

Figure 2. Plot of $\log K_L$ vs. ΔH^* (○) and total charge on metal complex vs. ΔS^* (×) for a series of tetradentate nickel(II) chelates.

complexes. Therefore, $\text{Ni}(\text{tren})\text{MeGly}^{2+}$ may exist in solution in two forms, one with *tren* acting as a tetradentate ligand and another as a tridentate one. This could explain the unexpectedly low ΔH^* value for $\text{Ni}(\text{tren})\text{MeGly}^{2+}$ hydrolysis. If one of the catalytic active species was $\text{Ni}(\text{tren})\text{MeGly}^{2+}$ with *tren* acting as a tridentate ligand, than its formation constant value would be smaller and its Lewis acidity higher than if it was acting as a tetradentate donor. Therefore, ΔH^* for $\text{Ni}(\text{tren})\text{MeGly}^{2+}$ hydrolysis could be an average value for the catalytic effects of two complexes, one with *tren* binding as a tridentate ligand and the other as a tetradentate donor.

In summary, these studies indicate that both the Lewis acidity and the charge of a metal chelate are important in determining its catalytic activity toward amino acid ester hydrolysis, and that previous studies^{18,19} indicating that only one of the two effects was important were probably fortuitous. Moreover, other effects such as strain and steric considerations,

the number of donor groups, and probably the stereochemistry of the metal chelates are important. It is probably for the latter reason that no correlation is observed to exist between $\log K_L$ and the values of ΔH^* and ΔS^* for the metal nitrilotriacetate promoted hydrolysis of MeGly .

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Porphyryns. 34.¹ Phosphorus Complexes of Octaethylporphyrin

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Abstract: The synthesis and optical spectra of previously unreported complexes of octaethylporphyrin (OEP) with phosphorus are described. Phosphorus, like arsenic and antimony, can assume oxidation states of III and V in the porphyrin hole. (Bi forms only a III complex.) The complexes have the forms $(\text{OEP})\text{P}^{\text{III}}\text{X}^-$ and $(\text{OEP})\text{P}^{\text{V}}(\text{X})_2\text{Y}^-$, with X an anionic ligand and Y^- a counterion. Iterative extended Hückel calculations rationalize the fact that the V species have normal porphyrin absorption and emission spectra while the valence III species show extra absorption bands and no fluorescence. The extra bands of the III species are attributed to charge transfer transitions $a_{2u}(3p_z)$ (phosphorus) $\rightarrow e_g(\pi^*)$ (ring), that strongly interact with the normal porphyrin excited (π, π^*) states.

The metalloporphyrin derivatives of group 5a elements have been the subject of recent experimental²⁻⁴ and theoretical³ studies. These compounds are of interest chemically and spectroscopically because the central atoms As and Sb can exist in both the formal oxidation states III and V. Bismuth is known only as the III complex. Theory predicted and new experiments proved^{3,4} (contrary to the original identification²) that the valence V species has the form $(\text{P})\text{M}^{\text{V}}(\text{X})_2\text{Y}^-$ and has a normal optical absorption spectrum. In this notation (P) stands

for the porphyrin ring, M stands for As or Sb, X stands for an anionic ligand such as OH or Cl, and Y^- stands for a nonligand counterion such as Cl^- or ClO_4^- . By normal absorption we mean a visible-near-uv spectrum consisting only of Q(π, π^*), B(π, π^*) (Soret), and N(π, π^*) (~ 330 nm) bands in the region $\lambda > 320$ nm. These compounds are pink in solution and show clear fluorescence and phosphorescence.

On the other hand, valence III species were predicted and shown to have form $(\text{P})\text{M}^{\text{III}}\text{Y}^-$ and a hyper absorption

Table I. Absorption and Emission Peaks for (OEP)P(X₂)⁺ Species

X ⁻	Solvent	A. Absorption: Wavelength (nm) ($\epsilon \times 10^{-4}$)				$\epsilon(Q_{00})/\epsilon(Q_{10})$
		B(0,0)	Q(1,0)	Q(0,0)		
OH ⁻	C ₂ H ₅ OH	403 (23.5)	541 (1.04)	583 (1.77)		1.7
OH ⁻	CH ₃ CN	402 (23)	541 (1.0)	583 (1.7)		1.7
HCOO ⁻	CH ₃ CN	399 (18)	531 (1.0)	571 (1.3)		1.3
CH ₃ COO ⁻	CH ₃ CN	400 (18)	536 (0.89)	575 (1.1)		1.2
F ⁻	CH ₃ CN	398 (20)	530 (0.95)	570 (1.1)		1.1
F ⁻	Acetone	399 (15)	534 (0.87)	574 (1.1)		1.2
CN ⁻	CH ₃ CN	398 (17)	531 (0.93)	571 (1.2)		1.3
O ₂ ⁻	CH ₃ CN	403 (13)	529 (1.5)	560 (1.4)		0.92
O ₂ ⁻	Acetone	406	530	561		0.97

X ⁻	Solvent	B. Emission: Wavelength (nm)						
		T, K	Q(0,0)	Q(0,1)	ϕ_r	T(0,0)	ϕ_p	τ_p
OH ⁻	EPA	77	585	645	0.1 ^a		0.001 ^b	
OH ⁻	30/70 ^c	77	586	644				
OH ⁻	90% EPA/10% C ₂ H ₅ I	77				737		7 ms
OH ⁻	CH ₃ CN	298	590	644	0.1 ^a			
CN ⁻	CH ₃ CN	298	580	621 (sh), 634	0.01 ^d			
F ⁻	CH ₃ CN	298	580	621, 634	0.01 ^d			

^a Rough. ^b Very rough upper limit. ^c 30% 1-butanol: 70% 3-methylpentane. ^d Very rough.

spectrum.³ Hyper spectra are defined as having relatively intense extra bands in the region $\lambda > 320$ nm, in addition to the Q, B, and N bands.^{5,6} In the M(III) case, like for porphyrin complexes of Sn(II) and Pb(II),^{7,8} the extra bands are attributed to charge transfer transitions of $a_{2u}(np_z) \rightarrow e_g(\pi^*)$ origin, probably strongly mixed with the normal (π, π^*) excited states. The hyper complexes are amber in solution, are non-fluorescent, but have weak, short-lived phosphorescence.³

Porphyrin complexes of almost all the metallic elements are known,^{5,6,9} as well as derivatives of two metalloids, arsenic and silicon. The ease with which the As, Sb, and Bi porphyrins are made² suggested that a similar synthesis should be attempted for phosphorus. The resulting complexes of phosphorus octaethylporphyrin reported in this paper seem to be the only ones known in which a nonmetal is coordinated to the porphyrin nucleus.^{5,6,9}

Experimental Section

Apparatus. The ion migration experiment utilized an apparatus like one previously described.¹⁰ The NMR data were gathered on a Varian Model CFT-20 Fourier transform instrument, using acetone-*d*₆ as a solvent and tetramethylsilane as an internal standard. The mass spectrum was determined on an AEI-MS 9 mass spectrometer, at an ionization potential of 70 eV. The basic optical apparatus has been recently described.¹¹ Briefly it consists of an exciting and a detecting monochromator at right angles, which provide respectively for excitation and emission spectra; a strobe lamp, oscilloscope, and signal averaging eductor were used for phosphorescence lifetime measurements. Emission was measured with a cooled RCA 8852 photomultiplier tube. A Cary 14 was used for absorption spectra.

Synthesis. (Dihydroxooctaethylporphyrinato)phosphorus perchlorate [(OEP)P(OH)₂⁺ClO₄⁻·H₂O or I]. Into a 50-ml three-necked reaction vessel were placed 100 mg of octaethylporphyrin free base [(OEP)H₂], 20 ml of pyridine (distilled from CaH₂ into the vessel under a stream of argon), followed by 2 ml of PCl₃. Dry argon was introduced through one neck and exited through another to a flask of water, which provided a positive gas pressure in the system. Through the third neck the PCl₃ was added and subsequent aliquots removed. This reaction mixture, maintained under an atmosphere of dry argon, was heated to 80–90 °C for 30 min. Reaction was monitored by taking the absorption spectra in dry benzene of aliquots of the reaction mixture. Disappearance of the (OEP)H₂ spectrum and appearance of the hyper spectrum (see below) indicated completion.

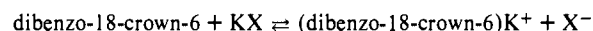
The reaction mixture was then reduced to dryness on a rotary evaporator, removing the pyridine and excess PCl₃. The residue was taken up in CH₂Cl₂/H₂O and extracted several times with CH₂Cl₂.

The CH₂Cl₂ fraction was evaporated to dryness, the residue taken up in a minimum amount of methanol, and filtered to remove insoluble (OEP)H₂. A volume of water about five times that of the methanol was added, after which unidentified precipitate formed and was filtered off. Dropwise addition of an aqueous NaClO₄ solution precipitated the desired compound, I, which was filtered off, washed with water, and dried under vacuum. Yield: 28 mg, 21%. Calcd for (OEP)P(OH)₂ClO₄·H₂O, C₃₆H₄₈N₄PClO₇: C, 60.46; H, 6.76; N, 7.83; P, 4.33. Found: C, 60.30, H, 6.57; N, 8.04; P, 4.50.

Related Species [(OEP)P(X)₂⁺ClO₄⁻]. Exchange of the OH ligands of I by use of acids such as HCl, HF, CH₃COOH, etc. as has been done for Sn(IV) complexes⁸ was unsuccessful. When dissolved in CH₂Cl₂, the complex is demetalated by dilute aqueous acid, and when dissolved in solvents such as ethanol, acetone, and acetonitrile, does not react even when anhydrous HCl or HBr is dissolved in high concentration.

Crown ethers have found usage as compounds to assist the solubilization of inorganic salts in aprotic solvents via complexation of the cation.^{12,13} In solution the anions of such salts are thought to be very weakly solvated (i.e., "naked fluoride", "bare acetate"). Some anions in acetonitrile and acetone solution are nucleophilic enough to replace the OH⁻ ligands bound to phosphorus.

Procedure. I was dissolved at $\sim 10^{-5}$ M in the dry solvent (Table I) in the absorption cell. A few milligrams of the crown ether 18-crown-6 (Aldrich Chem. Co.) was added and dissolved, and the absorption spectrum taken. The crown ether does not affect the absorption spectrum. A few crystals of the desired potassium salt were added, and the spectrum was taken again. The equilibrium constant in water for complex formation,



has $K \sim 2$; since a comparable or greater value for K is expected in our solvents, the concentration of X⁻ should be much greater than the concentration of porphyrin.

The following anions (as the K salts) were investigated: replacement of OH⁻: F⁻, CN⁻, HCOO⁻, CH₃COO⁻, "O₂⁻"; no replacement: N₃⁻, SCN⁻, Cl⁻, Br⁻, I⁻. Table I indicates the spectral data for those complexes in which OH⁻ was replaced. It cannot be determined from the spectra whether both OH⁻ ligands were replaced. Undoubtedly an equilibrium is established between the OH⁻ and the displacing anions. The absorption spectra show no evidence for the presence of two species, except for the acetate; however, excitation spectra and emission spectra for both the acetate and the formate are essentially similar to I, which is much more fluorescent than either acetate or formate. Thus a small amount of I in solution overwhelms emission from the other two ligand species. The emission and excitation spectra of the cyanide and fluoride complexes are in agreement with the presence of a single fluorescing and absorbing species. Addition of an

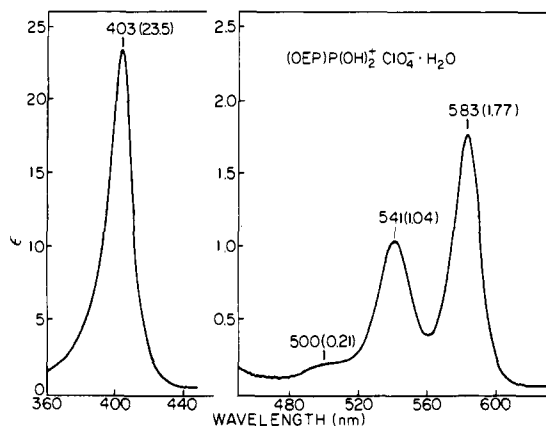


Figure 1. Absorption spectrum of (dihydroxo)(octaethylporphyrinato)phosphorus(V) perchlorate in ethanol. Peak wavelengths (in nm) and molar extinction coefficients (ϵ in $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are indicated.

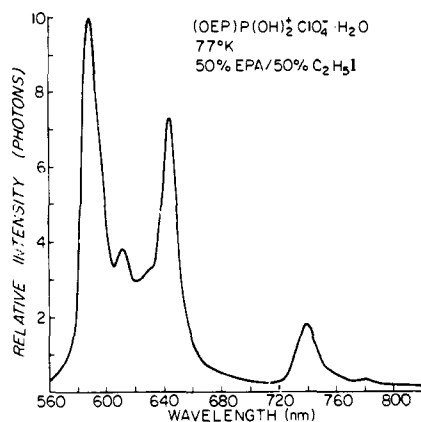


Figure 2. Emission spectrum of (dihydroxo)(octaethylporphyrinato)phosphorus(V) perchlorate in EPA:ethyl iodide (1:1) at 77 K.

enormous excess of crown ether and potassium salt does not change the spectra, so it seems likely that the species present, at least for CN^- and F^- , is the disubstituted one.

Addition of water to the fluoride, acetate, and formate solutions quantitatively converted the complexes back to I. The cyanide solutions were unstable and turned green after 15–30 min, probably due to nucleophilic attack on the ring itself.

The ligands designated as " O_2^- " deserve special comment. Using potassium superoxide, these complexes form in acetonitrile and acetone. The presence of the superoxide anion¹⁴ suggests that the species formed is $(\text{OEP})\text{P}(\text{O}_2)_2^+$. However, KO_2 reacts with water to produce HO_2^- , and there could be enough water present to generate sufficient hydroperoxide to form the peroxide complex. However, sodium peroxide only slowly generates the observed complex (KO_2 generates it instantly) and contains 10% NaO_2 , which may be the reacting compound. Unlike the other $(\text{OEP})\text{P}(\text{X})_2^+$ species, solutions of the "superoxide" complex show only a very weak fluorescence, and excitation spectra indicate that none of the emitting species is the primary absorber.

The use of a crown ether has proved to be a useful technique for exchanging ligands on complexes for which other methods are unsuitable and should be applicable to other porphyrins. For example, we have used this method to make $(\text{OEP})\text{Ga}(\text{F})$ from $(\text{OEP})\text{Ga}(\text{OH})$. This reaction can also be effected by aqueous HF in acetone/ CH_2Cl_2 . (J. W. Buchler, private communication).

Physical Characterization. Ion Migration. By use of an ion migration apparatus¹⁰ the cationic nature of the porphyrin was established. Of course this had been strongly indicated by its precipitation with ClO_4^- .

NMR. The spectrum obtained was typical of (OEP) metalloporphyrins.² The protons of the OH ligands were not observed, but this is not unexpected:¹⁵ triplet (CH_3) δ 1.84; quartet (CH_2) 4.06; singlet (CH) 9.83.

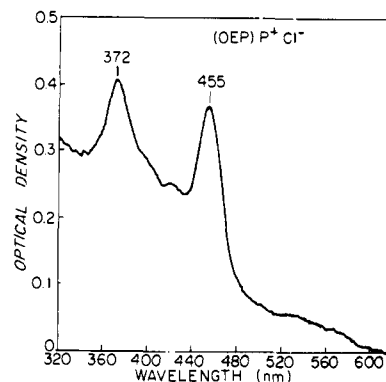


Figure 3. Absorption spectrum in dry benzene of reaction mixture (see text) after disappearance of free base octaethylporphyrin. Principal peaks (wavelengths indicated) presumed due to (octaethylporphyrinato)phosphorus(III) chloride (see text).

Mass Spectrum. For the ion $(\text{OEP})\text{P}(\text{OH})_2^+$, $\text{C}_{36}\text{H}_{46}\text{N}_4\text{PO}_2^+$, a principal mass peak is expected and observed at 597 au.

Infrared Absorption. The spectrum, taken in KBr disk, shows characteristic bands due to ClO_4^- (624 and 1080 cm^{-1}), H_2O and OH ($\sim 3400 \text{ cm}^{-1}$) in accordance with the proposed formula. A band is found at 890 cm^{-1} that is close to the range associated with P-OH stretch (1040 – 910 cm^{-1}). Since phosphorus is in an unusual chemical environment, a shifted value for P-OH stretch could be expected.

Results

Optical Spectra. Figure 1 shows the absorption spectrum taken for $(\text{OEP})\text{P}(\text{OH})_2^+$ in ethanol. In Table I we list the wavelength and molar extinction coefficient of the principal peaks. Also in Table I we list the absorption peaks of related compounds obtained by exchanging other anionic ligands for (OH^-) .

The emission spectrum is reported in Figure 2. This spectrum was taken in a mixture of 50% EPA (ethyl ether, isopentane, ethanol, 5:5:2), and 50% ethyl iodide. We use this solvent for reporting the emission because no phosphorescence is observed in pure EPA. The fluorescence spectrum is the same with and without ethyl iodide. We roughly estimated the fluorescence quantum yield as $\Phi_f \sim 0.1$ by comparison to (Eti)-Zn. We should note that excitation spectra showed that the principal emission peaks came from the main absorbing species. There is a Stokes shift between the Q(0,0) band in absorption and emission of $\sim 90 \text{ cm}^{-1}$. A comparable Stokes shift is obtained for the analogous As and Sb complexes.³

Because the phosphorescence is not observed in the absence of an external heavy atom effect, we could not directly determine the triplet lifetime of the unperturbed compound. To obtain an idea of the lifetime we compared the lifetimes of $(\text{OEP})\text{As}(\text{OH})_2^+$ and $(\text{OEP})\text{P}(\text{OH})_2^+$ in 90% EPA and 10% ethyl iodide. The As complex showed a nonexponential decay that could be fit with a double lifetime of 5 and 10 ms; the signal for the phosphorus species was much weaker, and only a single lifetime of 7 ms could be extracted, although there are indications of a short-lived component. In pure EPA the As complex also shows a double lifetime of 35 and 75 ms. These results suggest that the lifetime of the $(\text{OEP})\text{P}(\text{OH})_2^+$ triplet in EPA (with no ethyl iodide) is probably longer than 50 ms. An upper limit for the phosphorescence yield in EPA is estimated as $\phi_p < 0.001$.

Figure 3 shows the absorption spectrum in dry benzene of an aliquot of the fresh reaction mixture. The spectrum is typical of the hyper species. In the case of $(\text{OEP})\text{Bi}^{\text{III}}$ (hyper), the characterization of the species is now quite complete, including an x-ray structure.^{4b} In the case of the $(\text{OEP})\text{Sb}^{\text{III}}$ the characterization is quite good.³ For the Sb and As cases, conversion from the hyper species (identified as valence III) to the normal

Table II. Parameters Used for IEH Calculations^a

Phosphorus orbital exponents (bohr radii ⁻¹)	1.8806 (3s)	1.6288 (3p)
Phosphorus orbital ionization energies (eV)		
First	-18.3390	-11.0480
Second	-28.9040	-20.0290
Bond lengths (Å)		
P(V) to N	1.90	
P(V) to O	1.55	
O to H	0.98	
P(III) out of plane	0.50	
P(III) to N	2.10	
Bond angles (deg)		
N-P(V)-N	180	
O-P(V)-O	180	
P(V)-O-H	109	
N-P(III)-N	152	

^a For other parameters see ref 17.

species (well characterized as valence V) proceeds smoothly. Arguing by analogy, we identify the spectrum of Figure 3 with the species (OEP)P⁺Cl⁻ (however, see Discussion). Although undoubtedly contaminated by other absorbing species, the spectrum has peaks at 372 and 455 nm that are similar in position and relative intensities to the spectrum of (OEP)As⁺Cl⁻ and (OEP)Sb⁺Cl⁻. The latter has recently been published.¹⁶

Like the other hyper species, the hyper phosphorus is apparently nonfluorescent. No fluorescence from the reaction mixture could be detected using a black light. We did not look for phosphorescence.

Theoretical

The iterative extended Hückel (IEH) model was used to calculate molecular orbitals and energies for (dihydroxo)-(porphinato)phosphorus(V) cation and (porphinato)phosphorus(III) cation to explain their optical properties. The theory of the IEH model applied to porphyrins has been described in detail in Zerner and Gouterman¹⁷ and calculations on similar group 4a porphyrins have been reported.⁷ Analogous calculations on group 5a porphyrins have also been carried out.^{3,16}

Our proposed geometry for both phosphorus porphyrins is included in Table II. The value of 1.90 Å taken for the P-N distance is somewhat longer than a typical P-N single bond, which ranges from 1.75 to 1.80 Å. Use of this latter value, however, implies a porphyrin core diameter that is smaller than any metalloporphyrin for which x-ray data are available. The P-O bond length is consistent with other hydroxo-phosphorus bonds determined by x-ray diffraction. The bond angles are consistent with x-ray diffraction data from (OEP)Sb(OH)₂⁺ClO₄⁻.^{4a} Hydroxo hydrogens were placed as shown in Figure 3 to obtain two planes of symmetry for efficient computing.

The geometry of (P)P^{III+} has the phosphorus atom 0.5 Å above the center of the porphyrin ring. The longer phosphorus to nitrogen distance reflects the larger radius of P(III). Schematic diagrams for the two structures are given in Figure 4 where the resulting molecular orbital energies are shown. The chloride counterion was not included in the calculation because an ion migration experiment with (OEP)Bi^{III+} species likewise indicates dissociation of the counterion.³

Orbital ionization energies and basis set orbital exponents for phosphorus are in Table II. The ionization energies were computed from tables in McGlynn¹⁸ and single Slater orbital exponents for 3s and 3p atomic orbitals were computed from Cusachs and Corrington.¹⁹ Porphyrin ring coordinates are the

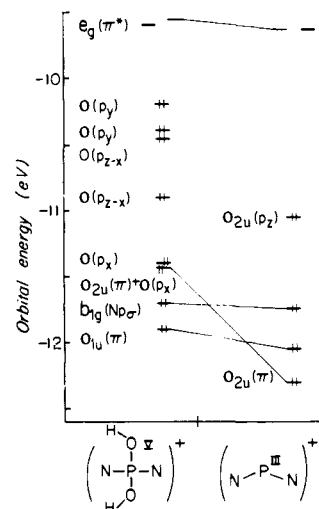


Figure 4. Molecular orbital energy levels obtained by the iterative extended Hückel model for (dihydroxo)(porphinato)phosphorus(V) and (porphinato)phosphorus(III) cations. Geometry in center of ring is shown. For P(III) species the P atom is 0.5 Å out of plane.

same as used in earlier IEH studies^{7,17} except for the nitrogen positions which depend on the central atom.

The IEH orbital energies (Figure 4) for the (P)P(OH)₂⁺ species are quite analogous to the orbitals reported earlier for (P)Si(OH)₂.⁷ However, all the levels for the phosphorus complex are 0.3 eV more negative; this is expected because of the change from a neutral to a cationic species. The top filled orbitals include a_{1u}(π), a_{2u}(π), and b_{1g}(Npσ), as found for, say, Zn(II).¹⁷ However, as in the case of (P)Si(OH)₂,⁷ there are five orbitals of primarily O character among the top filled. (The present calculation on the phosphorus complex differs from the earlier calculation on the silicon complex⁷ in that, in the earlier case, the Si-O-H bonds were taken as 180°; i.e., the molecule was forced into D_{4h} symmetry for computational economy.) Due to location of the -OH bonds over the nitrogen atoms and the near degeneracy of O(p_x) and a_{2u}(π), the mixing of these orbitals is probably exaggerated (Table III).

Another feature of these calculations that deserves some comment is the location in Figure 4 of four oxygen orbitals between a_{2u}(π) and e_g(π*). While general arguments have been given showing that IEH calculations generally underestimate charge transfer transition energies,²⁰ even allowing for this correction the diagram predicts that the transitions O(p) → e_g(π*) lie at lower energies than the (π,π*) ring transitions. There is no evidence for this from the emission or absorption spectra. We should note that these orbitals lie in about the same energy region as shown in Figure 4 for all dihydroxo porphyrin complexes of group 4a⁷ and group 5a³ calculated so far. Their location on the energy diagram appears to be a systematic artifact of the IEH method. This problem does not arise for chloride ligands.^{3,7,16} On the other hand, the orbital b_{1g}(Npσ) appears to be correctly placed when allowance is made for the underestimation of the charge transfer transition energy b_{1g}(Npσ) → e_g(π*).

We might note that the average energy calculated for the four orbital transitions a_{1u}(π) → e_g(π*) responsible for the Q,B bands^{21,22} is 2.08 eV. This is 0.025 eV (200 cm⁻¹) smaller than the average energy for the four orbital transitions calculated for the comparable (P)As(OH)₂⁺ complex.³ This, perhaps, correlates with the fact that there is a red shift between As(V) and P(V) complexes of 400 cm⁻¹ [T₁(π,π*)], 360 [Q(π,π*)], and 125 [B(π,π*)].

The IEH calculation for (P)P^{III+} is also shown in Figure 4. The presence of a top filled orbital labeled a_{2u}(p_z) indicates

Table III. Results of Iterative Extended Hückel Calculations

A. Orbital Energy						
Orbital	(P)P ^V (OH) ₂ ⁺ Energy (eV)	% π	% O	Orbital	(P)P ^{III+} Energy (eV)	% π
e _g x (π*)	-9.59	99	1	e _g (π*)	-9.65	99
e _g y (π*)	-9.56	96	4			
O(p _y)	-10.19	0	90			
O(p _x)	-10.39	0	80			
O(p _z -x)	-10.45	0	74			
O(p _z -y)	-10.88	0	67			
O(p _x)	-11.41	0	47			
a _{2u} (π) + O(p _x)	-11.42	74	17			
				a _{2u} (p _z)	-11.06	80
b _{1g} (Npσ)	-11.71	0	5	b _{1g} (Npσ)	-11.75	
a _{1u} (π)	-11.80	100	0	a _{1u} (π)	-12.05	100
				a _{2u} (π)	-12.30	90

B. Charge Density			
	(P)P ^V (OH) ₂ ⁺	(P)P ^{III+}	
P	+0.76	+0.21	H
O	-0.39		N
			(P)P ^V (OH) ₂ ⁺
			(P)P ^{III+}
			+0.30
			-0.14
			-0.09

that a hyper absorption spectrum will be obtained due to the presence of the CT transition $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$ in the region of the four orbital (π, π^*) transitions. This same result has been found for the other group 5a porphyrins of valence III³ and for the group 4a porphyrins of valence II. Again, in comparing the IEH results of Figure 4 to the optical spectrum of Figure 3, allowance must be made for the systematic underestimation of CT energies by the one electron energy difference in the IEH model. We believe that the bands observed at 372 and 455 nm represent a mixture of the B(π, π^*) excited state with the CT transition $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$. (We have designated the phosphorus p_z orbital by D_{4h} symmetry notation, although the molecule calculated had the phosphorus out-of-plane, to emphasize the fact that the CT transition has the same symmetry of the main (π, π^*) absorption bands.) We might note that no absorption band is observed in the near-IR, in agreement with the notion that this CT band occurs at higher energy than indicated by the energy difference between the IEH orbital energies.

The (P)P^{III+} is predicted to be nonplanar, although the actual distance out-of-plane is not very precisely determined. With the phosphorus in plane the orbital energy $a_{2u}(3p_z)$ is raised in energy because of antibonding interaction with the $a_{2u}(\pi)$ orbital, which has large electron density on the central N atoms. Under these conditions, the IEH calculation shows the $a_{2u}(3p_z)$ orbital only 0.4 eV below the $e(\pi^*)$ in poor agreement with an observed transition in the near-uv.

The fact that the energy of $a_{2u}(3p_z)$ is so sensitive to the distance of the phosphorus atom out of plane suggests that insofar as the excited states have CT character, the P atom will tend to move back into the plane. (That is, with only one electron in $a_{2u}(3p_z)$, there is less nonbonding repulsion.) Thus the CT excited states should have different potential curves with regard to this displacement than the ground state. Moreover, as the P atom moves out of plane, the (p_x, p_y) orbitals of the phosphorus increasingly mix with the empty $e_g(\pi^*)$ orbitals of the ring, giving spin-orbit coupling a high dependence on the P distance out of plane. The expectation of change in potential curves associated with change in spin-orbit coupling may account for the fact that no hyper complex of group 4a and 5a elements fluoresce. (A weak, short-lived phosphorescence has been documented in the hyper complexes of As, Sb, and Bi.³)

Discussion

Chemistry. The synthesis of the phosphorus porphyrins was based on that employed for the complexes of As, Sb, and Bi, but differs in certain respects. The hyper species (OEP)As⁺ and (OEP)Sb⁺ are easily oxidized ((OEP)As⁺ oxidizes immediately on exposure to air or water); H₂O₂ rapidly converts (OEP)Sb⁺ to (OEP)Sb(OH)₂⁺ in aqueous or alcoholic solution. Attempts to oxidize the hyper phosphorus compound with H₂O₂ or Cl₂ resulted in demetalation or conversion to some other unidentified compound. If the reaction mixture was diluted with water to hydrolyze the excess PCl₃, an amber solution was obtained whose absorption spectrum was quite similar to that in dry benzene, but blue shifted, and which was stable for a period of several hours, gradually reverting to (OEP)H₂. This solution did not precipitate ClO₄⁻, as does (OEP)Sb⁺. Attempts to isolate the hyper compound via column chromatography on neutral alumina grade IV using various solvents resulted in conversion of most of the product to free base and some to the normal compound. The behavior of this hyper porphyrin is, therefore, somewhat different from other members of the group, and the stoichiometry (OEP)P⁺Cl⁻ assumed by analogy and spectral similarity to the other members may not be completely correct.

(OEP)P(OH)₂⁺Cl⁻ is the product formed during the evaporation of the reaction mixture. This salt, like (OEP)As(OH)₂⁺Cl⁻ and (OEP)Sb(OH)₂⁺Cl⁻, is soluble in water and precipitates large singly charged anions such as ClO₄⁻, I⁻, and PF₆⁻. It is stable toward acid for several hours when dissolved in ethanol, but is susceptible to conversion to the (OEP)H₄²⁺ dication when dissolved in CH₂Cl₂ or CHCl₃, which typically contain HCl via decomposition of the solvent. By this latter behavior the normal phosphorus porphyrin would belong to stability class III (demetalated by HCl/H₂O-CH₂Cl₂). Arsenic and antimony normal porphyrins have been assigned to stability class I, the most stable;⁵ however, other evidence suggests somewhat less stability.^{3b}

Optical Spectra. The spectral shape and molar extinction coefficients of the P(V) complexes are characteristic of normal porphyrins.⁶ The fluorescence shows the expected mirror image relationship to absorption. It is interesting to note the principal ways the (OEP)P^V(OH)₂⁺ complex differs from the comparable arsenic and antimony compounds: In absorption the

visible Q bands are red-shifted about 10 nm compared to As(V) and Sb(V) complexes; moreover, the ratio of $\epsilon[Q(0,0)]/\epsilon[Q(1,0)]$ is 1.6 for P(V) compared to 1.06 for As(V) and 0.83 for Sb(V) complexes. The phosphorescence maximum systematically shifts red: 702 nm for Sb(V), 716 nm for As(V), and 737 nm for P(V) complexes.

The absorption spectrum of the putative (OEP)P⁺Cl⁻ differs more from the hyper compounds of As, Sb, and Bi than those differ among themselves. This is at least in part because there are undoubtedly other absorbing species in the initial reaction mixture—as evidenced by variations in spectra from one synthesis to the next. (The As and Sb reactions, by contrast, yield nearly 100% conversion to the hyper compounds as the first step in their syntheses.) The bands at 455 and 372 nm are blue shifted from the corresponding bands in As, Sb, and Bi which occur around 470 and 380 nm; this is a shift in the opposite direction from the red shift in the normal compounds. There is no definite maximum in the region of 580 nm, where the other hyper compounds have their weakest visible band. Finally, the band at 420 nm in Figure 3 has no correspondence among the other analogues; it is likely a by-product as its relative intensity changes between syntheses.

Theoretical. The IEH model calculates electronic configuration for (P)P^{III+} and (P)P^V(OH)₂⁺ complexes in a manner much the same as the analogous complexes of As, Sb, and Bi and the very similar valence II and IV complexes of group 4a elements. The results are in accord with normal absorption and fluorescence for the P(V) species; the P(III) species should show extra absorption bands due to the allowed CT transition $a_{2u}(3p_z) \rightarrow e_g(\pi^*)$. Moreover, the IEH model provides a rationale for the lack of fluorescence because the potential curve of the CT excited state with regard to displacement of the P(III) atom out of the porphyrin plane should be quite different from that of the ground state or the (π, π^*) excited states.

Conclusion

(Dihydroxooctaethylporphyrinato)phosphorus perchlorate, as the first reported “nonmetallic” porphyrin, completes the derivatives of group 5a, since a nitrogen porphyrin seems unlikely. These porphyrins are interesting chemically in that the central atoms (excepting Bi) assume oxidation states III and V and both species are cations; optically, because the spectra of the two oxidation are quite different in absorption and emission; structurally because the atoms in III are out of plane while V is in plane; biologically, due to the electronic similarity between the III species and cytochrome P-450;¹⁶ and theoretically, because the utility of the extended Hückel method was supported when it rejected the initially formulated valence and structure and predicted the current correct formulations.

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