modifications of the SDP-PLUS series of programs.

Bulk Coulometry and EPR Studies of Fluorodiphosphine Clusters II and III. To determine the number of electrons involved in each redox couple of clusters II and III, the bulk coulometric measurements were generally performed as described in detail for the pentakis derivative III. To an argon-flushed cell for bulk electrolysis was added 0.107 g (0.08 mmol) of $Co_4(CO)(PPh)_2[(F_2P)_2NMe]_5$ and 35 mL of THF containing 0.3 M TBAP. The 0/+1 redox couple was first examined by constant-potential electrolysis at +1.0 V vs. SCE and 25 °C. The current gradually diminished as the electrolysis proceeded (total time ~1 h). No current flow was observed after passage of 7.91 C (theoretical value 7.85 C). This afforded a value of n = 1.01, consistent with the proposed redox couple as a one-electron oxidation process. At this point, a small aliquot of the electrolysis solution was examined by EPR spectroscopy. However, the solution was EPR-silent. The solution was reduced back to the neutral starting cluster at a potential of 0.0 V vs. SCE at 25 °C. Reduction of the radical cation to III required 7.53 C and afforded a value of n = 0.95. Next, the neutral solution of III was reduced to its radical anion at a potential of −1.5 V vs. SCE in the constant-potential mode. After the passage of 7.91 C, the current flow ceased, which afforded a value of n = 1.05 for the 0/−1 redox couple. EPR analysis of the radical anion solution was negative. The absence of EPR signals in these type of clusters has also been previously noted. This situation may arise from the cobalt cluster, which is composed of Co(II).[53] Such Co(II) complexes are known to relax rapidly, which generally precludes the EPR resonances under normal conditions ($T > 77$ K). Finally, the radical anion was reoxidized to the neutral III at a potential of 0.0 V vs. SCE to yield a value of n = 0.63. This suggested that some material loss had occurred. Similar experiments were performed with II to afford values of a = 1.05 (0/+1 couple) upon oxidation and n = 0.79 for reduction of the radical cation back to the neutral II. Reduction of II to the radical anion led to n = 0.93, and reoxidation of the radical anion to II yielded n = 0.66. As in cluster III, solutions of both the radical cation and the radical anion derived from II were EPR-silent.

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Supplementary Material Available: Lists of bond lengths, bond angles, and general temperature factor expressions of the fluorophosphine and phenyl groups (5 pages); a list of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Phthalocyanine π-Cation-Radical Species: Photochemical and Electrochemical Preparation of $[ZnPc(-1)]^{\bullet+}$ in Solution

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The π-cation-radical species of ZnPc, $[ZnPc(-1)]^{\bullet+}$ (Pc = phthalocyanine), has been formed quantitatively as a stable product in solution following photochemical reactions with visible-region light in the presence of electron acceptors. The photolyses were carried out by excitation into the phthalocyanine's Q band ($\lambda > 580$ nm), with carbon tetrabromide as an irreversible electron acceptor. The neutral parent species could be regenerated following photooxidation by the addition of sodium dithionite. Cyclic voltammetry of neutral ZnPcL species identified the ring oxidation potentials; for ZnPc(py) and ZnPc(im) (py = pyridine; im = imidazole). In dimethylacetamide, there is one oxidation couple at 0.70 and 0.71 V vs. SCE, respectively, and there are two reduction couples, at −0.96 and −1.28 V vs. SCE, for the pyridine complex, and at −0.98 and −1.53 V vs. SCE, for the imidazole complex. Each of these reactions was reversible on the cyclic voltammetry time scale. The electrochemical and photochemical oxidation products were characterized by absorption, magnetic circular dichroism (MCD), and electron paramagnetic resonance (EPR) spectroscopies. Four clearly resolvable, optical transitions, centered at 440, 500, 720, and 825 nm, are observed in the absorption spectrum of the cation radical species. The MCD spectrum shows that the transition at 500 nm is nondegenerate, while the transitions at 440, 720, and 825 nm appear to be degenerate. EPR spectra obtained from frozen solutions of the π cation radicals gave isotropic g values that are characteristic of the oxidation at the phthalocyanine ligand (the g values were between 2.0055 and 2.0068).

Introduction

The phthalocyanines and porphyrins enjoy a growing importance as potential photo- and electrocatalysts for energy conversion processes,[1-5] as they are highly colored, exhibit diverse redox activity, and are relatively photochemically stable. Compared with the analogous porphyrin compounds, phthalocyanines are generally more resistant to ring degradation.[1] However, photochemical processes involving these ring compounds are only poorly developed, even though the chemistry of the excited states of molecules with so many π electrons is likely to be extensive. As part of our studies on the use of photochemically induced charge separation as the initial reaction step in a molecular solar cell,[6] we have examined the electrochemical and photochemical oxidation of zinc phthalocyanine (ZnPc) in solution.

Zinc phthalocyanines have been shown to exhibit photocatalytic properties, for example as photosensitizers for the reduction of methylviologens[7-9] and water.[10] It is known from cyclic voltammetry (CV) measurements that ZnPc undergoes chemical oxidation at the ring rather than at the metal center,[11] resulting in the formation of a phthalocyanine π cation radical on the CV time scale. Because of the very limited solubility of ZnPc in many nonpolar solvents, spectra of $[ZnPc(-1)]^{\bullet+}$ species have been

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obtained either from transient species, with lifetimes in the order of microseconds,[3] or as thin films in the solid state, where chemical[12] or electrochemical oxidation[13] was used.

Characteristic spectral changes are observed when thin films are oxidized to the π-cation-radical species.[12,13] However, due to extensive intermolecular (Davydov) coupling effects, these solid-state spectra are quite different when compared with their respective solution spectra. Significant broadening is observed in all the bands in the electronic spectrum of neutral species.[14-16] We see that Davydov effects are still significant in the π-cation-radical spectra in the data of Myers et al.[12] and Green and Faulkner.[13] This makes the assignment problem very difficult for absorption spectra of species such as the ring-oxidized π cation radical, where numerous overlapping bands are to be expected. To the best of our knowledge, no optical spectra have been published for a stable sample of the π-cation-radical species of ZnPc in solution. Indeed, solution spectra are only available for the radical cations of RuPc,[17,18] CuPc, H_2Pc, and MgPc,[19] and FePc and CoPc.[20,21] No magnetic circular dichroism (MCD) spectra of such species have been published previously, with the exception of our study of $[RuPc(-1)]^{\bullet+}$.[17]

The attractiveness of spectra recorded in solution for the $[ZnPc(-1)]^{\bullet+}$ species is that a direct comparison can be made with the large number of data already published for neutral M(Pc) complexes in solution. Because no charge-transfer transitions are expected in ZnPc between the metal and the ring at low energy, in either the oxidized or neutral species, it should be possible to use the available theoretical calculations to assign the observed bands to individual transitions.[12-24]

Photochemical studies of a range of metallophthalocyanines in solution using ultraviolet light for excitation[25-27] indicate that the redox processes take place via ligand-centered, singlet $n\pi^*$ states. An example of this type of reaction is hydrogen abstraction from the solvent following irradiation into the MPc's excited states.[26] However, excitation into the phthalocyanine's Q band populates both the lowest energy $\pi\pi^*$ singlet and the lowest lying triplet states. Because the singlet lifetime is so short, it is the phthalocyanine's triplet state that is subsequently quenched by electron transfer to an electron acceptor.[3,25] Ohno and coworkers[8,28] have reported a transient spectrum following irradiation into the Q band of ZnPc in the presence of the Co(III) complexes of 1,10-phenanthroline, 2,2′-bipyridyl, and 2,2′:6′,2″-terpyridyl that has the same band centers as the spectrum measured following chemical oxidation.[12] However, a stable oxidation product has not yet been characterized in solution following photooxidation of any ZnPc complex.

In recent papers, we have reported that the photoinduced, one-electron oxidation of a range of porphyrins[29-31] and of ruthenium phthalocyanine (RuPc)[17] takes place readily in the presence of alkyl halide acceptors. In this paper, we describe the preparation of the photooxidized product of ZnPc, where the photolysis was carried out at room temperature in methylene chloride solutions containing carbon tetrabromide as an electron acceptor. Electrochemical measurements were used to provide ground-state redox potentials for use in calculating the exergonicity of the photochemical reaction. The $[ZnPc(-1)]^{\bullet+}$ complexes were characterized by absorption and MCD spectroscopy.

Experimental Section

Materials and Methods. Most metalated phthalocyanines are relatively insoluble in the nonpolar organic solvents that are useful in both electrochemical and photochemical redox studies. In particular, we have found that while many porphyrins are readily photooxidized in dry methylene chloride,[29-31] ZnPc is almost insoluble in this solvent. Axial ligation of ZnPc results in complexes that exhibit considerably higher solubility in methylene chloride. Examples include complexes of pyridine, cyanide, and imidazole. Typically, ZnPc (Kodak) was Soxhlet-extracted with pyridine (py), evaporated to dryness, and then washed with hexanes to remove excess pyridine. This resulted in a complex formulated as ZnPc(py), since ZnPc is known to bind only one axial ligand.[32] The cyano (CN^-) and imidazole (im) complexes were prepared by refluxing ZnPc in dimethylacetamide (DMA), in the presence of excess ligand, for 5 h, after which the $ZnPc(CN^-)$ and ZnPc(im) complexes were isolated by evaporating the DMA to dryness. While potassium imidazolate was used in the preparation of the imidazole complexes described here, exactly the same optical data were obtained when imidazole (im) was used. We assume that under the experimental conditions used to make the ZnPc(L) complexes, hydrolysis occurs and imidazole is formed. All solvents were freshly distilled. Potassium imidazolate (K^+Im^-), tetraethylammonium perchlorate ($[Et_4N]ClO_4$, Kodak; TEAP), tetrapropylammonium perchlorate ($[Pr_4N]ClO_4$, Kodak; TPAP), ferrocene (Kodak; fc), and carbon tetrabromide (CBr_4, Kodak) were recrystallized before use. Sodium cyanide (Fisher) was used without further purification.

Electrochemistry. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a platinum wire as the auxiliary electrode and a platinum bead as the working electrode. A saturated calomel electrode (SCE) or a silver wire was used as a reference electrode. The ferrocene couple (fc^+/fc) was used as internal standard.[33] The SCE was separated from the solution by a very fine glass frit, and in order to minimize liquid–liquid-junction potentials, a salt bridge containing agar, saturated with potassium chloride, was placed adjacent to the SCE. Another bridge, containing the solvent and the electrolyte, was similarly placed adjacent to the phthalocyanine solution. The cell was sealed with a Teflon stopper that had holes for the nitrogen bubbler, working electrode, auxiliary electrode, and silver-wire reference electrode.

An "H" cell was used for exhaustive electrolyses in which the two compartments were separated by a fine glass frit. The working electrode, consisting of a cylindrical platinum gauze (Johnson-Matthey, diameter 13 mm and height 40 mm), and the silver-wire reference electrode were housed in one compartment. The auxiliary electrode, consisting of a 22 mm by 15 mm platinum plate, was housed in the other. The silver wire was placed in an air-saturated electrolyte solution for at least 30 min prior to use to form the Ag^+ required by the Ag^+/Ag reference couple that is provided by the silver wire.

All electrochemical work was carried out under an atmosphere of dry, deoxygenated nitrogen. The nitrogen was deoxygenated with the BASH catalyst,[34] which contains metallic copper on a high-surface-area matrix. Electrochemical measurements were carried out with a Princeton Applied Research Model 273 electrochemical system controlled by an IBM Instruments S9001 computer, using the computer program ELECTRA.[35] The number of moles of electrons transferred in reactions of the type $ZnPc(-2) \rightarrow [ZnPc(-1)]^{\bullet+} + ne^-$ was confirmed for the first oxidation step by fitting the coulometry data to an equation that relates charge with elapsed time, $Q_t = Q_0(1 - e^{-kt})$,[36] where Q_t is the charge in coulombs at elapsed time t, Q_0 is the charge at the completion of the electrolysis, and

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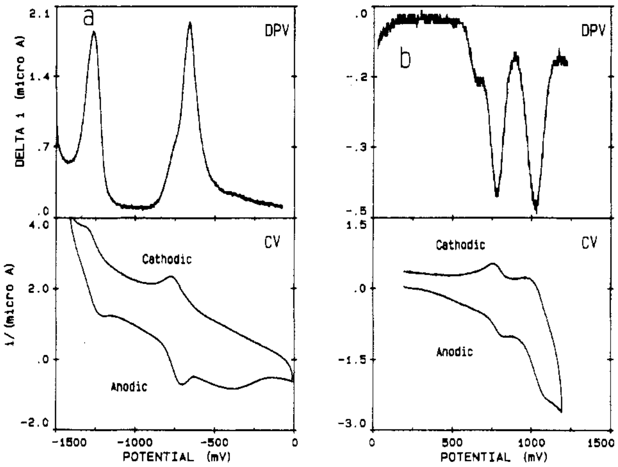

Figure 1. CV and DPV voltammograms of ZnPc(im) dissolved in DMA containing 0.1 M tetrapropylammonium perchlorate: (a) reduction; (b) oxidation. Silver wire was used as an internal reference electrode, while ferrocene was used as an internal standard. The potential axis can be expressed in terms of the saturated calomel electrode (SCE) with use of details given in ref 43. The half-wave potential of the peak at 1.0 V vs. silver wire is 0.71 V vs. SCE, the peak at 0.80 V vs. silver wire is 0.47 V vs. SCE, the peak at −0.65 V vs. silver wire is −0.96 V vs. SCE, and the peak at −1.20 V vs. silver wire is −1.53 V vs. SCE. Following the American polarity convention,[52] the positive current is cathodic and the negative current is anodic.

k is the rate of electron transfer. A least-squares minimization program, BARD,[37] was used to fit the data.

Spectroscopic Measurements. Absorption spectra were obtained with Cary Model 219 and 17 spectrometers. Molar extinction coefficients for ZnPc(CN$^-$) (ϵ_{670} = 235 000 L mol^{-1} cm^{-1}), ZnPc(im) (ϵ_{670} = 178 000 L mol^{-1} cm^{-1}), ZnPc(py) (ϵ_{670} = 240 000 L mol^{-1} cm^{-1}), and ZnPc (ϵ_{670} = 300 000 L mol^{-1} cm^{-1}) were determined in DMA and used to calculate the concentration of ZnPc in solution. MCD spectra were obtained at room temperature with a JASCO J500 C spectropolarimeter controlled by an IBM Instruments S9001 computer using the computer program CDSCAN5.[38] A field of 5.5 T was obtained from an Oxford Instruments SM2 superconducting magnet. The signal was calibrated with aqueous solutions of Co(SO$_4$), where the intensity of the negative band at 510 nm was taken as $\Delta\epsilon_M = -1.897 \times 10^{-2}$ L mol^{-1} cm^{-1} T^{-1}. EPR spectra were recorded on a Varian E-12 EPR spectrometer equipped with a Varian E-257 temperature controller and interfaced to a Nicolet 1180 computer through a Nicolet Explorer III digital oscilloscope. EPR measurements were made from glassy phthalocyanine solutions in 4 mm o.d. quartz tubes. The absolute values of the g factors were determined against a carbon black standard. The data were plotted on an HP 7550A digital plotter using the spectral data management program Spectra Manager.[39]

Photochemical Measurements. Photochemical experiments were carried out in the following manner. An aliquot of the metallophthalocyanine complex was dissolved in nitrogen-saturated methylene chloride to which CBr$_4$ had been added. The solutions were irradiated in the Q-band region with light from a 300-W tungsten–halogen projector lamp, with a Corning CS 2-73 high-energy (580 nm) cutoff filter to filter out light below 580 nm. Quantum yield measurements, employing actinometry with Reinecke's salt, KCr(NH$_3$)$_2$(NCS)$_4$,[40] were carried out with a PTI Quantacount, in conjunction with an LPS 200 power supply and a 100-W mercury lamp. The Reinecke salt was prepared by recrystallizing the ammonium form, (NH$_4$)Cr(NH$_3$)$_2$(NCS)$_4$ (Baker), from an acidic potassium nitrate solution. Quantum yields were determined by monitoring absorption bands in the spectral regions where absorption by the parent phthalocyanine was negligible (~500 nm), following irradiation at 20 °C of a 1-cm cell containing the M(Pc) species in methylene chloride, with CBr$_4$ added as the acceptor, using the Q-band wavelength of 670 nm.

Results and Discussion

I. Electrochemistry. Electrochemical techniques are well-established as routes to the production of porphyrin π cation radicals.[41,42] However, probably because of the low solubility of phthalocyanines in nonpolar solvents, far less data are available concerning the electrochemical generation of phthalocyanine π cation radicals in solution.[18]

Table I. Half-Wave Potentials of the ZnPc(L) Species Dissolved in DMA Containing 0.1 M Tetrapropylammonium Perchlorate

	$E_{1/2}$, V (vs. fc$^+$/fc)[a]	$E_{1/2}$, V (vs. SCE)[b]
ZnPc(py)	0.23	0.70
	−1.43	−0.96
	−1.75	−1.28
ZnPc(im)	0.24	0.71
	−1.45	−0.98
	−2.00	−1.53
ferrocene	0.00	0.47

[a] fc = ferrocene. [b] $E_{1/2}$ values vs. the saturated calomel electrode (SCE) were obtained by adding $E_{1/2}$(fc$^+$/fc) = 0.47 V to the $E_{1/2}$ vs. fc$^+$/fc values listed in the table, with use of details given in ref 43.

Typical cyclic voltammetry (CV) and differential pulse voltammetry (DPV) response curves are shown in Figure 1 for ZnPc(im). The use of water-based reference electrodes, such as the saturated calomel electrode (SCE) and the normal hydrogen electrode (NHE), in nonaqueous electrochemistry inevitably introduces an unknown contribution of liquid-junction potential into the measured potential. In order to avoid this problem, a silver wire was used as an internal reference electrode and the ferrocenium/ferrocene (fc$^+$/fc) couple was used as an internal standard. Thus, the potentials shown in Figure 1 are referenced to the internal silver-wire reference electrode. The potentials of the couples determined from such traces can then be restated in terms of the well-known fc$^+$/fc couple as follows: the $E_{1/2}$(fc$^+$/fc) vs. the silver wire values are subtracted from the $E_{1/2}$(ZnPc) vs. the silver wire values. The $E_{1/2}$(ZnPc) vs. SCE values were obtained by adding $E_{1/2}$(fc$^+$/fc) vs. sce values to the respective $E_{1/2}$(ZnPc) vs. fc$^+$/fc couple values.[43] The half-wave potentials for the im and py complexes are listed in Table I. All the $E_{1/2}$ values quoted in the text are referenced to the SCE couple in this manner. The value of $E_{1/2}$(fc$^+$/fc) vs. SCE is highly dependent on the solvent and electrolyte used.[44] We obtained $E_{1/2}$(fc$^+$/fc) values in methylene chloride and DMA of 0.47 V and in acetonitrile of 0.44 V, in each case with TPAP as the supporting electrolyte.

The CV and DPV of ZnPc(CN$^-$) gave inconsistent results, most likely due to the fact that the cyanide ion can be readily oxidized by organic radicals as follows:[45]

$$[\mathrm{MPc}(-1)]^{\bullet +} + \mathrm{CN}^- \rightarrow \mathrm{MPc}(-2) + \mathrm{CN}^\bullet$$

$$2\mathrm{CN}^\bullet \rightarrow (\mathrm{CN})_2$$

which depletes the concentration of the MPc π cation radical.

Because the charging effects are far less important than in the traditional CV experiment, the DPV experiment has a clear advantage over the CV experiment, and well-resolved signals are obtained for dilute solutions.[36] The half-wave potentials from CV curves have been calculated as $(E_{\mathrm{oxid}} + E_{\mathrm{red}})/2$, while for DPV curves the half-wave potential corresponds to E_{min} or E_{max}. The anodic to cathodic peak ratios were essentially unity over scan rates that ranged from 100 to 8000 mV/s for the im and py complexes. The anodic to cathodic peak separation was close to 60 mV and was essentially independent of scan rate, confirming

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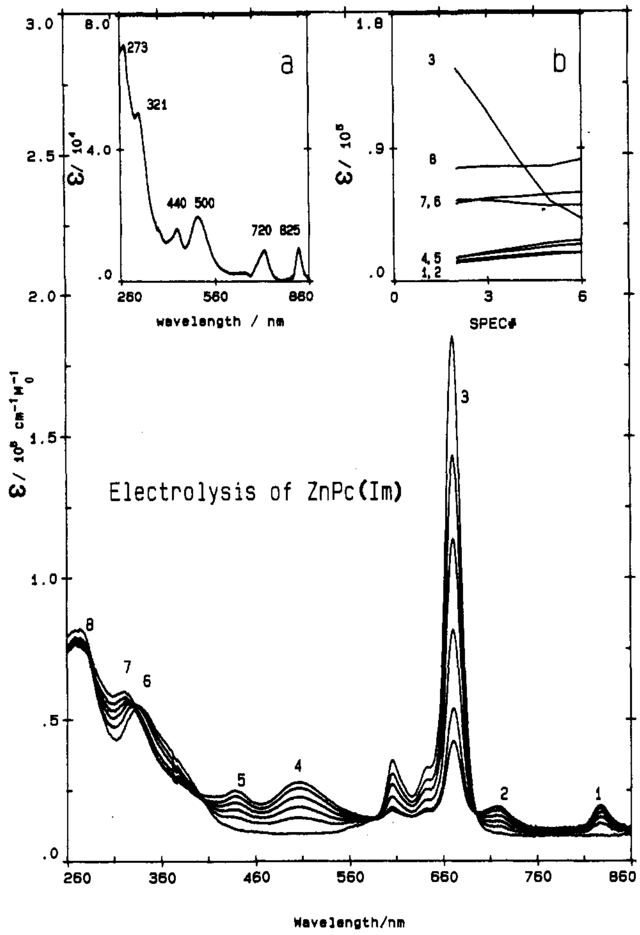

Figure 2. Absorption changes observed as controlled-potential coulometry was performed at 0.71 V vs. SCE on ZnPc(im) dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate. Inset a is the spectrum obtained when the spectrum due to the remaining (18%) neutral species was subtracted from the final spectrum. Inset b shows the time dependence of changes in intensity of individual bands during electrolysis. Traces 1, 2, 4, 5, and 7 correspond to bands due to the oxidized species, centered at 825, 720, 500, 440, and 321 nm, respectively, while traces 3, 6, and 8 correspond to bands due to the unoxidized species, centered at 670, 335, and 273 nm, respectively.

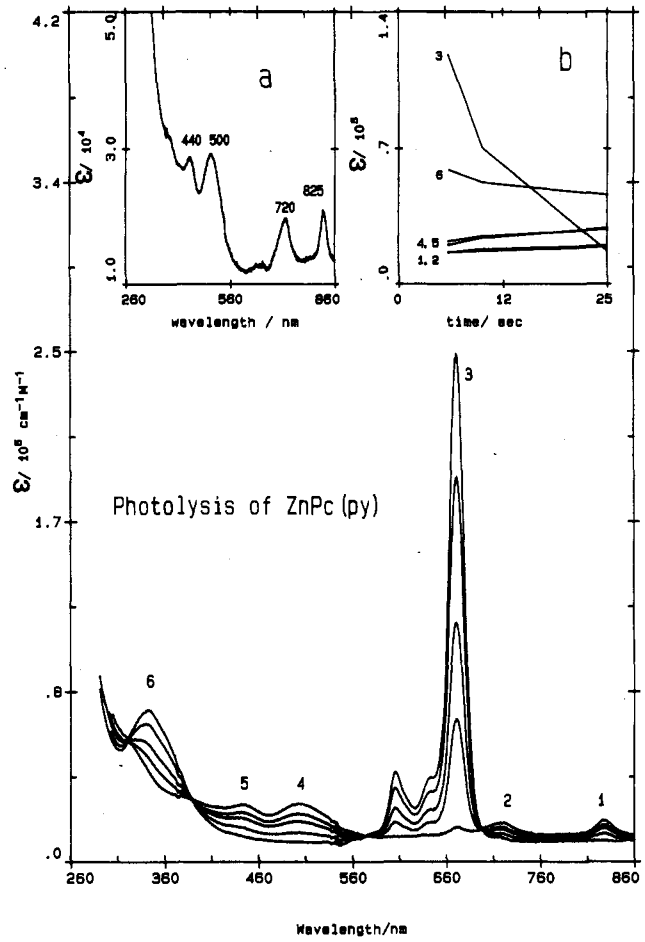

Figure 3. Absorption changes observed during the photochemical oxidation of ZnPc(py) dissolved in methylene chloride containing 10^{-3} M CBr_4. Inset a is the spectrum obtained when the spectrum due to the remaining (3%) neutral species was subtracted from the final spectrum. Inset b shows the time dependence of the changes in intensity of individual bands during electrolysis. Traces 1, 2, 4, and 5 correspond to bands due to the oxidized species, centered at 825, 720, 500, and 440 nm, respectively, while traces 3 and 6 correspond to bands due to the unoxidized species, centered at 670 and 335 nm, respectively.

the reversibility of the system and showing that n, the number of moles of electrons involved in each electron-transfer step, was approximately unity.[36]

The peak at 1.00 V vs. silver wire (0.71 V vs. SCE), in Figure 1, corresponds to the oxidation of the phthalocyanine ligand, forming $Zn^{II}(Pc^-)$, while the two negative pairs correspond to the reduction of the phthalocyanine ligand, giving $[ZnPc(-3)(im)]^{\bullet -}$ at −0.65 V vs. silver wire (−0.98 V vs. SCE) and $[ZnPc(-4)(im)]^{2-}$ at −1.20 V vs. silver wire (−1.53 V vs. sce). These values are in accord with those previously reported by Lever et al. for ZnPc dissolved in dimethylformamide,[11] the slight differences being due to solvent and axial ligand effects.

Isosbestic changes are observed in the absorption spectrum when complexes of ZnPcL, where L = py, im, and CN^-, are dissolved in methylene chloride containing 0.05 M $[Et_4N]ClO_4$ and exhaustively electrolyzed at the anodic peak potentials of the positive peaks ($E_{1/2}$, = ~0.70 V vs. SCE). Figure 2 shows spectral changes recorded during a typical electrolysis of ZnPc(im). Inset a in Figure 2 shows an absorption spectrum for the $[ZnPc(-1)]^{\bullet +}$ π-cation-radical species calculated by subtracting the spectrum due to the residual, unoxidized, neutral species from the spectrum recorded at the end of the electrolysis. Inset b shows the time dependence of the intensity of each resolved band at various stages during the electrolysis.

II. Photochemistry. Although there have been several reports of the formation of metallophthalocyanine π-cation-radical species using chemical[12,46,47] and electrochemical[13,19] techniques, studies using photochemical procedures have been solely concerned with the production of transient species.[25-27] Unlike those of the corresponding porphyrin species,[1] the lowest energy excited singlet states of phthalocyanines are extremely short lived;[1,48] hence, only the lowest energy triplet states are useful for electron-transfer reactions in which π-cation-radical species can be formed. Irradiation of the ZnPcL complexes dissolved in methylene chloride that contained 10^{-3} M CBr_4 resulted in isosbestic changes in the absorption spectra, as shown in Figure 3 for ZnPc(py). Similar changes are observed during the electrochemical oxidation of the ZnPc(im) complex (Figure 2) and during the photochemical oxidation of RuPc.[17,49] In view of these similarities, the final photooxidation product in the ZnPcL species is also identified as a π cation radical. The neutral ZnPcL species could be regenerated by reduction of the photooxidized species with sodium dithionite.

The mechanism for this photoredox reaction is based on increasing the exergonicity of the redox reaction through the use of the lowest energy, triplet state of the metallophthalocyanine as the reductant state instead of the ground state. Therefore, the

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Table II. Quantum Yields for the Photochemical Formation of $[ZnPc(-1)(L)]^{\bullet+}$ Species and EPR Parameters Measured for These Species Dissolved in Methylene Chloride Containing 10^{-3} M CBr_4

complex	Q_{redox}	g	bandwidth, G
ZnPc(im)	0.011	2.0055	3.8
ZnPc(py)	0.001	2.0059	4.0
ZnPc(CN⁻)	0.006	2.0068	4.0

reduction potential of the metallophthalocyanine triplet state has to be greater than that of the acceptor in order to form, spontaneously, the M(Pc) π cation radical as a product. The redox potential of the excited triplet state of the ZnPc complexes, written as a couple involving the excited state ZnPcL* as $[ZnPc(-1)(L)]^{\bullet+}/[ZnPc(-2)(L)]^*$, can be estimated from the relationship $E_{1/2}(MPc^{\bullet+}/MPc^*) \simeq E_{1/2}(MPc^{\bullet+}/MPc) - E_T$ (in V) to be equal to −0.44 V vs. SCE, where the ground-state redox potential, $E_{1/2}(MPc^{\bullet+}/MPc)$, is 0.70 V vs. SCE and the energy of the triplet state (E_T) is 1.14 eV.[48] This compares with the redox potential for CBr_4 of $E_{1/2} = -0.30$ V vs. SCE.[50] If acceptors such as CBr_4 are used, then the photoreduced products that form will be unreactive toward the $MPc^{\bullet+}$ species.

The experimental results for the photooxidation of ZnPc can be explained by using the scheme

$$ZnPcL \xrightarrow{h\nu} ZnPcL^*$$

$$ZnPcL^* + CBr_4 \rightarrow [ZnPc(-1)L]^{\bullet+} + CBr_3^{\bullet} + Br^-$$

Because the $CBr_3^{\bullet}$ species can rapidly dimerize, the reaction is irreversible and leads to the formation of the stable phthalocyanine π cation radical. The quantum yields of formation of the three complexes studied are shown in Table II. These quantum yields are very low, much lower than comparable zinc porphyrin values (the room-temperature photooxidation of ZnTPP proceeds with a quantum yield of 16%[30]). However, the oxidation of the ZnPc complexes does take place quantitatively, with insignificant side reactions, so photochemistry is still an attractive route for the formation of the π-cation-radical species in solution.

The EPR spectra obtained from frozen (at 79 K) solutions of the cation radicals gave isotropic g values (Table II) that are close to the free-electron value of 2.0023. The range of values listed in Table II, 2.0055–2.0068, appears to be characteristic of oxidation of the phthalocyanine ring in the presence of a metal; e.g., for $[RuPc(-1)(py)_2]^{\bullet+}$, $g = 2.010$,[18] and for $[Co^{III}Pc(-1)]Br_2$, $g = 2.004$.[12]

III. Absorption and MCD Spectra. Typical spectral behavior following the ring oxidation of porphyrins[41] is a general broadening of the spectra, together with a decrease in the intensity of the bands. From the data presently available for $[MPc(-1)]^{\bullet+}$ species,[11,17-19] it appears that while a loss of intensity in the visible region occurs, the remaining bands are not any broader than those in the spectra of the neutral species and it is probably the appearance of several new bands that results in the apparent broadening. In each of the spectra of the oxidized $[ZnPc(-1)(L)]^{\bullet+}$ species studied in this work (Figures 2 and 3), we observe the same four bands in the visible and near-IR regions; these are centered near 440, 500, 720, and 825 nm. Changes in the Soret band region, at $\lambda < 400$ nm, are more complicated, being more dependent on the axial ligand. In place of the series of continuously overlapping bands that span the 690–330-nm region for $[MP(-1)]^{\bullet+}$,[41,42] we find relatively isolated bands that span the region from 820 to 250 nm, each much less intense than bands in the neutral spectrum. Thus in Figure 3, the spectral changes induced by the photolysis are dominated by the disappearance of the intense Q band. The intensities of the newly formed absorption bands, identified as 1, 2, 4, 5, and 7 in Figure 2 and 1, 2, 4, and 5 in Figure 3, are plotted in the insets in the two figures and show an increase at roughly the same rate and reach a plateau near the completion of each reaction. This, together with the sharp isosbestic points in both photochemical and electrochemical preparations, is a good indication that the appearance of the four new bands results from the formation of the same species, namely the ZnPc π cation radical. The one-electron electrooxidations shown in Figures 2 and 3 proceed cleanly and reversibly over many cycles.

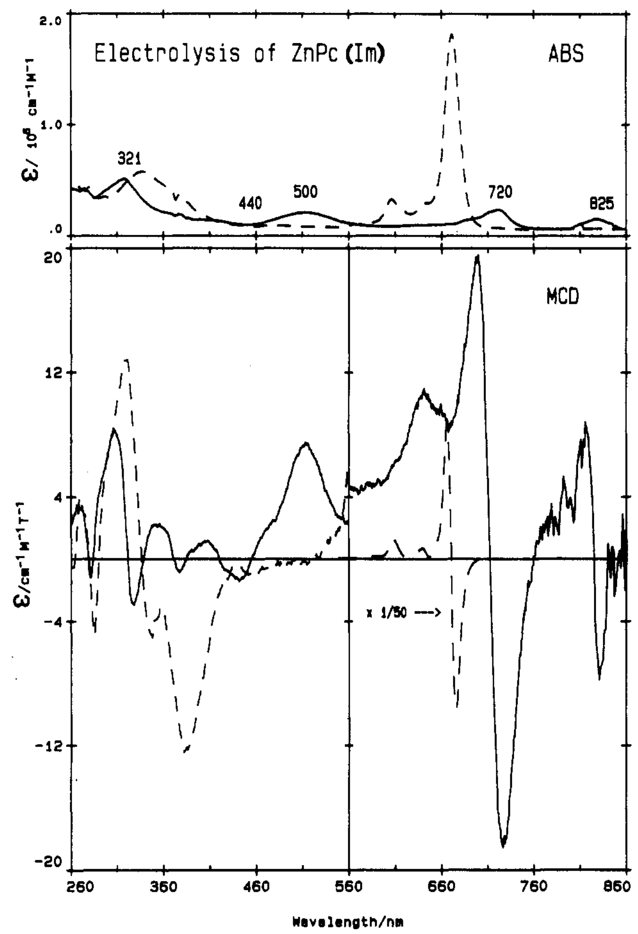

Figure 4. Absorption and MCD spectra recorded after the controlled-potential oxidation (at 0.71 V vs. SCE) of ZnPc(im) dissolved in methylene chloride containing 0.05 M tetraethylammonium perchlorate. The solid lines show spectra of the $[ZnPc(-1)]^{\bullet+}$ series.

The MCD spectrum provides far more information than the absorption spectrum alone about the number of transitions and the degeneracy of those transitions, which together make up the observed spectral envelope in systems as complicated as that of the π-cation-radical species. In order to obtain good estimates of the band centers, it is necessary to deconvolute the observed spectra, and this will be described in detail in a subsequent paper.[51] The absorption and MCD spectra recorded for the ZnPc(im) complex, before and after a controlled-potential coulometry experiment was carried out, are shown in Figure 4. The MCD spectrum is a particularly sensitive probe and shows that there is no remaining neutral species at the end of the electrochemical oxidation. The broken line in Figure 4 shows the spectra of the neutral ZnPc.

The MCD spectrum shown in Figure 4 can be qualitatively analyzed in terms of three derivative line shapes, centered under the 825-, 700-, and 325-nm bands, and a prominent, positive B term under the 500-nm band. Because of the very low signal intensity in the π-cation-radical MCD spectrum (the intensity scale spans $\Delta\epsilon \approx 40$ L mol^{-1} cm^{-1} T^{-1}), compared with the spectrum of the unoxidized complex (with a span at 670 nm of ~500 L mol^{-1} cm^{-1} T^{-1}), any residual unoxidized complex would dominate the spectrum at 670 nm. Therefore, all the bands recorded should

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arise from the π-cation-radical species. Analysis by band deconvolution of the spectra of both the neutral and oxidized ZnPc species[51] shows that there are many more transitions in these spectra than are apparent from such a qualitative analysis. However, the essence of the analysis presented here remains correct: the transitions at 825, 720, and 325 nm are degenerate, while the 500-nm transition is nondegenerate. Because the partially filled HOMO, in the $a_{2u}(2)a_{1u}(1)$ configuration, allows transitions from low-lying π MO's, we assign the 825-nm band to such a π–π transition. The Q band is associated with the 720-nm band, being identified from the MCD spectrum by its degeneracy and complement of vibronic overtone bands lying to higher energy. The 500-nm band must be a transition from nondegenerate, low-lying π MO's or possibly from low-lying σ, n-type orbitals on the ring nitrogens to the a_{1u} π MO.

Conclusions

Photolysis of ZnPc in solutions containing alkyl halide acceptors results in the quantitative formation of the π-cation-radical species. The lack of side reactions makes this an attractive method of preparing the π-cation-radical species of main-group phthalocyanines. With transition-metal phthalocyanines, metal-centered reactions may quench the π-ring excited state in competition with ring oxidation.

Qualitative analysis of the magnetic circular dichroism spectrum of the $[\text{ZnPc}(-1)]^{\bullet+}$ species suggests that the Q band is at 720 nm and that the bands at 825 and 500 nm arise from π–π transitions into the partially filled a_{1u} MO.

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Macrocyclic Dicarbinolamine Complexes of Nickel(II) with Planar $N_4(N_2)$ Ligands: Synthesis and Spectral and Electrochemical Properties

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Macrocyclic complexes of nickel(II) with highly unsaturated planar tetraaza $[N_4(N_2)]$ type ligands have been synthesized and characterized. These complexes are derived by the template condensation of the ligands 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BG) and 5-methyl-1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BMG) with *o*-phenylenediamine (opdn), 3,4-dimethyl-*o*-phenylenediamine (dmopdn), and 3-methyl-*o*-phenylenediamine (dat) in the presence of nickel(II) acetate. Each of these complexes displays spectral, magnetic, and conductance behavior characteristic of square-planar nickel(II) complexes. The electrochemical properties as studied by cyclic voltammetry and polarography indicate the quasi-reversible nature of these systems. In all the complexes the dicarbinolamine moiety is found to be present, which is confirmed by IR, ^{1}H NMR, and mass spectral data. Molecular model (CPK models) studies clearly show that the phenyl groups must be perpendicular to the plane of the molecule and the hydroxyl groups are trans to each other. The factors governing the stabilization of the dicarbinolamine moiety are discussed.

Introduction

The synthesis and study of macrocyclic complexes, in which a large ligand structure maintains donor atoms in a planar fashion around the metal ion, represent an important current objective in the study of transition-metal systems. This is particularly true in the case of ligands containing N_4 donors as they serve as simple models for biologically occurring molecules such as heme proteins, cyanocobalamin, chlorophyll, and other related systems. The isolation and characterization[1] of nickel(II) porphyrins from oil and oil shale lend further support to the choice of transition-metal complexes of tetraaza macrocyclic ligands as biomodels.

Some metal-directed template condensations lead directly to conjugated metal complexes. Examples are metal-directed (a) condensation of propargylaldehyde with *o*-phenylenediamine,[2] (b) tetramerization of *o*-aminobenzaldehyde,[3] and (c) condensation of *o*-phenylenediamine with 2,4-pentanedione.[4] The completely conjugated macrocyclic complexes studied comprise neutral,[3] monoanionic,[5] and dianionic ligands primarily of 14-membered rings. The increasing unsaturation in the macrocyclic ligand results in the reduction of core size, which is found to exhibit more pronounced effects in 14-membered rings.

Earlier investigations on 14-membered highly conjugated systems have essentially dealt with imine type complexes with only a few reports[6-8] on the imine–carbinolamine and dicarbinolamine varieties. The monocarbinolamine metal complexes obtained from the aliphatic dicarbonyl and diamine compounds are rather unstable when compared to their aromatic analogues. It has been reported[9] that the free carbinolamines obtained from the aliphatic compounds are very difficult to isolate and are very sensitive to acids. The earlier reports on the isolation of dicarbinolamine complexes did not describe in detail the conditions under which the stabilization of such moieties are possible. Tasker et al.[10] have recently reported the isolation and X-ray crystal study of a macrocyclic dicarbinolamine complex obtained by the template condensation of 2,6-diformylpyridine and dihydrazinobipyridine in the presence of Zn(II) ion. However, they have not made an in-depth analysis of the reasons for the stabilization of such moieties. Nor there was any attempt to synthesize a series of

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