phyrin derivatives. Second, within the framework of ligand-field theory, it is only possible to explain the magnetic properties in terms of a ^2E ground state with a first excited state some 200–400 cm^{-1} away, composed of varying amounts of $^6A_1$ and $^2E_1$ character, *and* by varying the ligand-field parameters slightly with temperature. Whatever the true description of the ligand field or of the vibronic nature of these systems the end observation (in the phenomenological description) of temperature-dependent parameters is necessary. Although not very satisfying, this latter requirement may well be compatible with the known geometry of other metal porphyrin compounds. Third, with these calculated parameters the observed NMR isotropic shifts can at least be reproduced quantitatively although the derived coupling constants are probably not unique. This is because they depend so critically on very small changes in the ligand-field parameters and so on the calculated pseudocontact shifts which in turn contribute quite substantially to the experimental shift.

The relation between electronic structure and biological activity is of particular current interest with several groups of workers actively engaged in preparing new synthetic model complexes, and particularly iron porphyrin derivatives, with this in mind. Although it is not yet established whether the particular electronic state of the iron atom controls or activates the biological function, the reverse is certainly true in that many different natural and synthetic iron complexes of this nature exhibit wide-ranging magnetic properties concomitant with the three nearly equienergetic, interacting ground states.

Acknowledgment. Very profitable discussions with Professor R. L. Martin and Drs. K. S. Murray, H. A. O. Hill, and P. D. Skyte are acknowledged.

Registry No. Fe(OEP)(3-Cl-py)$_2$ClO$_4$, 71414-31-8; Fe(OEP)(4-ac-py)$_2$ClO$_4$, 75149-73-4; Fe(OEP)(3-ac-py)$_2$ClO$_4$, 75172-95-1; Fe(OEP)(py)$_2$ClO$_4$, 71414-34-1; Fe(OEP)(*N*-me-im)$_2$ClO$_4$, 71414-35-2.

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Porphyrins. 41.[1] Phosphorus Mesoporphyrin and Phthalocyanine

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It is shown that synthesis of phosphorus porphyrins occurs from a pyridine–PBr_3 intermediate, and an improved synthetic procedure is given for P(MesoDME)(OH)$_2^+$ (MesoDME = mesoporphyrin dimethyl ester). The ^{31}P NMR spectral peaks occur between $\delta = -183$ and -197, depending on the solvent. The two protons of P(MesoDME)(OH)$_2^+$ can be titrated with $pK_{a1} = 9.53$ and $pK_{a2} = 12.20$, values obtained by monitoring the optical spectrum over the pH range 8–13 and the wavelength range 515–600 nm. Qualitatively the Q(0,0) or α band shifts from 583 nm at pH 7 to 561 nm at pH 13.3. This hypsochromic shift is attributed to back-bonding between the filled $O(p_x,p_y)$ and the empty $e_g(\pi^*)$ orbitals. The fluorescence lifetime decreases with increased pH: 4.1 (pH 7), 3.1 (pH 10), 2.6 ns (pH 13). A stable phosphorus phthalocyanine complex, P^{III}(Pc), can be made. It has a sharp Soret band at 442 nm. Its unusual visible spectrum is attributed to the four-orbital transitions $a_{1u}(\pi)$, $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$. A strong red fluorescence at 660 nm has a lifetime of 3.0 ns. There is also evidence for a P^V(Pc) species with a visible absorption like that of Zn(Pc) but with no fluorescence.

Introduction

Over the past 15 years considerable research has gone into the preparation of porphyrin complexes with various metals, with the result that porphyrin complexes are known with nearly every metal and semimetal in the periodic table.[2-4] One of the last type of complexes reported is those of phosphorus.[5,6] Since the initial report from our laboratory,[5] we have carried out further studies of phosphorus porphyrins. Our interest arises because phosphorus is the lightest atom forming a metalloporphyrin where the "metal" shows two oxidation states, in this case P^{III} and P^V; hence ab initio studies of the two oxidation states should prove easier than for transition-metal porphyrins, which contain d electrons. A second interest arises because of the possible biological use of phosphorylated porphyrin, since "demetalation" produces harmless phosphate ions rather than toxic metals.

In this paper we report the results of further investigations of these species: (1) an improved synthetic method that suggests that "metalation" occurs from a reactive pyridine–PBr_3 intermediate; (2) the acid–base properties of phosphorylated mesoporphyrin; (3) preliminary studies of the ^{31}P NMR spectra of phosphorylated porphyrins; (4) the synthesis of phosphorus phthalocyanine, which shows a fluorescent P^{III}(Pc) species and a nonfluorescent P^V(Pc) species.

Synthesis of Phosphorus Mesoporphyrin

The first reported synthesis was of the phosphorus octaethylporphyrin (OEP) complex; it proceeded in two steps (eq 1 and 2). Step 1 required 30 min in pyridine at 80–90 °C,

$$H_2(OEP) + PCl_3 \rightarrow P^{III}(OEP)^+Cl^- + 2HCl \quad (1)$$

$$P^{III}(OEP)^+Cl^- + H_2O + {}^1/_2O_2 \rightarrow P^V(OEP)(OH)_2{}^+Cl^- \quad (2)$$

with a mole ratio of PCl_3 to H_2(OEP) of 120:1. We were unable to carry out (1) in any solvent but pyridine. In particular it failed to go in amines, quinoline, or 2-picoline. Step 2 was presumed due to the presence of air and water.[5] In practice the oxidation step often failed, with the resulting re-formation of the free base H_2(OEP). Overall yields for P^V(OEP)(OH)$_2^+$ were never better than 30% and often were very poor. The second reported synthesis was of the P^V tetraphenylporphyrin (TPP) complex.[6] The reaction was carried out in pyridine with $POCl_3$, requiring 24 h at reflux temperature with a mole ratio of $POCl_3$ to H_2(TPP) of ~60:1.

In trying to improve the synthesis, we found that PBr_3 was better than PCl_3, and PI_3 gave no reaction. The following pieces of evidence show that PBr_3 forms a new, highly reactive species in pyridine. (1) On addition of PBr_3 to pyridine, the solution turns a bright, straw yellow color. (2) The PBr_3–pyridine solution reacts far more violently with paper than does either neat PBr_3 or pyridine. (3) Both neat $^{31}PBr_3$ and $^{31}PBr_3$ in CH_2Cl_2 show a structured line at $\delta = 228$.[7] In contrast,

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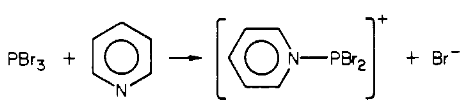
Table I. Absorption and Emission Data for Phosphorus Porphyrin and Phthalocyanine

compd	solvent	absorption peaks[a]						fluorescence lifetimes, ns[b]
$P(MesoDME)(OH)_2^+$	H_2O, pH 7					541 (1.0)	583.5 (1.57)	4.15 ± 0.04
$P(MesoDME)(OH)_2^+$	H_2O, pH 10					535 (0.98)	575 (1.47)	3.05 ± 0.04
$P(MesoDME)(OH)_2^+$	H_2O, pH 13					527 (1.09)	561 (1.25)	2.60* ± 0.08
$P^{III}(Pc)$	pyridine	413 (0.65)	435 (1.25)	442 (2.15)	597 (0.25)	626 (0.5)	655 (1.0)	3.02 ± 0.02
$P^V(Pc)$	pyridine				413 (0.2)	593 (0.3)	653 (1.0)	no emission

[a] Wavelengths in nm. Absorbance ratios in parentheses. [b] Measured by Thomas.[14] Errors are standard deviations. These times are fit by convoluting an exponential decay with the detector response function except for the * time, which was fit to $A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$ with $(\tau_1, \tau_2) = (2.60 \pm 0.08, 0.52 \pm 0.18)$ ns and $A_1/A_2 = 3.3 \pm 0.7$. However τ_2 may be an artifact. A single exponential decay gave a poorer fit with $\tau = 2.38 \pm 0.06$ ns.

the ^{31}P NMR spectrum of PBr_3 in pyridine shows a structureless line at $\delta = 218$; in pyridine–CH_2Cl_2 (1:1) the structureless line is at 223. [It is necessary to keep these samples under Ar when both PBr_3 and pyridine are present, as the mixture forms a hard white solid when exposed to air.]

We suggest that the intermediate is of the form


(3)

This is analogous to known phosphorus trihalide reactions with secondary amines[8] (eq 4). Complexes of arsenic, antimony,

$$PX_3 + 2R_2NH \rightarrow R_2NPX_2 + [R_2NH_2]X \quad (4)$$

and bismuth trihalides with pyridine are known.[9] Conductometric titration of pyridine (0.1 M in nitrobenzene) with PBr_3 showed that the conductivity reaches a limiting value at equimolar ratio, consistent with eq 3. Our titration results are similar to those reported by Roper and Wilkins,[10] who titrated 2,2′-dipyridyl in nitrobenzene with trihalides MX_3 (M = As, Sb, Bi) and deduced a reaction analogous to eq 3. Note that the observed small change in ^{31}P NMR δ is consistent with no change in coordination number, as proposed in eq 3. [Change in the overall species charge generally has only a small effect on δ.[7]]

An improved small-scale synthesis of phosphorylated mesoporphyrin can be carried out by using the py–PBr_3 intermediate as follows. Free-base mesoporphyrin dimethyl ester (H_2(MesoDME)) was made from hemim by using the methods described by Falk.[11] Under an inert atmosphere, either argon or nitrogen, the py–PBr_3 intermediate was prepared by adding 0.05 mL of PBr_3 to 2 mL of pyridine. From this yellow solution, 0.05 mL was added to a 0.5-mL pyridine solution $\sim 1 \times 10^{-3}$ M in H_2(MesoDME). The mole ratio of PBr_3 to porphyrin is ~25:1. Over a 1-h period at room temperature the initial red free-base fluorescence gradually faded, and the initial deep purple color became greenish yellow. We believe that this step represents reaction 5. Oxidation of the P^{III}

$$\text{py–}PBr_3 + H_2(\text{MesoDME}) \rightarrow P^{III}(\text{MesoDME})^+ + Br^- + 2HBr + \text{py} \quad (5)$$

species to P^V was effected by addition of 0.05 mL of a solution of 0.05 mL of Br_2 in 2 mL of pyridine under an inert atmosphere. The reaction proceeded immediately at room temperature. The observed lack of fluorescence suggests that this step represents eq 6. Then ~0.5 mL of H_2O under inert

$$P^{III}(\text{MesoDME})^+ + Br_2 \rightarrow P^V(\text{MesoDME})Br_2^+ \quad (6)$$

atmosphere was added, which hydrolyzed the excess PBr_3 and also replaced the Br^- ligands by OH^-. The solution was then opened to the air and diluted with ~20 mL of pH 6–7 aqueous buffer. This step neutralized the acid generated by step 5 and by the hydrolysis of the excess PBr_3. The solution now showed the characteristic orange fluorescence of the P^V(MesoDME)$(OH)_2^+$ complex. For purification of the complex, the buffered solution (20 mL) was extracted with ~25 mL of CH_2Cl_2. The aqueous layer, which contains the various inorganic salts, was discarded, and the CH_2Cl_2 layer was then extracted with ~25 mL of H_2O. The water layer was a clear purple solution with optical spectra (see below) characteristic of P(MesoDME)$(OH)_2^+$. While the method of preparation leaves the nature of the counterion in doubt, proton NMR studies showed that the species remains the dimethyl ester.

The synthesis just described is effective in producing optical spectra that we attribute to the P^V(porphyrin)$(OH)_2^+$ species for mesoporphyrin dimethyl ester, octaethylporphyrin, tetraphenylporphyrin, and tetrakis(perfluorophenyl)porphyrin. However, it was not effective with porphine or tetrabenzporphyrin even at 90–100 °C reaction temperatures.

On a larger scale, a similar ratio of PBr_3 and Br_2 to porphyrin was used, again under inert atmosphere. However, PBr_3 and Br_2 may be added directly to the porphyrin in pyridine.

Absorbance Titration

P^V(MesoDME)$(OH)_2^+$ shows color changes at basic pH. For these changes to be studied, solutions with fixed porphyrin concentration were prepared volumetrically in buffer solutions ranging from pH 6–13. The latter were prepared according to specifications as in ref 12. Solutions of higher pH were prepared by using 0.1, 0.2, and 0.4 M KOH, for which we assume that pH = 14 + log $[OH^-]$. To prevent CO_2 from lowering the pH, all solutions above pH 11 were stored in plastic containers under Ar. The phosphorylated MesoDME has $\sim 10^{-2}$ M solubility in H_2O at pH 7 but becomes rather less soluble above pH 10, requiring the use of more dilute solutions.

The absorption peaks for three pHs are listed in Table I. In Figure 1 the spectra are shown in the two pH ranges where isosbestic points are observed. These spectra suggest that there are two titratable protons and hence three species: P(Me-

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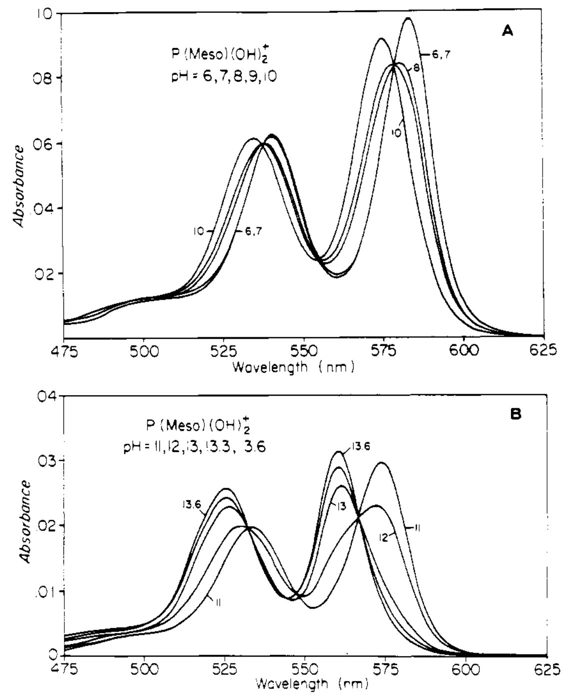

Figure 1. Absorbance of dihydroxo(mesoporphyrinato)(dimethyl ester)phosphorus [$P(Meso)(OH)_2^+$]: A, pH values 6–10; B, pH values 11–13.6. The concentrations for B were one-third those for A.

soDME)$(OH_2)^+$ = X, P(MesoDME)O(OH) = Y, and P-(MesoDME)O_2^- = Z. [Here O_2 stands for dioxo, not dioxygen.] The acid equilibrium constants are

$$K_{a1} = [Y][H_3O^+]/[X] \quad (7)$$

$$K_{a2} = [H_3O^+][Z]/[Y] \quad (8)$$

We shall here assume that the activity and the concentrations of these species are the same; we also assume that $[H_3O^+]$ is from the pH of the buffer solutions, as discussed above.

For determination of the acid dissociation constants, K_{a1} and K_{a2}, we studied the absorbances $A(\lambda,\text{pH})$ for a series of solutions containing equal total amounts of phosphorus porphyrin. In this series then

$$A(\lambda,\text{pH}) = A_x(\lambda)x + A_y(\lambda)y + A_z(\lambda)z \quad (9)$$

$$K_{a1} = y[H_3O^+]/x \qquad K_{a2} = z[H_3O^+]/y \quad (10)$$

$$x + y + z = 1 \quad (11)$$

Here x, y, and z are the mole fractions of the three species X, Y, and Z defined above; $A_x(\lambda)$, $A_y(\lambda)$, and $A_z(\lambda)$ are the absorbance values of solutions of the same concentration as our total concentration of phosphorus porphyrin but containing only X, Y, and Z, respectively.

The general problem of determining pK_{ai} and $A_i(\lambda)$ values from spectrophotometric data $A(\lambda,\text{pH})$ has been recently discussed by Meloun and Cermák.[13a] They present a method based on minimizing the sum of the squares of the residuals (eq 12). Here $A_{\text{exptl},i}$ are the measured $A(\lambda,\text{pH})$ values; $A_{\text{calcd},i}$

$$U = \sum_{i=1}^{N} w_i(A_{\text{exptl},i} - A_{\text{calcd},i})^2 \quad (12)$$

are determined from the parameters pK_{ai} and $A_i(\lambda)$ with eq 9–11; the w_i are statistical weights usually set at unity. In their procedure an initial guess is made of the pK_{ai} and $A_i(\lambda)$, and a heuristic trial and error procedure is used to minimize U.

(13) (a) Meloun, M.; Cermák, J. *Talanta* **1979**, *26*, 569. (b) Shankland, D., to be submitted for publication.

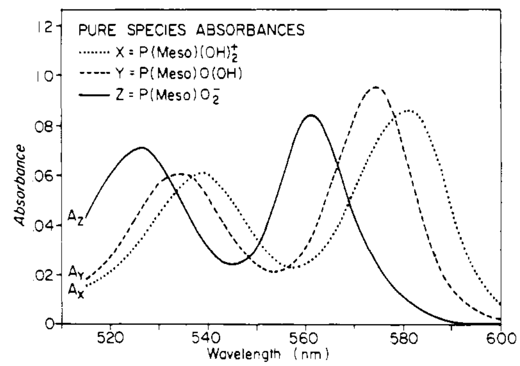

Figure 2. Absorbance curves for $P(Meso)(OH)_2^+$ = X, P(Meso)O(OH) = Y, and $P(Meso)O_2^-$ = Z deduced from the titration data of Figure 1.

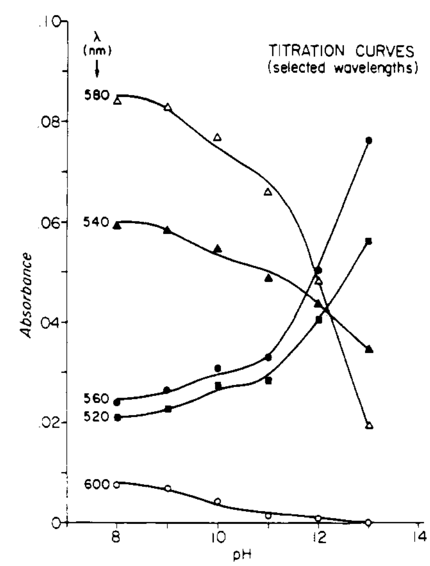

Figure 3. Titration curves $A(\lambda,\text{pH})$ for various λ showing experimental points (circles, squares, and triangles) and fitted curves (lines).

This problem was solved for use[13b] in a slightly different manner based on that fact that the K_{ai} parameters enter eq 9–11 quite differently from the parameters $A_i(\lambda)$. Thus for any particular wavelength there are five unknowns: $A_x(\lambda)$, $A_y(\lambda)$, $A_z(\lambda)$, K_{a1}, A_{a2}; however if measurements are done on a second wavelength, only three more unknowns are introduced. U was minimized by providing an initial guess for the K_{ai}. Equations 10 and 11 then allow determination of x, y, and z for any particular pH. This gives for each wavelength a set of linear equations (eq 13), where the subscript pH runs

$$x_{\text{pH}}A_x(\lambda) + y_{\text{pH}}A_y(\lambda) + z_{\text{pH}}A_z(\lambda) = A(\lambda,\text{pH}) \quad (13)$$

over the different pH values measured. The linear equations (eq 13) allow formal solution for the $A_i(\lambda)$ based on a standard least-squares procedure. The sum of the squares of the residuals, U, is determined. A nonlinear least-squares procedure is then used to minimize U as a function of K_{a1} and K_{a2}. The best values are $K_{a1} = 2.96 \times 10^{-10}$ and $K_{a2} = 6.34 \times 10^{-13}$. Figure 2 shows the final spectra deduced for the three porphyrin species, and Figure 3 shows titration curves for selected wavelengths.

[On the first runs, data were used for pH = 7, 8, 9, 10, 11, 12, and 13. However, study of the residuals indicated systematic error for the pH 7 data, which was then dropped. The accuracy of the K_{ai} values is ~2%, which is the deviation between two determinations of the K_{ai} using half the data. The final K_{ai} values are then based on all $A(\lambda,\text{pH})$ data: 6 pH values and 35 wavelengths from 515 to 600 nm. The calculated absorbances generally agreed with the experimental

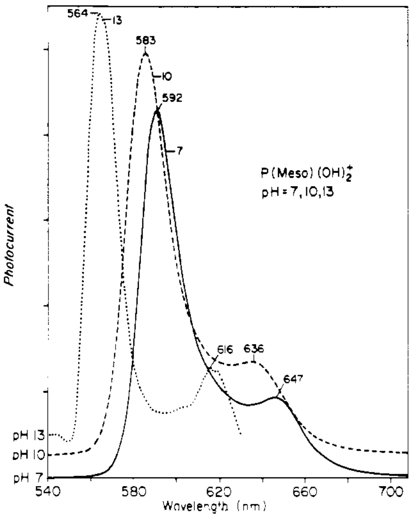

Figure 4. Fluorescence spectra for phosphorylated mesoporphyrin at pH 7, 10, and 13 (taken on a Perkin-Elmer 650-10S; uncorrected for the wavelength dependent response of the detection system).

within ±0.001 unit, with a few points off as much as ±0.003.]

Emission. Figure 4 shows the emission spectra of phosphorylated mesoporphyrin dimethyl ester taken at pH 7, 10, and 13. It can be seen that the fluorescence shifts to the blue over this pH range in the same manner as the absorption; the excitation spectra of the fluorescence shift similarly. Thus our spectra suggest that the equilibrium between the various acid-base forms of phosphorylated mesoporphyrin remains much the same for the first excited singlet state as for the ground state.

The fluorescence lifetime was measured by Dr. J. C. Thomas exciting with a picosecond dye laser and using time-correlated single-photon counting. The full system is described elsewhere.[14] The lifetimes are reported in Table I. It can be seen that at higher pH the lifetime decreases. We examined the pH 13 solution for phosphorescence at 77 K; however, none was observed. [Phosphorescence in EPA-ethyl iodide (1:1) has previously been reported.[5]]

Discussion. The blue shift observed on deprotonation of $P(MesoDME)(OH)_2^+$ has a natural explanation in terms of the taxonomy of metalloporphyrin electronic spectra.[4] *Hypsoporphyrins* have a blue-shifted visible and near-UV spectrum.[4] Previously known hypsoporphyrins have transition metals with filled $e_g(d_\pi)$ orbitals. The porphyrin visible and near-UV bands arise from transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$.[4] The blue shift of hypsoporphyrins is attributed to back-bonding of the filled $e_g(d_\pi)$ into the empty $e_g(\pi^*)$ orbitals, which pushes up the energy of the $e_g(\pi^*)$ orbitals, thus increasing the energy gap for the optical transitions. Iterative extended Hückel (IEH) calculations on $P(\mathbf{P})(OH)_2^+$ and $Si(\mathbf{P})(OH)_2$[5,15] ($\mathbf{P}$ = porphine) show filled orbitals of the oxygen atoms in the Fermi energy region (i.e., the energy region of the HOMO and LUMO, highest occupied and lowest unoccupied molecular orbitals). Qualitatively we expect these filled orbitals to go up in energy in $P(\mathbf{P})O_2^-$, which has four high-energy filled orbitals $e_g(O_\pi)$, $e_u(O_\pi)$. [O_π refers to oxygen $2p_x$, $2p_y$ orbitals with x and y axes parallel to the porphyrin plane.] The higher energy for $e_g(O_\pi)$ would then give rise to increased back-bonding with $e_g(\pi^*)$, thus explaining the observed hypso shift of the visible spectra with deprotonation.

Previously known transition-metal porphyrins that were hypso, if they showed emission, show little fluorescence and

Table II. ^{31}P NMR Data

sample	compd^a	solvent	ref	δ
1	$P(OEP)(OH)_2ClO_4$	$(CD_3)_2CO$	*b*	−183, −191^d
2	$P(MesoDME)(OH)_2PF_6$	$(CD_3)_2CO$	*b*	−190
3	$P(MesoDME)(OH)_2PF_6$	CD_3OD	*c*	(−192),^{e} −193^f
4	$P(MesoDME)(OH)_2PF_6$	5:3 CD_3OD–D_2O	*c*	(−186), (−194),^{e} −195
5	$P(MesoDME)(OH)_2X$	D_2O	*c*	(−196),^{e} −197

^{a} Abbreviations: OEP = octaethylporphyrin; MesoDME = mesoporphyrin dimethyl ester. ^{b} H_3PO_4 in D_2O; corrected by −5 ppm so that the main PF_6^- peak occurs at δ = −145. ^{c} Glycerophosphoryl choline; main PF_6^- peak observed at δ = −144.7. ^{d} The −191 peak ~2/3 as intense as the −183 peak. ^{e} Peaks in parentheses ~1/6 as intense as main peak. ^{f} T_1 for this line was found to be 2.1 s.

strong phosphorescence with lifetime $\tau_p < 3$ ms, because the back-bonding from $e_g(d_\pi)$ into $e_g(\pi^*)$ introduces strong spin-orbit coupling.[4] In the present case, the back-bonding from $e_g(O_\pi)$ into $e_g(\pi^*)$ should introduce only a little spin-orbit coupling; thus the deprotonated compounds continue to show strong fluorescence.

^{31}P NMR Spectra

A Bruker WH-360 NMR spectrometer operating at 145 MHz in the pulsed Fourier transform mode was employed for the experiment. No proton decoupling was used, and the sample temperature was controlled to ±1 °C. The spectral width was 50 kHz. The positions of the signals were referenced to either an external phosphoric acid sample or an internal glycerophosphoryl choline signal.

The results are reported in Table II. It can be seen that the phosphorus resonance is observed between δ = −183 and −197 depending on complex, counterion, and solvent. These δ values are comparable to values reported[7] for PF_6^- (δ = −144) and $[P(C_{12}H_8)_3]^-$ (δ = −181) ($C_{12}H_8$ is biphenylene), which are also P^V six-coordinate species. Two features of the resonance are unexplained. (1) Sample 1 showed a doublet structure, which was also observed on a Varian CFT-20 instrument. The two peaks were unchanged with addition of 1% H_2O and with change of temperature from 20 to 40 °C. (2) Samples 3–5 showed weak satellite peaks slightly downfield from the main resonance (Table II).

Phosphorus Phthalocyanine

Synthesis and Optical Spectra. The preparation of phosphorus phthalocyanine begins with the addition of the py–PBr_3 intermediate (prepared as above) to a solution of free-base phthalocyanine ($H_2(Pc)$) in pyridine, all under an inert atmosphere. For this step, concentrations like that used for the synthesis of $P(MesoDME)(OH)_2^+$ are appropriate. The formation of phosphorus phthalocyanine occurs at 90–100 °C with a 1-h reaction time. We presume this represents a reaction similar to eq 5 producing a $P^{III}(Pc)$ species from $H_2(Pc)$. After the reaction with py–PBr_3, the reaction mixture is opened to air and added to ~100 cm^3 of buffered water (pH 7). The solid is collected by vacuum filtration and then is washed with water. The residue is redissolved in pyridine, and the solution is chromatographed on Al_2O_3. Any free base, which is only marginally soluble in pyridine, stays at the top of the column. A blue nonfluorescent band moves down the column first, on elution with pyridine; we believe this is a $P^V(Pc)$ species. The main product, which is green and red fluorescent follows with continued pyridine elution or with elution using pyridine–ethanol (1:1); we believe this is a $P^{III}(Pc)$ species. It should be noted that in solution $P^{III}(Pc)$ deteriorates in room light over several days. The absorption and emission spectra of the two species are shown in Figure 5 and 6. The absorbance maxima and fluorescence lifetimes are given in Table I.

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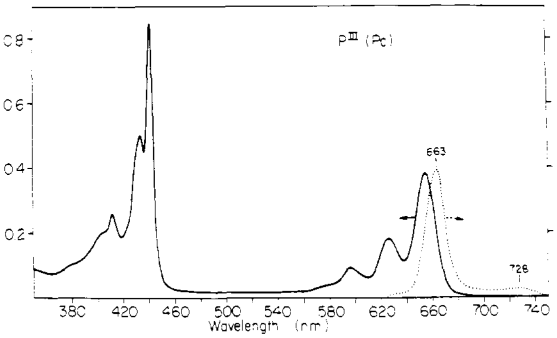

Figure 5. Absorption in pyridine–CH_2Cl_2 ($\sim$1:20) (solid line) and uncorrected emission (dotted line) in pyridine of $P^{III}(Pc)$. The 442-nm band has $\epsilon > 140\,000\ M^{-1}\ cm^{-1}$.

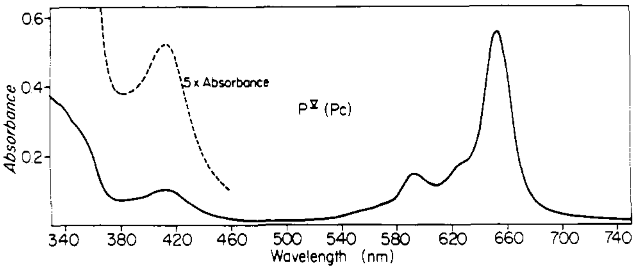

Figure 6. Absorption in pyridine of $P^V(Pc)$. No emission is observed.

Species Characterization. The main basis of our characterization of the two phosphorus phthalocyanine species are (i) the mode of synthesis, (ii) the optical spectra (see Discussion below), and (iii) analogies to phosphorus porphyrins. Certain points in favor of our identification should be stressed: we have synthesized the $P^{III}(Pc)$ species many times. Unlike the phosphorus porphyrin case, this stable phosphorus complex is obtained without introduction of Br_2. It should also be noted that the phthalocyanine ring tends to favor lower oxidation states of the central metal compared to porphyrin.[16]

Some further chemical characterizations of the $P^{III}(Pc)$ species were obtained.

Acids. When a few percent of trifluoroacetic acid (TFA) is added to an absolute ethanol solution of $P^{III}(Pc)$, a spectroscopic change is observed, which is largely reversible on addition of pyridine. When solid $P^{III}(Pc)$ is dissolved in neat TFA, the spectrum observed is identical with the acid phthalocyanine spectrum given by either $H_2(Pc)$ or $Li_2(Pc)$ in neat TFA. $P^{III}(Pc)$ is soluble in cold, concentrated H_2SO_4 with marked spectroscopic changes that are reversible on dilution with excess pyridine. Over several weeks the H_2SO_4 solutions appear unchanged if stored in the dark.

Bases. Upon addition of strong bases to solutions of $P^{III}(Pc)$ spectral changes occur; e.g., when tetramethylammonium hydroxide is added to a pyridine solution, the spectral peaks occur at 668, 616, 590, and 455 nm. Addition of HCl reverses the changes.

Solubility. Solid $P^{III}(Pc)$ goes into solution slowly at room temperature, and heated solutions remain supersaturated for several days before a fine flocculant precipitates. The solubility in cold solutions is *very slight* (solutions virtually colorless) for ethyl acetate, acetone, chloronaphthalene, tetrahydrofuran, 2,6-lutidine, and dimethylformamide; solubility is *slight* to *moderate* (absorbance below 4) for ethanol < dimethyl sulfoxide $\approx$ *N,N*-dimethylethanolamine < pyridine. The highest solubility observed is in hot chloronaphthalene.

A *mass spectrum* of $P^{III}(Pc)$ showed a strong peak at 545.4 amu, corresponding to a species $P(C_{32}H_{16}N_8)H_2^+$, i.e., $P(Pc)H_2^+$.

Only one sample of the blue, nonfluorescent material identified as $P^V(Pc)$ was obtained. We believe it was produced by air oxidation of $P^{III}(Pc)^+$ during the purification procedure. However, when 1 drop of 30% H_2O_2 is added to 10 mL of $P^{III}(Pc)$ in pyridine, the solution turns colorless overnight. That this treatment fails to give the reaction $P^{III}(Pc) \rightarrow P^V(Pc)$ may be explained by the observation that addition of the same amount of peroxide to $P^V(Pc)$ in pyridine causes the solution to turn colorless in 20 min. In contrast we should note that a similar peroxide treatment of Zn(Pc) has no effect.

Discussion. The optical spectrum of $P^{III}(Pc)$ is very unusual in having a sharp Soret band at 442 nm. While such a band is characteristic of porphyrins, phthalocyanines generally show a broad Soret band at $\sim$330 nm. A natural explanation for this unusual Soret band is possible for a $P^{III}(Pc)$ species. The characteristic visible and Soret bands of porphyrin arise from configuration interaction among the four-orbital transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$, where $a_{1u}(\pi)$ and $a_{2u}(\pi)$ are nearly degenerate.[4] Pariser–Parr–Pople[17,18] and "peel" electron calculations[19,20] show that in changing from porphyrin to phthalocyanine the energy of $a_{2u}(\pi)$ shifts down in energy relative to $a_{1u}(\pi)$; thus the visible absorption band of phthalocyanine is nearly pure $a_{1u}(\pi) \rightarrow e_g(\pi^*)$; furthermore the phthalocyanine Soret band contains not only $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ but also other transitions from more deeply buried π orbitals. In $P^{III}(Pc)$ we expect a new filled orbital $a_{2u}(3p_z)$ to be introduced into the Fermi energy region, where $3p_z$ is an orbital on phosphorus.[5,21] A porphyrin-like four-orbital situation is recreated with transitions $a_{1u}(\pi)$, $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$, so that a porphyrin type Soret band appears.

A curious feature of the $P^{III}(Pc)$ optical spectra is the strong fluorescence. This contrasts with studies on similar species $M^{III}(OEP)^+$ (M = P, As, Sb, Bi),[4,5,21] which show no fluorescence. We can provide a speculative explanation for this difference. There is some evidence that for $M^{III}(OEP)^+$ the M atom is out of plane.[5,21] Since $a_{2u}(3p_z)$ is antibonding with $a_{2u}(\pi)$, the transition $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$ may cause the metal to move back toward the plane. The coupling of shape change to the optical transition enhances the radiationless decay of the excited singlet. However, for $P^{III}(Pc)$ there is probably less antibonding character between $a_{2u}(3p_z)$ and $a_{2u}(\pi)$, since the latter is more deeply buried in phthalocyanine. Therefore, the P atom may be in plane in the ground state. This latter structure is also consistent with the observed chemical stability of $P^{III}(Pc)$. Hence there is no P atom movement coupled to the optical transition $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$, and the observation of fluorescence is accounted for.

Summary

Phosphorus is the first nonmetal to occupy the center of a porphyrin ring. We have shown that the insertion reaction proceeds from a reactive py–PBr_3 intermediate. We have examined the acid–base titration properties of the dihydroxo(mesoporphinato)phosphorus(V) complex and shown that the species can lose one or two protons. The deprotonated species provides the first example of a fluorescent hypsoporphyrin. The (phthalocyanato)phosphorus(III) complex can be made. It shows great acid stability. Its unusual sharp Soret band at 442 nm is attributed to four-orbital transitions $a_{1u}(\pi)$, $a_{2u}(3p_z) \rightarrow e_g(\pi)$. Phosphorus porphyrin and phthalocyanine thus provide novel variants to the known chemical and spec-

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troscopic properties of these macrocycle compounds.

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Registry No. $P(OEP)(OH)_2ClO_4$, 62638-18-0; $P(MesoDME)(OH)_2PF_6$, 75444-55-2; P, 7723-14-0; $H_2(Pc)$, 574-93-6; P(Meso)O(OH), 75431-38-8; $P(Meso)O_2^-$, 75431-39-9; PBr_3, 7789-60-8.

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Derivatized Lamellar Phosphates and Phosphonates of M(IV) Ions

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By means of a metathetical precipitation reaction, a broad series of crystalline and semicrystalline layered products which can have various organic groups affixed on the inorganic sheets of zirconium phosphate related structures has been prepared. These compounds are exceedingly thermally stable as shown by TGA measurements, and they are quite chemically stable in nonalkaline media. Crystallinity and particle size were found to depend on the conditions of preparation; the effect of the appended organic group on basal spacing was clearly evident by X-ray diffraction. IR spectra in all cases are consistent with the disposition of the groups as well. Surface area measurements have tended to verify the accessibility of the relatively vast internal surface of the compounds, as have some intercalation reactions.

Introduction

Recent investigations have shown the viability and desirability of "heterogenization" of various solution phase agents onto certain solid supports.[1] The bulk of this work has involved inorganic substrates such as silica[2] or organic polymers based mainly on polystyrene.[3] In the former case, affixation has usually been accomplished by reacting terminal trichloro- or trimethoxysilyl compounds with pendant inorganic hydroxyl groups; in the latter, phenyl rings on the polymer backbone were typically derivatized with appropriate coordinating functions. In both approaches, the strategy was to anchor ligating groups onto the solids prior to incorporation of an active metal site. There are alternative methods of obtaining essentially the same sort of products such as polymerization of the metal-site-containing monomer to get the product in one step[4] or reaction of allyl organometallic compounds directly with hydroxylic surfaces.[5] Generally, the concept has proven to be feasible, but problems of activity loss primarily due to accessibility to sites and attrition have plagued investigators.[6]

Recognizing that both the inorganic and organic supports previously employed have an intrinsically disordered disposition of sites upon or within them, we considered the possibility of using a highly ordered source of handles for subsequent anchoring. One obvious class of candidates possessing an array of planar handles is the inorganic hydroxylic layered compounds, epitomized by certain of the clay minerals such as montmorillonite or hectorite. In fact, these materials have been derivatized with some passive organics,[7] and recently attempts at incorporating active catalysts via ion exchange of interlayer cations have been described.[8] Typically, site–site distances are on the order of 25 Å, leading to relatively low capacities. Moreover, ion-exchanged groups tend to be labile and/or mobile under most conditions. Nevertheless, the idea of using layered solids for supports is a compelling objective, for the vast potential internal surface could be highly advantageous. If sites situated within the bulk of a suitable layered solid can be prepared and shown to be accessible to exterior species (via intercalation), one might expect enhanced selectivity for certain reactions to result from the two-dimensional nature of the site environment,[9] as well as minimal attrition due to the chelating effect of a bilayered situation of ligands. High site densities would also be expected if intersite distances were considerably smaller than in the clays.

Crystalline layered zirconium phosphate[10] presents an ideal model on which to test the foregoing ideas. It contains on its lamellar surfaces a hexagonal array of hydroxyl groups spaced about 5.3 Å apart (see Figure 1). This leads to an area per site of 24 Å^2, which is quite suitable as a cross-sectional limit for many affixed substituents. It is known to undergo intercalative ion exchange and inclusion with a broad series of species.[11] Although it was our initial intention to attempt to attach organic functions to the pre-formed phosphate via the pendant hydroxyl group as done by Yamanaka,[12] and also with silicas,[2] we found that a far superior approach involved direct precipitation of the derived phosphate (or phosphonate) with Zr^{4+} or other tetravalent metal ions (eq 1).

$$M^{4+} + 2(HO)_2P(=O)OR \text{ or } (HO)_2P(=O)R \rightarrow M(O_3POR)_2 \text{ or } M(O_3PR)_2 \quad (1)$$

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