Acc. Chem. Res. **1982,** *15,* 73–79

Metalloid Porphyrins and Phthalocyanines

PHILLIP SAYER, MARTIN GOUTERMAN,* and CHARLES R. CONNELL

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received July 27, 1981 (Revised Manuscript Received November 18, 1981)

The remarkable complexing ability of porphyrin and related macrocycles has permitted the synthesis of complexes with nearly every metal in the periodic table. In addition, complexes containing the semimetals and nonmetals of groups 4A and 5A have been made, some of which have only recently been characterized. For these compounds, the term *metallo*porphyrin is inappropriate. As discussed in this Account, these compounds share some unique chemical and spectroscopic properties. We use the terms *metalloid porphyrin* and *metalloid phthalocyanine* to refer to compounds of those rings which incorporate an element from groups 4A, 5A, or 6A. The structure of these macrocycles can be found in Figure 1 of ref 1. The reader is referred to a recent compendium for details of nomenclature, especially of peripheral substitution on the porphyrin ring.[2]

These porphyrins are of interest because at least two valence states are accessible to the central atom. As summarized in Table I and discussed below, the redox chemistry is not fully clarified. The lower valent metalloid complexes show unusual *p-type hyper* absorption spectra, in contrast to the *normal* absorption of the higher valent metalloids. These spectroscopic types are from a recent scheme that classifies and rationalizes porphyrin electronic spectra[1] and will be discussed in context below. Chemically, certain of the complexes exhibit behavior that is unusual for synthetic porphyrins—such as water solubility, ionic character, and aqueous acid–base chemistry—all involving the central atom and associated ligands.

Background

Synthetic tin complexes of biologically derived porphyrins (e.g., hematoporphyrin) have been known since the last century. The first group 5A derivative was evidently made by Hill in 1924.[3] He treated hematoporphyrin in pyridine with arsenic trichloride and observed the amber-brown solution now known to be characteristic of the $\mathrm{As^{III}}$ complex. He did not isolate the product, but noted that it was unstable with respect to reversion back to the parent hematoporphyrin free base. Interestingly, in the same paper he reported the synthesis of lead hematoporphyrin (which would have been $\mathrm{Pb^{II}}$) and noted its spectral similarity to the arsenic hematoporphyrin.

Table I
Summary of the Redox Chemistry of Metalloid Porphyrins and Phthalocyanines[a]

porphyrins	refs	phthalocyanines	refs
? $\mathrm{Si^{IV}}$		? $\mathrm{Si^{IV}}$	
? $\mathrm{Ge^{IV}}$		$\mathrm{Ge^{II}} \leftarrow \mathrm{Ge^{IV}}$	57
$\mathrm{Sn^{II}} \rightleftarrows \mathrm{Sn^{IV}}$	*b*, 24, 69	$\mathrm{Sn^{II}} \rightleftarrows \mathrm{Sn^{IV}}$	9, 13, 51, 60
$\mathrm{Pb^{II}} \rightleftarrows \mathrm{Pb^{IV}}$	25, 32	$\mathrm{Pb^{II}}$?	
$\mathrm{P^{III}} \rightarrow \mathrm{P^{V}}$	7	$\mathrm{P^{III}} \rightarrow \mathrm{P^{V}}$(?)	14
$\mathrm{As^{III}} \rightarrow \mathrm{As^{V}}$	6, 17, 18	$\mathrm{As^{?}}$	
$\mathrm{Sb^{III}} \rightleftarrows \mathrm{Sb^{V}}$	6, 17, 18	$\mathrm{Sb^{?}}$	
$\mathrm{Bi^{III}}$?		?	

[a] Arrow indicates redox accomplished in one manner or another. See text and references for details. [b] See Figure 1.

Complexes with other members of groups 4A and 5A are more recent. Silicon porphyrin was reported in 1967[4] and germanium in 1969.[5] In addition to the germanium complex, Treibs[5] described the synthesis of As, Sb, and Bi derivatives, work extended by Buchler and Lay.[6] The first phosphorus porphyrin appeared in 1976.[7]

As dyestuffs of commercial importance and as close relatives of the porphyrins, the phthalocyanines have also received considerable attention. Linstead and co-workers made many metal complexes with these ligands (see the review by Lever[8]) including tin,[9] lead,[9] and antimony[10] derivatives. Kenney and co-workers synthesized silicon,[11] germanium,[12] tin,[13] and lead[13] phthalocyanines and demonstrated novel and interesting structural properties of these molecules, including intermolecular polymerization via associated ligands. Eleven years after a prediction by Lever,[8] phosphorus complexes with phthalocyanine were reported.[14]

The history of many of these compounds has been

Phillip Sayer was born in 1943. He received a B.A. from the University of Colorado in 1966. His Ph.D. studies, completed in 1971, were done at the University of Washington under Professors Martin Gouterman and Rex Robinson on the spectroscopic and analytical properties of tetraphenyl group 4A and 5A compounds. Currently he is a Research Associate at the University of Washington.

Martin Gouterman was born in 1931 in Philadelphia where he grew up. His higher education was obtained at the University of Chicago, from which he graduated in 1958 with a Ph.D. in Physics. He was a Research Associate and faculty member in Chemistry at Harvard University from 1958 to 1966. Since then he has been a member of Chemistry faculty at the University of Washington. His primary research efforts have been on the spectra and electronic structure of porphyrin molecules.

Charles R. Connell was born in California in 1947. He obtained a B.S. in Mathematics and an M.S. in Physical Sciences from Stanford University before entering graduate studies in Chemistry at the University of Washington. His Ph.D. research, carried out under Professor Martin Gouterman and completed in 1977, elucidated the structure and valence of group 5A metalloporphyrins. He is currently working at Hewlett-Packard in Palo Alto, CA.

---

(1) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.

(2) Bonnett, R. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, Chapter 1.

(3) Hill, R. *Biochem. J.* **1925,** *19,* 341.

(4) Boylan, D. B.; Calvin, M. *J. Am. Chem. Soc.* **1967,** *89,* 5472.

(5) Treibs, A., *Liebigs Ann. Chem.* **1969,** *728,* 115.

(6) Buchler, J. W.; Lay, K. L. *Inorg. Nucl. Chem. Lett.* **1974,** *10,* 297.

(7) Sayer, P.; Gouterman, M.; Connell, C. R. *J. Am. Chem. Soc.* **1977,** *99,* 1082.

(8) Lever, A. P. B. *Adv. Inorg. Chem. Radiochem.* **1965,** *7,* 27.

(9) Barrett, P. A.; Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1936,** 1719.

(10) Barrett, P. A.; Frye, D. A., Linstead, R. P. *J. Chem. Soc.* **1938,** 1157.

(11) Joyner, R. D.; Cekada, J.; Linck, R. G.; Kenney, M. E. *J. Inorg. Nucl. Chem.* **1960,** *15,* 387.

(12) (a) Joyner, R. D.; Kenney, M. E. *J. Am. Chem. Soc.* **1960,** *82,* 5790. (b) Kane, A. R.; Yalman, R. G.; Kenney, M. E. *Inorg. Chem.,* **1968,** *7,* 2588.

(13) Kroenke, W. J.; Kenney, M. E. *Inorg. Chem.* **1964,** *3,* 251, 696.

(14) Gouterman, M.; Sayer, P.; Shankland, E.; Smith, J. P. *Inorg. Chem.* **1981,** *20,* 87.

0001-4842/82/0115-0073$01.25/0

marked by some confusion as to the valence of the coordinated atom. Falk, in his monograph,[15] refers to tin(II) porphyrins when in fact such complexes are highly unstable to oxidation to Sn^{IV} species, and published spectra of Sn porphyrins (see, for example, ref 16) are always Sn^{IV}, with one exception noted below. Similarly, the valencies of the group 5A metalloids As, Sb, and Bi octaethylporphyrins given in a preliminary report[6] have been reversed by later work.[17,18] Theoretical calculations on the electronic spectra were instrumental in elucidating the structure of the group 5A derivatives.[17]

The electronic absorption and emission data on these complexes are still incomplete, especially as regards the low-valent species. Further work is warranted on theoretical and other grounds: (i) Absorption spectra characteristic of low valence porphyrins closely resemble spectra from a group of naturally occurring enzymes, the cytochromes P-450, whose anomalous absorption spectra have been explained by analogy to Sb^{III} octaethylporphyrin.[19,20] (ii) The unusual (for a synthetic porphyrin) water solubility and presumably nontoxic breakdown products of phosphorus porphyrins suggest potential uses of these substances in biological and medical applications.[21] (iii) Finally, the solid-state properties may show some surprises given the ionic character of many of these species and the possibility of electron transport via bridging ligands and/or some type of redox mechanism involving the central atom.[22,23]

Group 4A: Sn and Pb Porphyrins

Tin porphyrins are easy to make. A variety of solvents can be used, and metal insertion into free base porphyrin, $H_2(\mathbf{P})$, proceeds at moderate temperatures using stannous salts as the metal source. (We shall use **P** to refer to any porphyrin, regardless of substituents.) If the reaction is carried out in air, the only observed product is the Sn^{IV} porphyrin. Probably because of the use of stannous salts, earlier workers assumed that the resulting complexes were Sn^{II}. However, if a carefully dried and deoxygenated pyridine and anhydrous $SnX_2(X = Cl, Br)$ system is used, one obtains in solution a species of very different spectral character first reported by Whitten.[24] Figure 1 shows the visible absorption spectrum of $Sn^{II}(OEP)$ prepared in our laboratory on an inert atmosphere/vacuum system from $H_2(OEP)$ and $SnBr_2$. After the $Sn^{II}(OEP)$ spectrum was recorded the absorption cell was briefly opened to air and resealed and the spectrum recorded again; this procedure was repeated. The resultant series of spectra (Figure 1) show the various intermediate mixtures during the conversion of $Sn^{II}(OEP) \rightarrow Sn^{IV}(OEP)X_2$. Several isosbestic points indicate that this oxidation is quantitative. The identity of the ligands X is not certain; most likely they are either Br^- from the excess $SnBr_2$ or OH^- from water and air. No attempt was made to isolate the unstable $Sn^{II}(OEP)$; therefore identification rests entirely on this *hyper* spectrum, its resemblance to the spectra of other well-characterized porphyrins of Pb^{II} and group 5A elements and its quantitative conversion to the Sn^{IV} species.

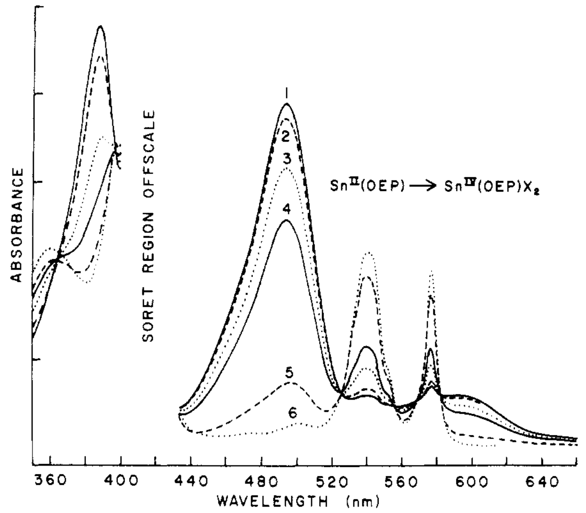

Figure 1. $Sn^{II}(OEP)$ and $Sn^{IV}(OEP)X_2$: Absorption spectra observed when $SnBr_2$ reacts with $H_2(OEP)$ in pyridine under inert atmosphere (curve 1) and the reaction mixture is subsequently opened to air (curves 2 to 6). Some $Sn^{IV}(OEP)X_2$ is present in the first spectrum. (The visible spectra and the near-UV spectra are from different runs.)

A discussion of *normal* and *hyper* porphyrin electronic spectra is found in ref 1. It will suffice here to note that normal spectra result from $\pi \rightarrow \pi^*$ transitions of the aromatic macrocycle, giving rise to the visible Q bands ($\epsilon \sim 20000\ M^{-1}\ cm^{-1}$) and a near-UV B (or Soret) band around 400 nm ($\epsilon \sim 400000\ M^{-1}\ cm^{-1}$). Both fluorescence and phosphorescence are observed. In contrast, *p-type hyper* porphyrin spectra are characterized by two Soret bands at ~350 and ~450 nm and a weaker group of visible bands further to the red. These spectra are found for valence M^{II} in group 4A and M^{III} in group 5A; fluorescence has not been found, but phosphorescence is generally observed. The extra Soret band is attributed to the presence of an allowed np_z(metal) $\rightarrow \pi^*$(porphyrin) charge-transfer transition in the visible–near-UV region. Clearly $Sn^{IV}(OEP)X_2$ is normal and $Sn^{II}(OEP)$ is hyper. The latter has no detectable fluorescence; phosphorescence, while perhaps expected, has not yet been looked for.

Lead porphyrins are long known. Synthetic procedures similar to those used for Sn are effective in producing Pb^{II} derivatives.[25,26] The Pb^{II} porphyrins are easily demetalated due, no doubt, to the large distance of the Pb from the plane of the four nitrogen atoms, found to be 1.174 Å in *meso*-tetra-*n*-propylporphyrin.[27] Similarly, a preliminary study of $[Bi^{III}(OEP)]NO_3$ found

---

(15) Falk, J. E. "Porphyrins and Metalloporphyrins"; Elsevier: Amsterdam, 1964.

(16) Dorough, G. D.; Miller, J. R.; Huennekens, F. M. *J. Am. Chem. Soc.* **1951**, *73*, 4315.

(17) Connell, C. R., Ph.D. Thesis, Department of Chemistry, University of Washington, Seattle, 1977.

(18) Stoppa, H., Doctoral Dissertation, Rheinisch-Westfälische Technische Hochoschule, Aachen, Federal Republic of Germany, 1976.

(19) Hanson, L. K.; Eaton, W. A.; Sligar, S. G.; Gunsalus, I. C.; Gouterman, M.; Connell, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 2672.

(20) Dawson, J. H.; Trudell, J. R.; Barth, G.; Linder, R. E.; Bunnenberg, E.; Djerassi, C.; Gouterman, M.; Connell, C. R.; Sayer, P. *J. Am. Chem. Soc.* **1977**, *99*, 641.

(21) Labbe, R. F., personal communication.

(22) Mitulla, K.; Hanack, M. *Z. Naturforsch.* **1980**, *356*, 1111.

(23) Ukei, K. *Acta Crystallog., Sect. B* **1973**, *29B*, 2290.

(24) Whitten, D. G.; Yau, J. C.; Carroll, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 2291.

(25) Gouterman, M.; Schwarz, F. P.; Smith, P. D.; Dolphin, D. *J. Chem. Phys.* **1973**, *59*, 676.

(26) Buchler, J. W. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 5; also in ref 1, Vol. I, Chapter 10.

(27) Barkigia, K. M.; Fajer, J.; Adler, A. D.; Williams, G. J. B. *Inorg. Chem.* **1980**, *19*, 2057.

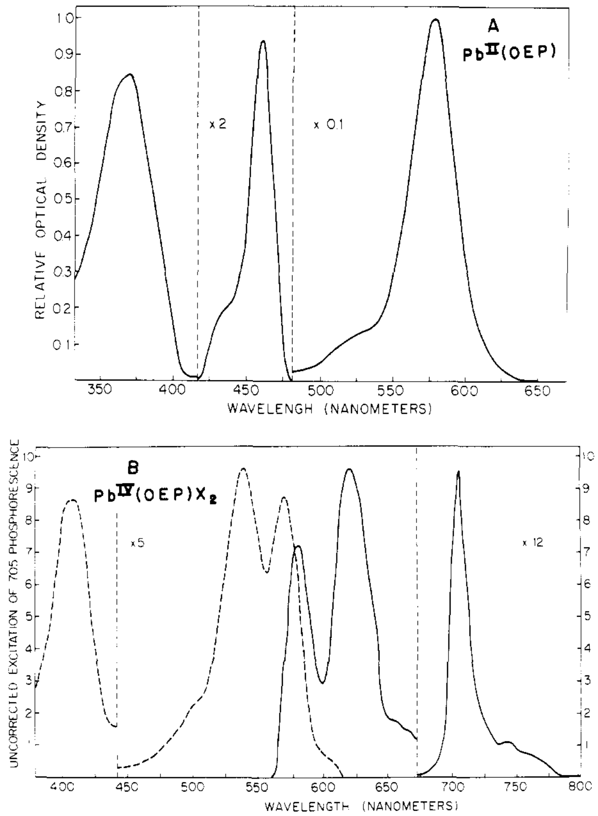

Figure 2. (A) Pb^{II}(OEP): Absorption spectrum in CH_2Cl_2 at 298 K. (B) Pb^{IV}(OEP)X_2: uncorrected excitation spectrum (dashed) and corrected emission spectrum (solid) in CH_3OH at 77 K. (In this and in subsequent figures ×2, × 0.1, etc. indicate multiplicative factors to be applied to the bands in the regions indicated.) Reprinted with permission from ref 25. Copyright 1973, American Institute of Physics.

the distance of the Bi from the plane of the four nitrogens to be 1.09 Å.[28] This is in contrast to the planar six-coordinate geometries found for Sn^{IV}(TPP)Cl_2[29] (TPP = tetraphenylporphyrin) and Sn^{IV}(OEP)Cl_2[30] and the near planar structure of [Sb^{V}(OEP)(OH)$_2$]ClO_4·C_2H_5OH.[31] The increasing stability of the lower valence in the heavier elements of a group is evident in that Pb^{II} is more stable than the Pb^{IV}. The Pb^{IV}(OEP)X_2 porphyrin has been generated chemically with Cl_2[25] and electrochemically.[32]

Figure 2 shows absorption and emission spectra of Pb^{II}(OEP) and Pb^{IV}(OEP)X_2.[25] The Pb^{II} species exhibits a typical *hyper* spectrum, while Pb^{IV} is *normal* porphyrin type, with fluorescence and phosphorescence. A phosphorescence spectrum of Pb^{II}(Meso) [Meso = mesoporphyrin dimethyl ester] has been reported.[33]

Group 4A: Si and Ge Porphyrins

Silicon and germanium porphyrins, because of their more difficult synthesis, are relatively recent. $SiCl_4$ and $GeCl_4$ are used as metalloid carriers. The halide and free base porphyrin [e.g., H_2(OEP)] are dissolved in pyridine, sealed in a Carius tube, and heated (~170 °C) for several hours,[4,5,25] after which the contents are hydrolyzed in water and the porphyrin is extracted. A synthesis of Ge(P)Cl_2 [P = porphine] from $GeCl_4$ and H_2(P) occurs in quinoline in one hour at 230 °C.[12b] The more rigorous synthetic conditions, compared to stannous, points up a well-known observation in metalloporphyrin synthesis: metals in lower oxidation states, when available, are usually easier to insert than their high valent forms.[26]

The absorption and emission spectra of Si^{IV}(OEP)Cl_2 and Ge^{IV}(OEP)Cl_2 are *normal*,[25] very similar to the Sb^{V} spectra below. Among the M^{IV} complexes of group 4A, the most striking spectral change occurs in the ratio of fluorescence yield to phosphorescence yield, ϕ_f/ϕ_p, which decreases with increasing atomic number of the central atom. This effect, along with the concomitant decrease in τ_p, the phosphorescence lifetime, is a consequence of increasing spin–orbit coupling as the central atom becomes heavier.[25]

Group 5A: As, Sb, and Bi Porphyrins

Synthesis of the group 5A metalloid porphyrins, like group 4A, is straightforward. In a typical procedure, dry pyridine, the As or Sb halide (usually Cl or Br), and the free base porphyrin are heated or refluxed for up to 1 h.[5,6,17,18] The extent of reaction can be monitored by the disappearance of free base fluorescence from the solution. Excess MX_3 is hydrolyzed with methanol or aqueous buffer and the porphyrin isolated. As^{III} porphyrins are quite susceptible to oxidation and have been examined only in the original (degassed, dry) reaction mixture. Sb^{III} derivatives are more stable, and with precautions to minimize contact with oxidizing agents, can be isolated. Bi^{III} complexes are air stable; a Bi^{V} porphyrin is not yet known. Atmospheric oxygen or mild oxidizing agents are sufficient to convert the arsenic and antimony porphyrins from III → V.

That pyridine has been the only solvent in which As, Sb, and P porphyrins have been synthesized may relate to its ability to react with the trihalides of these elements,[34] forming a highly reactive complex postulated to be $[C_6H_5NMX_2]^+$ (M the metalloid).[7] Pyridine also favors the deprotonation of the free base porphyrin, exposing it to electrophilic attack. For the rather unreactive (and chemically rather different) bismuth salts, the nitrate is used for metalation; some improvement in yield is achieved by the use of refluxing dimethylformamide, a technique pioneered by Adler.[35]

Group 5A porphyrins are ionic, either [M^{III}(**P**)]$^+$Y$^-$ or [M^{V}(**P**)X_2]$^+$Y$^-$, where X$^-$ is an anionic ligand and Y$^-$ is an anionic counterion. The porphyrin cation and its counterion are separated in polar solvents.[17] While the compounds can be chromatographed, their ionic nature permits purification by precipitation from aqueous or water/alcohol solutions using such large anions as ClO_4^-, PF_6^-, or even NO_3^-, in the case of [Bi^{III}(OEP)]$^+$. The salt [Sb^{V}(TTP)(OSiPh$_3$)$_2$]PF_6 derived from *meso*-tetrakis(*p*-tolyl)porphyrin, H_2(TTP), crystallizes from acetone. The Sb–O–Si systems in the huge cation of this salt were prepared from [Sb^{V}(TTP)(OH)$_2$]OH and $SiClPh_3$.[18]

---

[28] Fitzgerald, A., preliminary study described in ref 17, pp 32–34.

[29] Collins, D. M.; Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6689.

[30] Cullen, D. L.; Meyer, E. F. Jr. *Acta Crystallog., Sect. B* **1973**, *29B*, 2507.

[31] Fitzgerald, A.; Stenkamp, R. E.; Watenpaugh, K. D.; Jensen, L. H. *Acta Crystallog., Sect B* **1977**, *33B*, 1688.

[32] Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *Inorg. Chem.* **1971**, *11*, 2766.

[33] Becker, R. S.; Allison, J. B. *J. Phys. Chem.* **1963**, *67*, 2669.

[34] Gibson, S.; Johnson, J. D. A.; Vining, D. C. *J. Chem. Soc.* **1930**, 1710. Roper, W. R.; Wilkins, C. J. *Inorg. Chem.* **1964**, *3*, 500.

[35] Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

Table II
Electronic Spectral Peaks (nm) for Metalloid Porphyrins

	absorption[b]				emission[b]				
compound[a]	solvent	band III	band II	band I	solvent	$T(0,0)$	τ_p	Φ_p	ref
			Valence III						
$P^{III}(OEP)^+$	C_5H_5N	372	455	~535	nd[c]				7
$As^{III}(OEP)^+$	CH_2Cl	378	457	565	CH_2Cl_2	750	50/330 μs[d]	≲0.002	17
$[Sb^{III}(OEP)]Cl$	CH_2Cl_2	379	460	570	EPA[e]	740	88 μs	0.003	17
$[Bi^{III}(OEP)]NO_3$	CH_2Cl_2	355, 370	460	572	EPA	745	13.6 μs	0.008	17
$[Bi^{III}(TTP)]NO_3$	C_6H_6	336, 355	467	651	nd				18

	absorption[b]				emission[b]							
compound	solvent	B-(0,0)	Q-(1,0)	Q-(0,0)	solvent	Q-(0,0)	Q-(0,1)	T-(0,0)	p	f	p	ref
					Valence V							
$[P^V(OEP)(OH)_2]ClO_4$	EtOH	403	541	583	EPA	585	645	737	7 ms[f]	~0.1	<0.001[f]	7
$[As^V(OEP)(OH)_2]^+$	EPA	402	532	568	EPA	574	631	716	35/75 ms[d]	0.076	0.003	17
$[Sb^V(OEP)(OH)_2]Cl$	EPA	397	532	570	EPA	569	624	702	26 ms	0.020	0.026	17
$[Sb^V(OEP)Cl_2]Cl$	EtOH	400	533	571	nd							17
$[P^V(TPP)(OH)_2]Cl$	MeOH	424	555	593	nd							37
$[As^V(TPP)(OH)_2]Cl$	CH_2Cl_2	425	554	596	nd							18
$[Sb^V(TPP)(OH)_2]Cl$	CH_2Cl_2	422	553	596	nd							18

[a] OEP = octaethylporphyrin; TTP = *meso*-tetrakis(p-tolyl)porphyrin; TPP = *meso*-tetraphenylporphyrin. For spectra of group 4A metalloids, see ref 25 for OEP, ref 16 for TPP, and ref 18 for TTP. [b] Absorption at room temperature; emission at 77 K; τ_p is phosphorescence lifetime; Φ_f, Φ_p are fluorescence and phosphorescence quantum yields. [c] Not determined. [d] A sum of two expontential decays: $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ with $A_1/A_2 = 2.5(As^{III})$ and $1.1(As^V)$ with $\tau_1 < \tau_2$. [e] EPA: diethyl ether, isopentane, ethanol (5:5:2 v/v). [f] 90% EPA/10% C_2H_5I.

The electronic spectra for the Sb^{III} and Sb^V complexes of OEP are shown in Figure 3. The Sb^{III} has a hyper absorption spectrum, no fluorescence, and weak, short-lived phosphorescence. The As^{III} and Bi^{III} optical spectra are similar, with the phosphorescence lifetime decreasing along the series $As^{III} > Sb^{III} > Bi^{III}$ (Table II). Another principal difference is that the absorption intensity ratio of band II/band III = 0.63, 0.77, and 1.53 for As^{III}, Sb^{III}, and Bi^{III} OEP complexes in CH_2Cl_2.[17] This change in intensity ratio is attributed to a shift to higher energy of the $np_z(\text{metal}) \rightarrow \pi^*(\text{porphyrin})$ charge-transfer transition along the series $As^{III} < Sb^{III} < Bi^{III}$. Such a shift is predicted by the iterative extended Hückel calculations.[17] The As^V and Sb^V species have normal metalloporphyrin spectra, with mirror-image fluorescence, and phosphorescence intensities and lifetimes comparable to those of Ge^{IV} and Sn^{IV} species.[25]

The existence of a lone pair of electrons on the M^{III} atoms suggests the possibility of Lewis base behavior for these complexes. However, preliminary experiments with triphenylboron and $AlCl_3$ showed no spectroscopic effect on $[Sb^{III}(OEP)]^+$ in solution,[17] while a careful examination of $[Bi^{III}(OEP)]^+NO$ revealed only a small spectral shift with increasing NO pressure.[36]

Group 5A: Phosphorus Porphyrins

The synthesis of phosphorus porphyrins is very similar to that of arsenic and antimony. PCl_3 and PBr_3 in dry pyridine react with several free base porphyrins (e.g., octaethylporphyrin,[7] tetraphenylporphyrin,[37] and mesoporphyrin dimethyl ester[14]) to yield the unstable P^{III} complex, which is oxidized by air during workup or by treatment with Br_2. Carrano and Tsutsui[37] used $POCl_3$ in refluxing pyridine to make $[P^V(TPP)X_2]^+$, which is in contrast to our failure to make a phosphorus porphyrin using P^V reagents. Their reaction time was much longer (24 h vs. ~2 h) and conditions more extreme (117 °C vs. 40–80 °C), and it is possible that reduction of $POCl_3$ to PCl_3 was occurring.

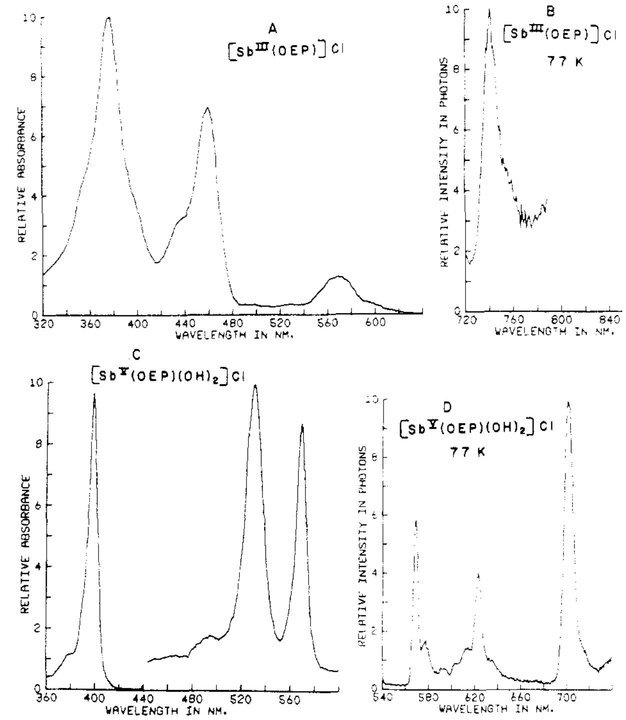

Figure 3. (A) $[Sb^{III}(OEP)]Cl$: Absorption spectrum in pyridine at room temperature. (B) $[Sb^{III}(OEP)]Cl$: Emission spectrum in EPA at 77 K. (C) $[Sb^V(OEP)(OH)_2]Cl$: Absorption spectrum in ethanol at room temperature. (D) $[Sb^V(OEP)(OH)_2]Cl$: Emission spectrum in EPA at 77 K. From ref 17.

The very stable $[P^V(OEP)(OH)_2]Cl$ is quite soluble in water and resistant to demetalation by acids in water or polar organic solvents such as ethanol. Unlike As^V and Sb^V porphyrins, P^V derivatives with hydroxide ligands undergo Brønsted acid–base reactions in solution. Successive deprotonation of the hydroxide ligands with increasing pH shifts the visible absorption bands to the blue, an effect attributed to increased backbonding from the filled $O(p_x,p_y)$ orbitals into the empty

---

(36) Sayer, P.; Chang, C. K., unpublished.
(37) Carrano, C. J.; Tsutsui, M., *J. Coord. Chem.* **1977**, *7*, 79.

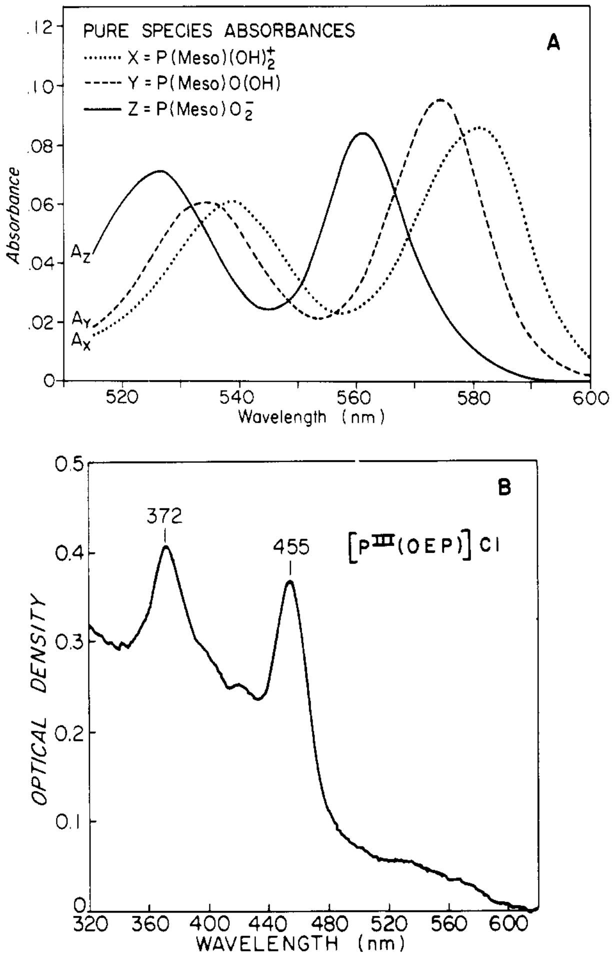

Figure 4. (A) Absorbance curves for $[P^V(Meso)(OH)_2]^+$ and its two deprotonated species in aqueous buffer as deduced from titration data. Meso = mesoporphyrin dimethyl ester]. From ref 14. (B) $[P^{III}(OEP)]Cl$: Absorption spectrum in dry benzene of pyridine reaction mixture after disappearance of $H_2(OEP)$. From ref 7.

ring $e_g(\pi^*)$[14] (see Figure 4). Titratable hydroxide protons have also been found on Al^{III}, Sn^{IV}, Cr^{III}, and Mn^{III} phthalocyanines.[8,38]

The absorption and emission of spectra of $[P^V(OEP)(OH)_2]^+$ compounds are quite normal.[7] The phosphorescence was observed only with ethyl iodide providing heavy atom enhancement.[7] The hyper absorption spectrum for the $[P^{III}(OEP)]^+$ species, which has proved difficult to isolate, is shown in Figure 4B; no luminescence of this species has been reported.

Group 6A: Selenium and Tellurium Porphyrins

Group 6A is the last stronghold of elements which might reasonably be expected to form porphyrin complexes, but for which none are presently known. This laboratory has accumulated results that strongly indicate complex formation, but as yet no well-characterized species has been isolated. By analogy to groups 4A and 5A, it is suspected that such derivatives might be of the form $[M^{IV}(P)]^{2+}$ and $[M^{VI}(P)X_2]^{2+}$, where X is a mononanionic ligand. Another reasonable compound is a neutral dioxo species $M^{VI}(OEP)(O)_2$. Synthetic efforts[39] have concentrated on the pyridine method, using $SeCl_4$ and $TeCl_4$ as metalloid sources. Like phosphorus and arsenic halides, $SeCl_4$ forms a pyridine adduct which can ionize in solution to give $[(C_6H_5N)_2SeCl_3]^+$.[40] However, this bis(pyridine) adduct is clearly sterically unfavorable compared to the monopyridine complexes of group 5A, and another synthetic route may be necessary.

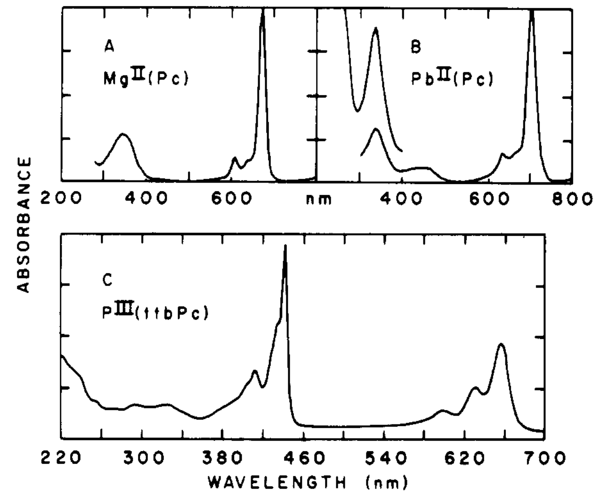

Figure 5. (A) $Mg^{II}(Pc)$: Normal absorption of a metallophthalocyanine in dimethyl sulfoxide. (B) $Pb^{II}(Pc)$: A hyper absorption spectrum (Pb out of plane) in dimethyl sulfoxide. (C) $P^{III}(ttbPc)$: A hyper absorption spectrum (P probably in-plane) in ethanol. (ttbPc = tetra-*tert*-butylphthalocyanine; A and B from ref 51.)

Absorption spectra of the reaction mixtures show evidence of new bands appearing in the 450-nm region, as expected for a hyper, lower valent complex.[39] Purification and isolation of the species responsible have not yet been accomplished.

Metalloid Phthalocyanines

The literature on the phthalocyanine (Pc) ring is quite extensive and has been the subject of a comprehensive review,[8] a monograph,[41] and shorter recent reviews.[42-44] Metallophthalocyanines can be made from the free base and a metal salt, as for porphyrins. They also are often made in a template reaction from phthalonitrile and the metal or the metal salt at ~300 °C. The ease with which they are made and their thermal and chemical stability are real advantages. Unsubstituted derivatives, however, are poorly soluble in most solvents, which can be a serious problem. Recently a tetra-*tert*-butyl Pc (ttbPc) has become available,[45,46] providing a soluble molecule with chemical and electronic properties quite similar to Pc.

The phthalocyanines generally have very intense visible absorption bands [600–700 mm ($\epsilon \gtrsim 10^5$ M^{-1} cm^{-1}) and broad Soret bands [~350 nm ($\epsilon \lesssim 10^5$ M^{-1} cm^{-1})]. Thus the visible bands are more intense and red-shifted with respect to the visible bands in porphyrins, and the Soret bands are broader and blue-shifted. Theoretical treatments account for these differences.[47-50] Figure 5A shows a typical normal spec-

---

(38) Elvidge, J. A.; Lever, A. P. B. *Proc. Chem. Soc.* **1959**, 123.
(39) Shankland, E.; Gouterman, M., unpublished.
(40) Cordes, A. W.; Hughes, T. V. *Inorg. Chem.* **1964**, *3*, 1640.
(41) Moser, F. H.; Thomas, A. L., "Phthalocyanine Compounds"; Reinhold: New York, 1963; ACS Monograph 157.
(42) Boucher, L. J. In "Coordination Chemistry of Macrocyclic Compounds", Melson, G. A., Ed., Plenum: New York, 1979; Chapter 7.
(43) Jackson, A. H. in ref. 1, Vol. I, Chapter 9.
(44) Kasuga, K.; Tsutsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67–95.
(45) Mikhalenko, S. A.; Barkanova, S. V.; Lebedev, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* (*Engl. Transl.*) **1971**, *41*, 2735.
(46) Geigy French Patent 1580683; *Chem. Abstr.* **1970**, *73*, 100057.

trum of a metallophthalocyanine.[51] In solution the phthalocyanines are typically blue to green while the porphyrins are generally red or amber.

Table III
Absorption Peaks (nm) for Metalloid Phthalocyanines

compound	solvent[a]	band III	band II	band I	ref
		Valence II			
$Ge^{II}(Pc)$	pyr	330	445	655	57
$Sn^{II}(Pc)$	EtOH	359	nr[b]	682	58
$Pb^{II}(Pc)$	vapor	332	420	698	51, 60
$Pb^{II}(Pc)$	Me_2SO	336	450	702	51, 60
$Pb^{II}(Pc)$	ClN	342	430	714	58
		Valence III			
$P^{III}(Pc)$	EtOH	325	438	651	*c*
$P^{III}(ttbPc)$	EtOH	325	441	656	*c*
$As^{III}(Pc)Cl$[d]	DMF	340[d]	nr	580[d]	61
compound		solvent	B(0,0)	Q(0,0)	ref
		Valence IV			
$Si^{IV}(Pc)(OC_5H_{11})_2$		bz	nr	673	55
$[Si^{IV}(Pc)(C{\equiv}C)]_n$		nr	nr	707	22
$Sn^{IV}(Pc)Cl_2$		ClN	363	701	60
$Sn^{IV}(Pc)Cl_2$		vapor	323	693	60

[a] pyr = pyridine; Me_2SO = dimethyl sulfoxide; ClN = 1-chloronaphthalene; EtOH = ethanol; DMF = dimethylformamide; bz = benzene. [b] Not reported. [c] This work; ref 14 reports spectra of $P^{III}(Pc)$ in pyridine with Q(0,0) absorption at 655 nm and emission at 663 nm. [d] Very anomalous; see text.

Group 4A Phthalocyanines. Complexes of group 4A have been studied from several aspects: X-ray structures have come out on $Sn^{II}(Pc)$[52] and $Sn^{IV}(Pc)Cl_2$;[53] the chemistry of the axial ligands of Si^{IV} and $Ge^{IV}(Pc)$ has been investigated;[54,55] and there is solid state work on the electrical conduction of $Pb^{II}(Pc)$[23] and alkyne bridges $Si^{IV}(Pc)$.[22] Kenney et al.[54,55] reported several quite different syntheses for these compounds and have discussed the axial ligand chemistry. In addition to the mononuclear complexes, Sn^{IV} also forms a binuclear $Sn^{IV}(Pc)_2$, in which the 8-coordinate tin ion is sandwiched between two Pc units.[9,56] While the electronic absorption and emission data for phthalocyanines is considerable (though less extensive than for porphyrins), comparatively little has appeared for group 4A. Si^{IV}, Ge^{IV}, and Sn^{IV} phthalocyanines exhibit normal spectra, similar to $Mg^{II}(Pc)$ in Figure 5A.

Optical data for the group 4A $M^{II}(Pc)$ species are somewhat confusing. By analogy with p-type hyperporphyrins, it is expected that corresponding spectral differences between valences II and IV in group 4A and III and V in group 5A metalloid phthalocyanines will be observed. This does indeed seem to be clearly the case for $Ge^{II}(Pc)$ and $[P^{III}(Pc)]^+$ (below). Stover et al.[57] reduced $Ge^{IV}(Pc)Cl_2$ with $NaBH_4$ or $SnCl_2$ to obtain $Ge^{II}(Pc)$, tabulated absorption data, but did not report luminescence. Their data, along with other metalloid phthalocyanine data, are included in Table III. The appearance of a new absorption band at 445 nm is strikingly similar to the 460-nm band of hyperporphyrins.

$Ge^{II}(Pc)$ is light sensitive but surprisingly resistant to oxidation to $Ge^{IV}(Pc)X_2$, in contrast to $Sn^{II}(Pc)$. Br_2, I_2 and 30% H_2O_2 were ineffective; ring oxidation and decomposition preceded the $Ge^{II} \rightarrow Ge^{IV}$ step. The Pc macrocycle is known to stabilize low-valence metal oxidation states; that it does so more for Ge^{II} than Sn^{II} (where we would naively expect the reverse order) may be a consequence of the smaller covalent radius of Ge^{II} which could allow it to fit tightly in plane, rather than exoplanar as is the case for $Sn^{II}(Pc)$[52] and $Pb^{II}(Pc)$,[23] which are reported to be 1.11 and 0.92 Å out of the plane of the four pyrrole nitrogens, respectively. A similar situation is found with $[As^{III}(OEP)]^+$ and $[P^{III}(OEP)]^+$: The P^{III} derivative appears to be somewhat more stable than the As^{III} compound.

The labile $Pb^{II}(Pc)$ is the only lead derivative presently known, though attempts have been made to prepare Pb^{IV} complexes.[54] Figure 5B shows the absorption spectrum of $Pb^{II}(Pc)$.[51] As with $Ge^{II}(Pc)$, a band at ~450 nm is seen, with an intensity relative to the Q and Soret bands that is less than that of $Ge^{II}(Pc)$ or $[P^{III}(Pc)]^+$. This spectrum is in agreement with one published by Berezin[58] but differs from that reported much earlier by Linstead et al.[59]

$Sn^{II}(Pc)$ is somewhat anomalous in that published data[51,58,60] do not indicate any extra absorption bands in the region 400–500 nm that can be identified as a hyper charge-transfer transition. However, the chemistry was not fully under control in the spectra from our laboratory.[51,60] and we believe such a band will be observed in $Sn^{II}(Pc)$.

Luminescence properties of these group 4 phthalocyanines have not been systematically investigated. In particular, it is not known whether the M^{II} derivatives are nonfluorescent like the corresponding porphyrins or fluorescent like $[P^{III}(Pc)]^+$ (see below).

Group 5A Phthalocyanines. The complexes "Sb(Pc)Cl" and "Sb_2Pc" have been prepared[10] by refluxing $SbCl_3$ and H_2Pc in chloronaphthalene, and Sb and phthalonitrile, respectively. The latter complex is of unknown structure. A compound, "chloroarsenic phthalocyanine" is reported,[61] derived from the useful replacement type reaction

$$MX_3 + Li_2Pc \rightarrow M(Pc)X + 2LiX$$

which utilizes dilithium phthalocyanine as a soluble Pc derivative whose labile lithium ions are readily displaced. The proposed formulas "Sb(Pc)Cl" and "$Sb_2(Pc)$" are supported by elemental analyses and chemical behavior, but the "chloroarsenic Pc" is incompletely characterized. No bismuth derivatives are presently known, and there are no reports on attempts to form other-valent species.

Practically nothing is known about the spectral characteristics of these complexes. "Sb(Pc)Cl" is described as bright green in solution, but no absorption

---

(47) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1970**, *18*, 1.

(48) McHugh, A. J.; Gouterman, M.; Weiss, C., Jr. *Theor. Chim. Acta* **1972**, *24*, 346.

(49) Henriksson, A.; Sundbom, M. *Theor. Chem. Acta* **1972**, *27*, 213.

(50) Henriksson, A.; Ross, B., Sundbom, M. *Theor. Chim. Acta* **1972**, 27, 303.

(51) Edwards, L., Ph.D. Thesis, Department of Chemistry, Harvard University, Cambridge, MA, 1969.

(52) Friedel, M. K.; Hoskins, B. F.; Martin, R. L.; Mason, S. A. *Chem. Commun.* **1970**, 400.

(53) Rogers, D.; Osborn, R. S *Chem. Commun.* **1971**, *840.*

(54) Esposito, J. N.; Lloyd, J. E.; Kenney, M. E. *Inorg. Chem.* **1966**, 5, 1979, and references therein.

(55) Kreuger, P. C.; Kenney, M. E. *J. Org. Chem.* **1963**, *28*, 3379.

(56) Whalley, M. J. *J. Chem. Soc.* **1961**, 866.

(57) Stover, R. L.; Thrall, C. L.; Joyner, R. D. *Inorg. Chem.* **1971**, 10, 2335.

(58) Berezin, B. D. *Russ, J. Phys. Chem.* (*Engl. Transl.*) **1962**, *36*, 258.

(59) Anderson, J. S.; Bradbrook, E. F.; Cook, A. H.; Linstead, R. P. *J. Chem. Soc.* **1938**, 1151.

(60) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292.

data are given. "Chloroarsenic Pc" precipitates as a blue material, with absorption maxima at 340 and 580nm.[61] The position of the visible band, if correct, is unusual for metallophthalocyanines. The compound is relatively stable toward acid.

A complex which we identify as $[\mathrm{P^{III}(Pc)}]^+$ is formed when $\mathrm{PCl_3}$ or $\mathrm{PBr_3}$ is added to a pyridine solution of $\mathrm{H_2(Pc)}$ and heated to ~90 °C for about 30 min.[14] Figure 5C shows the absorption of $[\mathrm{P^{III}(ttbPc)}]^+$. The intense band at 446 nm is possibly unique among phthalocyanines in having such a narrow bandwidth, since the Soret region of the Pc macrocycle is typically broad and structureless, as in Figure 5A. To date efforts to produce a $[\mathrm{P^{V}(Pc)X_2}]^+$ derivative by oxidation of $[\mathrm{P^{III}Pc}]^+$ have failed. Chromatography of a long-neglected reaction mixture yielded a small amount of a blue material whose absorption spectrum and behavior in an ion-migration experiment suggested the formulation $[\mathrm{P^{V}(Pc)X_2}]^+$.[14] Contrary to expectation, there is no fluorescence from this substance, and the identification must be regarded as tentative.

Strong fluorescence is observed from $[\mathrm{P^{III}(ttbPc)}]^+$ and $[\mathrm{P^{III}(Pc)}]^+$. This is in marked contrast to the lack of fluorescence from any $[\mathrm{M^{III}}(\mathbf{P})]^+$ species noted above. This has been attributed to an in-plane locus of the phosphorus atom in $[\mathrm{P^{III}(Pc)}]^+$, while the central atoms in $[\mathrm{M^{III}}(\mathbf{P})]^+$ species are generally out of plane.[7,14] (Recent theoretical studies[62] suggest that in $[\mathrm{P^{III}}(\mathbf{P})]^+$ there is quenching by a low-energy $\pi \rightarrow a_{1g}$ (σ^*) transition.)

Some question remains about whether the phosphorus phthalocyanines should be formulated as $[\mathrm{P^{III}(Pc)}]^+\mathrm{X}^-$ or as $\mathrm{P^{III}(Pc)X}$. Although ion migration tests show $[\mathrm{Sb^{III}(OEP)}]^+$ and $[\mathrm{Bi^{III}(OEP)}]^+$ are ions,[17] similar tests on phosphorus phthalocyanine give unclear results.[63] A silver nitrate test for chloride ion on "chloroarsenic Pc" in pyridine/ethanol was negative, but it was positive after exhaustive oxidation in hot nitric acid.[61] The mass spectral data on $[\mathrm{P^{III}(Pc)}]\mathrm{X}$ raise the possibility of another structure, since the mass peak of the main phosphorus phthalocyanine species corresponds to $[\mathrm{P(Pc)H_2}]^+$.[14] We have similarly found the mass peak for $[\mathrm{P(ttbPc)H_2}]^+$.[63]

Redox Studies

In Table I we have summarized the redox chemistry of the metalloid porphyrins and phthalocyanines, as discussed in the text above. In this section we wish to mention electrochemical studies as well as an unusual redox observed on vaporization.

There is a rich literature on porphyrin and phthalocyanine electrochemical redox reaction involving both the macrocyclic π electron system and/or the central atom.[64–68] While the electrochemical redox reactions of the central atom tend to be reversible for transition-metal porphyrins and phthalocyanines, the little data available on metalloid porphyrins show reversible reactions occur only on the ring. Thus $\mathrm{Sn^{IV}(OEP)(OH)_2}$ shows two reversible ring reduction waves, but the oxidation wave is irreversible.[68] A similar behavior is shown by $[\mathrm{Sb^{V}(OEP)(OH)_2}]\mathrm{ClO_4}$ and $[\mathrm{Sb^{III}(OEP)}]\mathrm{ClO_4}$, whose reversible reduction waves occur at −0.55 and −1.05 V [$\mathrm{Sb^V}$] and at −0.70 and −1.10 V [$\mathrm{Sb^{III}}$],[17] lower in absolute value than any metalloporphyrin so far reported.[66] Electrochemical analysis of $\mathrm{Pb^{II}(OEP)}$ is summarized in the unusual scheme[32]

$$\mathrm{Pb^{II}(OEP)} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{II}(OEP^+)} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{IV}(OEP)X_2}$$

On the other hand, one reversible ring reduction wave and two reversible oxidation waves are reported for $\mathrm{Si^{IV}(OEP)(OH)_2}$.[68]

An unusual redox is observed on vaporization, where metal reduction by homolytic cleavage has been reported. Thus on vaporization, the reaction $\mathrm{Sn^{IV}(TPP)X_2} \rightarrow \mathrm{Sn^{II}(TPP)}$ occurs.[69] A similar reaction occurs when $[\mathrm{Sb^{V}(OEP)(OH)_2}]^+$ is vaporized.[17]

Conclusions

By reviewing the data, we have shown that the cyclic tetrapyrrole compounds containing metalloids rather than metals have a distinctive chemistry and electronic spectroscopy characterized by two valence states of the metalloid that are difficult to interconvert. As a result the literature on the subject has been somewhat confused, and many of the species are incompletely characterized. A further complication is that the metalloid may be in plane or out of plane depending on the metalloid size and valence. The availability of a large number of such macrocycles with differing electronic and chemical character, in combination with these double valent metalloids, provides a fertile field both for future experimental and theoretical studies.

This work was supported by NSF Grant DMR-7823958. Professor Johann W. Buchler, while at the Technische Hochschule, Aachen, provided samples of the group 5A octaethylporphyrin complexes, without which our optical studies could not have been done. He also provided valuable comments on this paper. Professor Michael Hanack of the Universität Tübingen kindly provided samples of tetra-tert-butyl phthalocyanine. Eric Shankland worked on Se and Te porphyrins.

---

(61) Rutter, H. A., Jr.; McQueen, J. D. *J. Inorg. Nucl. Chem.* **1960**, *12*, 362.

(62) Rawlings, D.; Gouterman, M.; Davidson, E. R., work in progress.

(63) Callis, J. C.; Gouterman, M.; Pepich, B.; Sayer, P., unpublished.

(64) Fuhrhop, J.-H. *Struct. Bonding* **1974**, *18*, 1.

(65) Fuhrhop, J.-H. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; Chapter 14.

(66) See reviews by Castro, C. E. (Chapter 1), Felton, R. H. (Chapter 3), and Davis, D. G. (Chapter 4), in ref 1, Vol. V.

(67) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.

(68) Fuhrhop, J.-H.; Kadish, K.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.

(69) Edwards, L.; Dolphin, D.; Gouterman, M.; Adler, A. D. *J. Mol. Spectrosc.* **1971**, *38*, 16.