm.

at low temperatures, e.g., in glassy solutions at T = 77 K, exhibited vibronic structure with a separation $\Delta\nu \approx 1.3 \times 10^3$ cm^{-1} between successive peaks (Figure 1). These spectra, obtained by excitation by various wavelengths, remain the same with the exception of minor variations due to the appearance of additional vibration levels and changes in relative intensities.

The spectra described above can be explained by considering that the luminescence originates in an upper ligand-centered excited state as in the case of the porphyrins.[22] Indeed, the excitation spectra of Rh(pc)(CH_3OH)X, X = Cl^-, Br^-, and I^-, present maxima at $\lambda_{max} \approx 330$ nm (Figure 2). Such maxima, placed at wavelengths of the ultraviolet band N, constitute one major difference between the excitation and action spectra (see below).

Quantum yields of the violet emission have been measured for a number of phthalocyanines under different experimental conditions (Table I). Phthalocyanines with diamagnetic ions have small yields, $\phi \approx 10^{-3}$, and are not strongly dependent on temperature and solvent composition (Table I). One exception to this behavior is observed with Ru(pc)$(py)_2$, where the yield of emission varies one order of magnitude between room temmperature and 77 K. In addition, the emission yield of copper(II) phthalocyanine is one order of magnitude smaller than those of the phthalocyanines with diamagnetic ions (Table I). This difference in yields between phthalocyanines with paramagnetic and diamagnetic ions is similar to that observed between the yields of emission from the lowest lying $\pi\pi^*$ excited states.

Table I. Quantum Yields of Emission for Various Phthalocyanines for Excitation at 320 nm

compd[b]	solvent[a]	temp, K	$10^3\phi$
Rh(pc)(CH_3OH)Cl	CH_3CN	298	1.4
	CH_3CN	243	1.5
	9:1 ethanol-methanol	298	1.2
	9:1 ethanol-methanol	77	3.2
	CH_2Cl_2	298	1.3
	methanol	298	1.4
	4:1 benzene-CH_3CN	298	1.4
Rh(pc)(CH_3OH)Br	CH_3CN	298	1.2
	9:1 ethanol-methanol	298	1.3
	9:1 ethanol-methanol	77	3.1
Rh(pc)(CH_3OH)I	CH_3CN	298	1.4
	9:1 ethanol-methanol	298	1.3
	9:1 ethanol-methanol	77	3.6
Al(pc)Cl	9:1 ethanol-methanol	298	0.5
	9:1 ethanol-methanol	77	0.8
$[Co(pts)]^{3-}$	ethanol	298	0.5
	ethanol	77	1.6
$[Cu(pts)]^{4-}$	ethanol	298	0.035
	ethanol	77	0.04
Ru(pc)$(py)_2$	9:1 ethanol-methanol	298	0.77
	9:1 ethanol-methanol	77	8.5

[a] Deaerated solutions. [b] Abbreviations: pc = phthalocyanine; pts = tetrasulfophthalocyanine; py = pyridine.

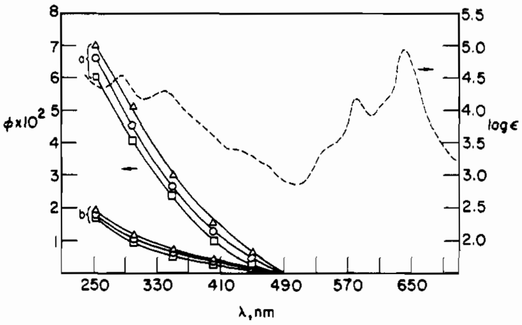

Figure 3. Action spectra showing the dependence of the quantum yields on excitation wavelength for Rh(pc)(CH_3OH)Cl (△), Rh(pc)(CH_3OH)Br (○), and Rh(pc)(CH_3OH)I (□) in (a) 2.5 M 2-propanol in CH_3CN and (b) 0.5 M 2-propanol in CH_3CN. The absorption spectrum of Rh(pc)(CH_3OH)Cl (---) has been superimposed on the action spectra.

Action Spectra. In order to find the relationship between the $n\pi^*$ photoreactive state and the photoemissive state, we have studied the dependence of the quantum yields on excitation wavelength. The stoichiometry of the photochemical reaction induced in 254-nm irradiations of Rh(pc)(CH_3OH)X, X = Cl, Br, and I, was previously reported.[3,6] The same stoichiometry, namely, $\phi_{X^-} = \phi_{Rh(pc)(solvent)_2^+}$, was obtained for ultraviolet irradiations, λ_{excit} <<ldq 500 nm, of the Rh(pc)(CH_3OH)X compounds in deaerated 2-propanol–acetonitrile solutions. We have verified again that for excitation at each particular wavelength there was no dependence of the Rh(pc)$(solvent)_2^+$ and X^- quantum yields on complex concentration or light intensity, namely, less than 3% variation for $10^{-5} \leq I_0 \leq 3 \times 10^{-4}$ einstein/L min.[23] Moreover, plots of the quantum yield vs. 2-propanol concentration reach a plateau for [2-propanol] ≥ 1.0 M. The action spectra obtained

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(22) An emission from the second excited singlet in porphyrins was reported by L. Bajema and M. Gouterman, *J. Mol. Spectrosc.*, **39**, 421 (1971).

(23) We have already reported that the transient response observed in flash photolysis of Rh(pc)(CH_3OH)X, X = Cl^-, Br^-, I^-, at $\lambda_{excit} \geq 280$ nm is the same as that observed at $\lambda_{excit} \geq 320$ nm.[6] We have confirmed in this work that the transient behavior is the same in the entire ultraviolet region, e.g., $260 \leq \lambda_{excit} \leq 500$ nm.

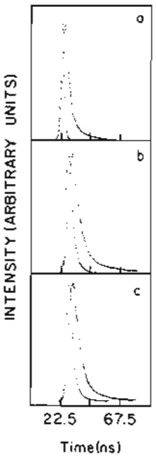

Figure 4. Time-resolved profile of the violet emission for (a) Rh(pc)(CH_3OH)Cl, (b) Rh(pc)(CH_3OH)Br, and (c) Rh(pc)(CH_3OH)I in deaerated CH_3CN at 298 K. Inner curves show the lamp's profile.

in photolyses of Rh(pc)(CH_3OH)X, X = Cl^-, Br^-, ad I^-, are reported in Figure 3.

A comparison of the photochemical properties of the rhodium(III) phthalocyanines at various excitation wavelengths reveals that the Rh(pc)(solvent)$_2^+$ and X^- products are formed by the same reaction mechanism previously reported for 254-nm irradiations.[6] In this regard the formation of the products can be described in a summarized form by eq 4–10.

$$\mathrm{Rh(pc)(CH_3OH)X} \xrightarrow[\phi_T]{+h\nu} n\pi^* \tag{4}$$

$$n\pi^* \xrightarrow{k_r} \mathrm{Rh(pc)(CH_3OH)X} \tag{5}$$

$$n\pi^* + \mathrm{SH} \xrightarrow{k_r'} \mathrm{Rh(pc)(CH_3OH)X} \tag{6}$$

$$n\pi^* + \mathrm{SH} \xrightarrow{k_R} \mathrm{Rh(\dot{p}c\text{-}H)(CH_3OH)X} + \mathrm{S}\cdot \tag{7}$$

$$\mathrm{S}\cdot + \mathrm{(CH_3)_2CHOH} \rightarrow \mathrm{SH} + \mathrm{(CH_3)_2\dot{C}OH} \tag{8}$$

$$\mathrm{Rh(\dot{p}c\text{-}H)(CH_3OH)X} \xrightarrow{\text{oxidant}} \mathrm{Rh(pc)(SH)_2}^+ + \mathrm{X}^- \tag{9}$$

$$2\mathrm{(CH_3)\dot{C}OH} \rightarrow \mathrm{(CH_3)_2CO} + \mathrm{(CH_3)_2CHOH} \tag{10}$$

The yields of the products Rh(pc)(solvent)$_2^+$ and X^-, abbreviated as ϕ_P, can be expressed as a function of the yield for the $n\pi^*$ formation, ϕ_T, and the rate constants for various transformations of the $n\pi^*$ species (eq 11). It follows from

$$\phi_P = \phi_T \frac{k_R[\mathrm{SH}]}{k_r + (k_r' + k_R)[\mathrm{SH}]} \tag{11}$$

eq 11 that the yields ϕ_P for a constant concentration of SH and/or $k_r < (k_r' + k_R)[\mathrm{SH}]$ (eq 12) will change with excitation

$$\phi_P \simeq \phi_T \frac{k_R}{k_r' + k_R} \qquad k_r < (k_r' + k_R)[\mathrm{SH}] \tag{12}$$

wavelength in a manner determined by ϕ_T. Figure 1 shows that ϕ_P does not depend on the ligand coordinated in the axial position. Moreover, ϕ_P increases with excitation energy from a threshold energy, $E_{th} \approx 243$ kJ/mol, which is the same for the three rhodium(III) complexes.

Excited-State Lifetimes. The observation of the upper emissive $\pi\pi^*$ state in laser flash photolysis is precluded by the time resolution of our apparatus. However, the decay of this state can be followed by means of the time dependence of the emitted light in single-photon counting experiments. Such intensity decreases with increasing time in a manner that cannot be fitted by a single exponential function (Figure 4). The best agreement between experimental and theoretical curves is obtained with a double-exponential function. This suggests two parallel paths for the emission. Such a complex decay of the intensity is exhibited by all the rhodium(III) complexes investigated in this work. Moreover, the rate of decay of the intensity is independent of medium conditions and monitoring wavelength, e.g., monitoring wavelengths 400 ≤ λ_{ob} ≤ 460 nm, and excitation wvelength, e.g., monochromatic excitation at λ_{excit} ≤ 360 nm, but shows a moderate dependence on the temperature (Table II).

Table II. Excited-State Lifetimes of Rh(pc)(CH_3OH)X Complexes

compd	solvent[a]	temp, K	τ_1	τ_2
λ_{excit} = 320 nm, λ_{ob} = 420 nm[b,d]				
Rh(pc)(CH_3OH)Cl	CH_3CN	298	3.8 ns	18.4 ns
	CH_3CN	243	3.5 ns	17.0 ns
	CD_3CN	298	3.8 ns	18.5 ns
	9:1 ethanol–methanol	298	3.6 ns	19.0 ns
	9:1 ethanol–methanol	77	3.9 ns	17.2 ns
Rh(pc)(CH_3OH)Br	CH_3CN	298	3.4 ns	21.2 ns
Rh(pc)(CH_3OH)I	CH_3CN	298	4.0 ns	19.1 ns
λ_{excit} = 640 nm, λ_{ob} = 500 nm[c,d]				
Rh(pc)(CH_3OH)Cl	CH_3CN	298	1.3 μs	2.5 μs
		225	6.7 μs	3.0 μs
Rh(pc)(CH_3OH)Br	CH_3CN	298	0.2 μs	2.5 μs
	CH_3CN	282	0.33 μs	2.7 μs
	CH_3CN	273	0.39 μs	2.7 μs
	CH_3CN	263	0.51 μs	2.9 μs
	CH_3CN	253	0.63 μs	2.85 μs
	CH_3CN	243	1.10 μs	2.64 μs
	CH_3CN	235	1.26 μs	2.70 μs
	CH_3CN	225	1.33 μs	3.20 μs
Rh(pc)(CH_3OH)I	CH_3CN	298	36 ns	1.8 μs

[a] Deaerated solutions. [b] Lifetimes for the disappearance of the 420-nm emission obtained with a single-photon counting technique. [c] Lifetimes for the disappearance of the lowest lying $^3\pi\pi$ species. Values were obtained as an average of 5–10 traces in laser flash photolysis. [d] The reported lifetimes were independent of complex concentration, e.g., [Rh] ≤ 10^{-4} M, and the intensity of the exciting pulse.

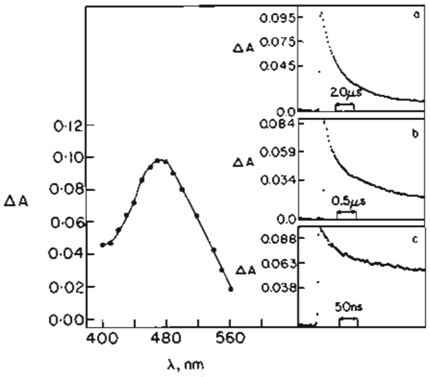

Figure 5. Absorption spectrum and transient behavior of the lowest $^3\pi\pi^*$ state in 640-nm laser flash photolysis of (a) Rh(pc)(CH_3OH)Cl, (b) Rh(pc)(CH_3OH)Br, and (c) Rh(pc)(CH_3OH)I in deaerated CH_3CN at 298 K.

The excitation of the rhodium(III) phthalocyanines at wavelengths of th first $\pi\pi^*$ allowed transition, namely, the Q band, produced transient spectra, λ_{max} = 500 nm, that can be attributed to the lowest $^3\pi\pi^*$ excited state (Figure 5).[6] This state disappears by a complex process with a lifetime that is independent of light intensity and complex concentration. Therefore, the complexity of the excited-state disappearance cannot be attributed to aggregation or self-quenching processes. The experimental traces can be fitted by a double-exponential function. The lifetimes obtained from curve fitting are considerably different from those obtained from the upper emissive state (Table II).

Discussion

We have previously reported that the ultraviolet photochemistry of the rhodium(III) phthalocyanines can be related to the population of ligand-centered $n\pi^*$ states.[1-6] Such states seem to have oxidation potentials that confer a considerable driving force to the abstraction of hydrogen from given donors (eq 1).[15] The monotonic growth of the yield with excitation energy (Figure 3) can be interpreted in terms of the yields for the conversion of the states populated by the absorption of light into the reactive $n\pi^*$ state. Such states are the result of ligand-centered $\pi \rightarrow \pi^*$ transitions and charge-transfer transitions that involve the electronic density of the axial and/or phthalocyanine ligands.[24-26] However, the independence of the action spectra on the nature of the axial ligand (Figure 3) suggests that for $Rh(pc)(CH_3OH)X$, $X = Cl^-, Br^-$, and I^-, the acido ligand to metal charge-transfer states, namely, $CT_{X\rightarrow Rh}$, make insignificant contributions to the population of the reactive $n\pi^*$ state. It is feasible that these charge-transfer states never achieve a very large population and experience, in addition, rapid conversions to lower lying states. This proposition is also in agreement with the reported absence of the charge-transfer photochemistry that is otherwise observed with isoelectronic complexes, namely, $Rh(NH_3)_5X^{2+}$ with $X = Cl^-, Br^-$, and I^- and $Co(pc)X^{4-}$ with $X = Cl^-, Br^-$, and SCN^-.[2,30,31]

The observation of the violet light emission in the ultraviolet excitation of the phthalocyanines demonstrates that the photonic energy is degraded in a complex manner that involves photochemical, radiative, and nonradiative pathways. Indeed, the 420-nm emission, observed in ultraviolet excitations of the Al(III), Rh(III), and Co(III) phthalocyanines, has been assigned to an upper ligand-centered electronic state. The independence of the quantum yield and lifetimes of the emission from solvent nature rules out the possibility of emission from $n\pi^*$ states. Moreover, the luminescence of the Al(III) complex and the independence of the emission from the nature of the axial ligand indicates that metal-centered states, namely, dd states, or charge-transfer states, $CT_{X\rightarrow Rh}$ or $CT_{pc\rightarrow Rh}$, cannot be responsible for the 420-nm emission; thus one must attribute such emission to a $\pi\pi^*$ state placed above the lowest lying $\pi\pi^*$ state. The lifetimes reported in Table II suggest that the 420-nm emission must originate in states with triplet multiplicity, e.g., $^3\pi\pi^*$.[32] The excitation spectra (Figure 2) show that this luminescent $^3\pi\pi^*$ state can be efficiently populated when phthalocyanines are excited at $\lambda_{excit} \approx 320$ nm, namely, within the N band. Although theoretical calculations demonstrate that the main contribution to the N-band intensity comes from allowed $\pi \rightarrow \pi^*$ transitions, there are also several ligand-centered $\pi\pi^*$ states whose conversions to the lowest lying $\pi\pi^*$ state are orbitally forbidden.[24] Such states have appropriate energies for emitting in the violet region and can be populated in 320-nm excitations. Therefore, it is possible that the mechanism of the 420-nm emission involves a trapping of a fraction of the excitation energy in these $\pi\pi^*$ states followed by competitive radiative and nonradiative pathways.

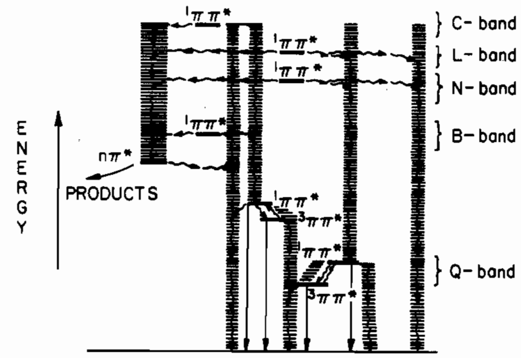

Figure 6. Schematic representation of the principal radiative and nonradiative transformations between excited states of rhodium(III) phthalocyanines. Charge-transfer and ligand field states have not been represented for the sake of clarity.

The relationship between the emissive $\pi\pi^*$ state and the reactive $n\pi^*$ state can be found by comparing the action spectra (Figure 3) and the excitation spectra (Figure 2). This comparison suggests that the states populated by excitation in the 290-nm band, B band, are later converted to the reactive $n\pi^*$ state but not to the upper $\pi\pi^*$ emissive state. Such a proposition must be complemented by the assumption that the states populated by excitation in the B band have a better communication with the lowest lying $^3\pi\pi^*$ and/or ground state than those populated by excitation in the N band, namely, at $\lambda_{excit} = 320$ nm. In this regard, the mechanism discussed above for the degradation of the photonic energy in ultraviolet photolyses of the phthalocyanines is summarized in Figure 6. Some details of the emissive-state relaxation have been omitted in Figure 6 and must be further discussed. Indeed, the 420-nm emission of the rhodium(III) phthalocyanines exhibited a complex time dependence that can be described by a double exponential (Figure 4). The complexities of this decay cannot be related to any ground- or excited-state association. Hence, if the rates of conversion between sublevels of the emissive triplet state are not greatly affected by the temperature, one possible explanation of the observed behavior is provided by the mechanism for the radiative relaxation of the lowest lying emissive state.[11]

The values of the lifetimes reported in Table II show that the rate of decay of the lowest lying $^3\pi\pi^*$ state depends on the axial ligand. The regular change of the properties of this state in the series of the chloro, bromo, and iodo complexes can be attributed to electronic perturbations induced by the axially coordinated species on the electronic levels of the phthalocyanine ligand. However, another explanation of this dependence can be based on the influence that metal–axial ligand vibrational levels might have on the values of the rate constants for the nonradiative relaxation of the triplet sublevels.[34-38] This vibrational contribution would be particularly

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(25) A. Henriksson, B. Roos, and M. Sundbom, *Theor. Chim. Acta*, **27**, 303 (1972).

(26) Although it is difficult to assess the exact position of the $CT_{X\rightarrow Rh}$ states, one approximate estimation of these energies can be obtained from values reported for the ground-state redox potentials,[27-29] the optical electronegativities,[30] and the electronic levels reported for various phthalocyanines.[24,25] These estimations suggest that the acido to rhodium(III) charge-transfer states must be ~11 kJ/mol above the similar states in the isoelectronic cobalt(III) complexes. Therefore the lowest lying $I^-(\pi) \rightarrow Rh(III)$ charge-transfer state must be in the violet region below the ligand $\pi \rightarrow \pi^*$ transition corresponding to the B band. For other halides, namely, Co^- and Br^-, the lowest lying $X^-(\pi) \rightarrow Rh(III)$ charge-transfer state must be above or at least near the energy of the $\pi\pi^*$ state corresponding to the B band.

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(30) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. Adamson and P. D. Fleischauer, Eds., Wiley-Interscience, New York, 1975, Chapter 3.

(31) P. C. Ford in "Concepts in Inorganic Photochemistry", A. Adamson and P. D. Fleischauer, Eds., Wiley-Interscience, New York, 1975, Chapter 5.

(32) Subnanosecond liftimes have been reported for the fluoerscence of several phthalocyanines.[10,33] One can expect similar lifetimes for the fluorescence of the Al(III), Co(III), and Rh(III) compounds.

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(35) K. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).

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(37) G. W. Robinson and R. P. Frosh, *J. Chem. Phys.*, **37**, 1962 (1962).

important if the nonradiative pathways determine the lifetimes of the $^3\pi\pi^*$ sublevels. Since there are insignificant changes in the spectrum of the lowest lying $^3\pi\pi^*$ state obtained with different axial ligands, the second alternative, namely, differences in the rate constants for nonradiative relaxation, seems to provide a better description of the observed behavior.[34–38]

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Registry No. Rh(pc)(CH_3OH)Cl, 81725-25-9; Rh(pc)(CH_3OH)Br, 81725-26-0; Rh(pc)(CH_3OH)I, 81725-27-1; Al(pc)Cl, 14154-42-8; $[Co(pts)]^{3-}$, 69087-63-4; $[Cu(pts)]^{4-}$, 67462-31-1; Ru(pc)$(py)_2$, 67588-46-9.

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(38) J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **18**, 1589 (1965).

(39) Notice that the temperature dependence of the rate constant is in agreement with the behavior expected for a weak-coupling mechansm.[36,40]

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Intermolecular vs. Intramolecular Reduction of Cobalt(III) Centers by Coordinated Pyridinyl Radicals

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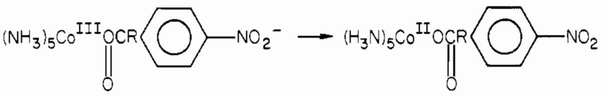
Four pentaamminecobalt(III) complexes, bound via a nonconjugated carboxylate to a pyridinyl derivative, were reduced by aliphatic free radicals. The primary site of reduction is shown to be the pyridinyl group. In one of the complexes studied an intramolecular electron transfer from the free radical to the cobalt center is observed, $k_{IET} = 4 \times 10^4$ s^{-1}. Surprisingly the coordinated pyridinyl radicals in the other complexes reduce another cobalt(III) center via an intermolecular process. The origin of the different patterns of behavior is discussed.

Introduction

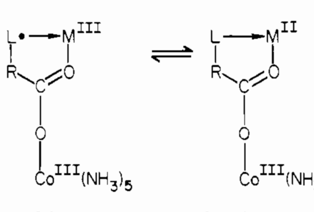
Our interest in the factors affecting the rate of intramolecular electron-transfer reactions prompted us to study the effect of "interrupted conjugation" on the rate of reduction of pentaamminecobalt(III) centers by pyridinyl radicals bound to the cobalt by an insulated carboxylate group. While this study was in progress, Hoffman et al. reported[2] results on the analogous reactions



(1)

Their results suggested that the rate of reaction 1 depends only slightly on the nature of –R– for R = CH_2, CH=CH, and $(CH_2)_3$.

The choice of complexes studied stemmed also from the suggestion[3] that the mechanism of reduction of $(NH_3)_5CoOC(O)RL$ by Eu^{2+} and Cr^{2+} involves intermediates of the type



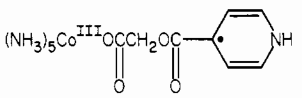
(2)

It seemed thus of interest to study the rates of the reaction

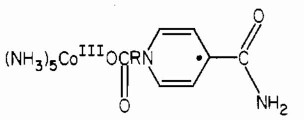
$$(NH_3)_5Co^{III}OC(O)RL^{-}\cdot \rightarrow (NH_3)_5Co^{II}OC(O)RL \quad (3)$$

Furthermore the ligands ^-O_2CRL were shown[4] to be catalysts for the reduction of cobalt(III) complexes by Eu^{2+}.

We report here the surprising result that we observed an intramolecular electron transfer only for the complex



whereas for complexes of the type

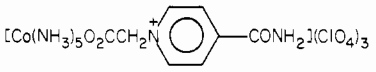


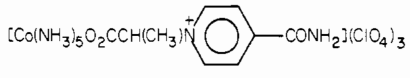
we observed intermolecular redox reactions of the type

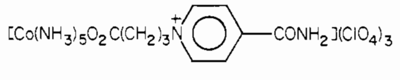
$$(NH_3)_5Co^{III}OC(O)RL^{-}\cdot + (NH_3)_5Co^{III}OC(O)RL \rightarrow (NH_3)_5Co^{III}OC(O)RL + (NH_3)_5Co^{II}OC(O)RL \quad (4)$$

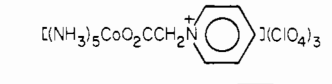
Experimental Section

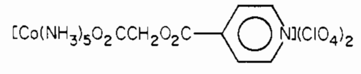
Materials. The complexes











were prepared according to procedures described in the literature.[5]

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