Theoret. chim. Acta (Berl.) 18, 1—13 (1970)

Commentationes

Porphyrins

XXI. Extended Hückel Calculations on Group IV Metal Complexes*

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Received March 4, 1970

Extended Hückel calculations are reported for tetravalent porphin complexes of $Si(OH)_2$, $Ge(OH)_2$, $GeCl_2$, and $SnCl_2$ and divalent complexes of Ge, Sn, and Pb. Divalent Ge porphin is expected to be planar and have the extra two electrons in the ring. Divalent Sn and Pb porphins are expected to be non-planar and have the extra two electrons on the metal. The possibility of a charge transfer transition $a_1(p_z) \rightarrow e_g^*(\pi)$ is noted, and its identication in available spectra of Sn and PbTPP is made. The electronic structure of the tetravalent species is similar to other metalloporphyrins except for the possibility of low lying ligand to porphin charge transfer states in the hydroxy complexes.

Für die vierwertigen Porphin-Komplexe des $Si(OH)_2$, $Ge(OH)_2$, $GeCl_2$ und $SnCl_2$ und die zweiwertigen Komplexe des Ge, Sn und Pb werden Berechnungen nach der erweiterten Hückelmethode durchgeführt. Von dem zweiwertigen Ge-Porphin wird erwartet, daß es planar ist und daß sich die beiden zusätzlichen Elektronen im Ring befinden, während von den zweiwertigen Sn- und Pb-Porphinen zu erwarten ist, daß sie nicht planar sind und die beiden zusätzlichen Elektronen sich am Metall befinden. Auf die Möglichkeit eines Charge-Transfer-Übergangs $a_1(p_z) \rightarrow e_g^*(\pi)$ wird hingewiesen, und dieser Übergang wird in gemessenen Spektren von Sn und PbTPP identifiziert. Die Elektronenstruktur der vierwertigen Verbindung ist denjenigen anderer Metallporphyrine ähnlich, außer der Möglichkeit niedrig liegender Ligand-Porphin-Charge-Transfer-Zustände in den Hydroxy-Komplexen.

Calculs de type Hückel étendu pour des complexes tétravalents de la porphine avec $Si(OH)_2$, $Ge(OH)_2$, $GeCl_2$ et $SnCl_2$ et des complexes divalents avec Ge, Sn et Pb. La porphine de Ge divalente est prévue plane avec les deux électrons supplémentaires dans le cycle. Les porphines divalentes de Sn et Pb sont prévues non planes avec les deux électrons supplémentaires sur le métal. On remarque la possibilité d'une transition de transfert de charge $a_1(p_z) \rightarrow e_g^*(\pi)$ et on l'identifie dans les spectres disponibles pour Sn et PbTPP. La structure électronique des espèces tétravalentes est semblable à celle des autres métalloporphyrines à l'existence possible près dans les complexes hydroxy d'états de transfert de charge de basse énergie entre le ligand et la porphine.

Introduction

Some of the previous papers in this series have been concerned with extended Hückel calculations on transition metal and alkaline earth porphins [1]. Recently, experimental information has been accumulating on Group IV metal complexes. Linstead [2] was the first to prepare Sn and Pb phthalocyanines. Although most phthalocyanines are very stable, the unusual chemical reactivity of the PbPc was thought due to the decreased stability of an out of plane metal.

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* Paper XX: Ake, R. L., Gouterman, M.: Theoret. chim. Acta (Berl.) 17, 408—416 (1970).

Dorough [3] observed that the absorption spectra of Pb(II) porphyrins differed significantly from the spectra of transition metal porphyrins. This result was attributed to differences in the size of the metal atoms. If size is the only factor, however, it would be difficult to explain the quite normal spectrum of barium porphyrin, for barium is larger than lead. Edwards [4–6] has recently made a detailed study of the vapor and solution spectra of a large number of metal porphyrins and phthalocyanines. In addition to the normal phthalocyanine visible spectrum, he found the PbPc and $SnCl_2Pc$ compounds gave extra bands around 500 mμ. The absorption spectra of the Sn porphyrins were very dependent upon the oxidation state of the metal. In fact the spectrum associated with Sn(II)TPP by Dorough has been identified by Edwards as being due to the Sn(IV) compound. Information about metal-nitrogen bond strengths, magnetic shielding, and molecular geometry has been obtained from the *ir* and *nmr* of tetravalent Si, Ge, and Sn porphyrins and phthalocyanines by Kenney and co-workers [7, 8]. These experiments also showed the effects on the above properties of substituting different ligands around the metal atom.

Because porphyrin is a divalent ligand while Group IV metals are either divalent or tetravalent, a number of questions arise: in particular, the location of the extra two electrons in the divalent complex. The data shows that Si and Ge are tetravalent, Pb is divalent, while both valences have been observed for Sn. The calculations herein were undertaken to determine the effect of metal valence on electron distribution and spectra. As will be seen, the calculations lead to several interesting experimental predictions.

Method and Geometric Considerations

The previously reported extended Hückel program [9] has been expanded to include overlaps with the 5*s*, 5*p*, 4*d* orbitals of Sn and the 6*s*, 6*p* orbitals of Pb. The 5*d* electrons of Pb were not included since calculations on Sn including and excluding the *d* electrons give essentially equivalent results. That is, for both Ge and Sn porphins the *d* electrons are completely localized. The parameters used for the Group IV metals are given in Table 1. No attempt was made to optimize the basis set exponentials because accurate Sn–N and Pb–N overlaps are not available for comparison.

Although the crystal structures of Group IV porphyrins have not been studied in detail, preliminary investigations indicate that Ge(IV) and Sn(IV) porphyrins have nearly planar ring systems [14]. Zerner and Gouterman in Paper IV [1] demonstrated that the *x*-ray coordinates of the various transition metal porphyrins give very nearly the same planar projection for the porphin moeity (Fig. 1). Consequently, only two geometric parameters were varied in our calculation: (1) the distance of the pyrrole nitrogen from the ring center; (2) the metal nitrogen bond distance. Hoard [15] has found that any porphyrin with a metal-nitrogen bond length greater than 2.01 Å should be non-planar; i.e., the maximum distance nitrogen can be displaced from the center of the ring is 2.01 Å. However, if the nitrogens are placed 2.06 Å from the center, the size of the central cavity in free base porphyrins, the results of our calculations do not appreciably change.

Table 1. *Extended Hückel parameters for* Si, Ge, Sn *and* Pb

A. Basis set exponentials[a] *(Bohr radii)*$^{-1}$

Si	$\zeta_{3s}=1.6344$	$\zeta_{3p}=1.4284$	
Ge	$\zeta_{4s}=2.0109$	$\zeta_{4p}=1.6951$	$\zeta_{3d}=5.4171$
Sn	$\zeta_{5s}=2.1257$	$\zeta_{5p}=1.8204$	$\zeta_{4d}=4.4925$
Pb	$\zeta_{6s}=2.3500$	$\zeta_{6p}=2.0655$	

B. Ionization potentials[b] *(eV)*

	$M \rightarrow M^{+} + (e)$		$M^{+} \rightarrow M^{++} + (e)$	
Si	d $s^2p^2 \rightarrow sp^2 + (s)$	-15.16	$s^2p \rightarrow sp + (s)$	-23.80
	$s^2p^2 \rightarrow s^2p + (p)$	-7.62	$s^2p \rightarrow s^2 + (p)$	-16.33
Ge	$s^2p^2 \rightarrow sp^2 + (s)$	-15.88	$s^2p \rightarrow sp + (s)$	-24.51
	$s^2p^2 \rightarrow s^2p + (p)$	-7.36	$s^2p \rightarrow s^2 + (p)$	-15.82
	$s^2p^2d^{10} \rightarrow s^2p^2d^9 + (d)$	-32.50^{c}	$d^9 \rightarrow d^8 + (d)$	-42.50^{d}
Sn	$s^2p^2 \rightarrow sp^2 + (s)$	-14.56	$s^2p \rightarrow sp + (s)$	-22.05
	$s^2p^2 \rightarrow s^2p + (p)$	-6.84	$s^2p \rightarrow s^2 + (p)$	-14.37
	$s^2p^2d^{10} \rightarrow s^2p^2d^9 + (d)$	-32.50^{e}	$d^9 \rightarrow d^8 + (d)$	-42.50^{e}
Pb	$s^2p^2 \rightarrow sp^2 + (s)$	-16.91	$s^2p \rightarrow sp + (s)$	-23.43
	$s^2p^2 \rightarrow s^2p + (p)$	-7.44	$s^2p \rightarrow s^2 + (p)$	-14.16

[a] From Ref. [10, 11].
[b] Based on data from Ref. [12].
[c] From Ref. [13].
[d] Estimated from Zn values.
[e] Chosen to agree with Ge values.

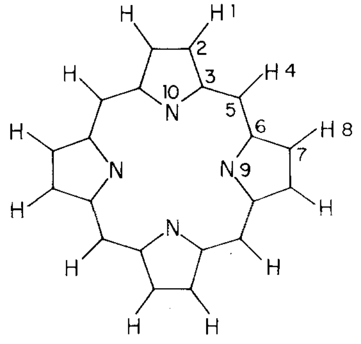

Fig. 1. Geometry and labeling of planar porphin

Since Group IV metal-nitrogen bond distances are not known exactly, the calculations were performed over a reasonable range of values (Table 2A). From a consideration of covalent radii, one would expect a Si-N distance somewhat less than 1.90 Å. However, this is the minimum value possible without significant distortion of the porphin skeleton. The Ge–N bond distances used for Ge(II) were based on known covalent radii and on the calculated ionic character in

Table 2. *Bond distances used in calculations*

A. Metal nitrogen bond distances of Group IV porphins (Å)

	Si(IV)	Ge(II)	Ge(IV)	Sn(II)	Sn(IV)	Pb(II)
planar	1.90	1.98	1.98	2.06	2.06	—
non-planar[a]	—	2.04	—	2.15 to 2.25	2.20	2.20 to 2.32

B. Metal ligand bond distance (Å)[b,c]

Si–O	Ge–O	Ge–Cl	Sn–O	Sn–Cl
1.64	1.79	2.10	2.05	2.31

[a] For all non-planar geometries the distance from N to projection of metal on plane is 2.01 Å.

[b] From Ref. [16].

[c] All O–H bond distances set at 0.984 Å.

porphyrin. Ge(IV) porphyrins are almost surely planar since the metal-nitrogen bond distance will decrease with an increase in the oxidation number of the metal. It is, therefore, reasonable to place the ligands on either side of the porphin ring (Table 2B).

Schlemper [17] found the Sn–N distance in Bis(8-hydroxyquinolate) to be 2.35 ± 0.04 Å. This molecule is a distorted octahedron with steric effects tending to increase bond distances; therefore, the porphin Sn–N distance is probably shorter. In addition, a bond length of that magnitude would mean that the Sn atom has to be 1.22 Å out of the molecular plane. Since this seems unlikely from what is known about the stability of Sn(II) complexes, the Sn–N distance was placed in the range 2.15–2.25 Å. A calculation on the planar Sn(II) porphin was carried out since this is an extreme form useful for comparison. The effective ionic radius of Sn(IV) is about 0.22 Å less than that of Sn(II) [18]. Consequently Sn(IV) complexes have a much greater likelihood of being planar. From a study of the *ir* absorption of $Sn(OH)_2Pc$ and SnX_2Pc, Kenney *et al.* [8, 19] support the view that Sn(IV) forms an octahedral complex. Since such evidence is never completely firm in complex molecules, calculations were made for two possible configurations of non-planar $Sn(IV)Cl_2$ porphin. Two extreme configurations were considered: the Cl atoms above the aza nitrogens; the Cl atoms above the bridged carbon atoms. In both cases the Cl–Sn–Cl angle was set at 109°. As will be shown in a later section, the predicted spectra for these two configurations should be very different. The decreased stability of Pb porphyrins and phthalocyanines indicates that the Pb is almost surely out of plane. The range of Pb–N distances was chosen on the basis of the 2.27 Å distance in $Pb(NS)_2NH_3$ [16].

After these calculations were completed, an interesting report on the effects of ring geometry on the triplet and singlet energies in metalloporphyrins became available to us [20]. The conclusions presented do not contradict any of our geometric considerations.

Results

A. Divalent Species

Fig. 2 gives a schematic representation of the top filled and lowest empty orbitals of the divalent Group IV porphins. As the metal atom moves out of the plane of the molecule, the symmetry point group changes from D_{4h} to C_{4v}. However, D_{4h} labels have been kept for those molecular orbitals which have essentially planar character.

Fig. 2 shows top filled orbitals $a_{1u}(\pi)$, $a_{2u}(\pi)$, and $b_{1g}(\mathrm{N}p_\sigma)$, which are definitely filled. The next higher energy orbital can be either the normally empty porphin $e_g(\pi)$ or the metal orbital $a_1(p_z)$. Because valence III seems highly unlikely, we shall assume that the remaining two electrons are either $(e_g)^2$ or $(a_1)^2$. The $(e_g)^2$ structures are shown in Fig. 2 as triplets, with one electron in each e_g orbital. The phthalocyanine dianions are also naively predicted to have $(e_g)^2$ structures, but are thought to be singlets [21]. However, whether singlets or triplet the $(e_g)^2$ structure can be expected to be quite reactive.

Although divalent Ge compounds exist, attempts to make Ge(II) porphyrins have so far been unsuccessful [14]. From Fig. 2 we see that with the Ge atom in plane the ground state would have $(e_g)^2$ structure, and so the compounds are expected to be very reactive. The figure also shows that with the Ge out of plane, the ground state may become $(a_1)^2$. However, the situation is ambiguous. When two electrons are placed in the a_1 molecular orbital (Fig. 2), its energy is raised above that of the empty $e_g(\pi)$. Two electrons in the $e_g(\pi)$ however, lower the empty a_1 below the $e_g(\pi)$ (not shown in the figure).

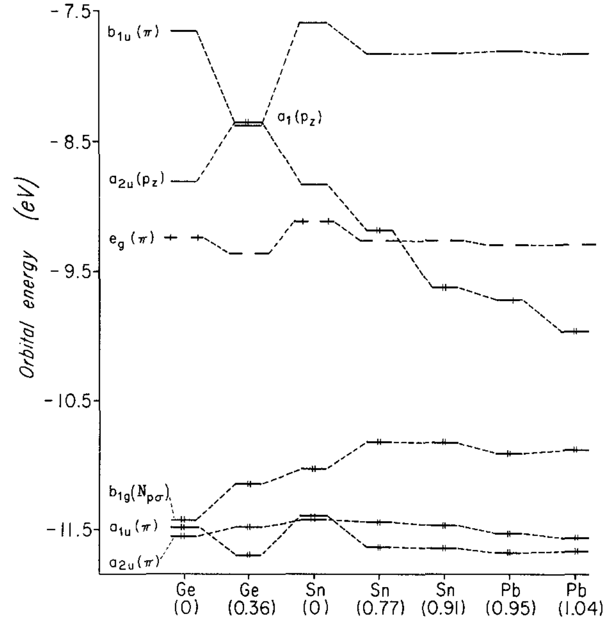

Fig. 2. Top filled and lowest empty MO's of divalent Group IV metal porphins. Numbers give metal distances in Å from plane. For full geometry, see Table 2

A similar geometry dependent electronic structure is calculated for Sn(II) porphyrins. With the Sn atom in plane, the ground state is predicted to be $(e_g)^2$. However, in contrast to Ge, a large non-planarity seems possible. With Sn 0.91 Å out of plane, the ground state is predicted to be $(a_1)^2$. Electronic spectra for Sn(II)TPP are reported by Edwards *et al.* [5]. The spectra are closer to known neutral porphyrin spectra than to either known monoanion or dianion spectra [22] and tend to support a ground state structure of $(a_1)^2$. Hence a Sn–N bond distance between 2.20 and 2.25 Å seems most likely.

From known radii Pb(II) porphyrin is clearly non-planar, and for any reasonable geometry a ground state $(a_1)^2$ is predicted. The spectra of Pb(II)TPP are relatively normal porphyrin spectra, in agreement with the electronic structure for a non-planarity of about 1 Å.

Although conclusions about geometry from extended Hückel calculations are generally tenuous, based on our spectral assignment, Sn(II) and Pb(II) are clearly predicted to be non-planar. This conclusion is not strongly dependent on the exact values used for the ionization potentials, which are rather uncertain for Pb because spin-orbit coupling is very strong in the atom and the extent of decoupling in the molecule is not clear. We performed calculations on Pb for various AOIP's representing different amounts of residual spin-orbit coupling in the molecule. The AOIP's used are given in Table 3, and the energies of the relevant MO's are given in Table 4. Since increasing the Pb–N by 0.05 Å affects the energy of the $a_1(p_z)$ about as much as lowering the AOIP by 1.5 eV, geometry is far more critical for determining the occupancy of this orbital than is the exact value for AOIP. We expect this to also hold for Ge(II) and Sn(II) porphins.

When the ground state is $(a_1)^2$, the energy level pattern for Sn(II) and Pb(II) porphins is very similar to other metal porphins [1]. The average of the two low

Table 3. *Ionization potentials (eV) of* Pb *for different amounts of residual molecular spin-orbit coupling*

Cases[a]	$M \rightarrow M^+ + e^-$		$M^+ \rightarrow M^{++} + e^-$	
	s	p	s	p
I	−16.036	−6.569	−23.430	−14.149
II	−16.909	−7.442	−23.430	−14.159
III	−17.782	−8.314	−23.430	−14.159

[a] Case III represents complete decoupling in the molecule and case I largest residual coupling.

Table 4. *Energy (eV) of* MO's *for different* AIOP's[a]

Case	a_{1u}	a_{2u}	b_{1g}	$a_1(p_z)$	$e_g(\pi)$
I	−11.663	−11.464	−10.864	−9.571	−9.289
III	−11.685	−11.685	−10.950	−9.897	−9.316
II	−11.683	−11.539	−10.911	−9.728	−9.308
II[b]	−11.683	−11.573	−10.893	−9.973	−9.310

[a] Unless otherwise noted, Pb–N distance = 2.27 Å.

[b] Pb–N distance = 2.32 Å.

Table 5. *Percent composition of* MO's *of* Sn(II) *and* Pb(II) *porphins*

	a_{2u}			b_{1g}	$a_1(p_z)$			$e_g(\pi)$
	porphin π	p_z of metal	s of metal	Np_σ	p_z of metal	porphin π	s of metal	porphin π
Sn(0)[b]	78	22	—	80	91	9	—	100
Sn(0.77)	60	30	4	81	64	20	13	99
Sn(0.91)	52	36	6	81	57	26	14	98
Pb(0.95)	50	36	5	81	57	28	11	98
Pb(1.04)	44	39	6	81	52	34	11	97

[a] Composition of $a_{1u}(\pi)$ is always 100% porphin π.

[b] Numbers give metal distance in Å from plane.

lying transitions for Sn(II), $a_{2u} \rightarrow e_g^*(\pi)$ and $a_{1u}(\pi) \rightarrow e_g^*(\pi)$, is 2.21 eV for the planar geometry and 2.27 eV for the non-planar compound while the value for Pb(II) is 2.31 eV. The average experimental value for transition metal porphyrins is 2.19 eV. The accuracy of the extended Hückel model is such that it is impossible, however, to confidently predict the position of the *Q* and *B* bands of Sn(II) and Pb(II) relative to other metal porphyrins.

As the metal move out of plane, the $a_{2u}(\pi)$ orbital loses porphin π character (Table 5). This loss might be reflected in a lower transition probability for the two main electronic bands in divalent Sn and Pb porphyrins. Dorough [3] found that the oscillator strength for the first two electronic transitions of PbTPP is in fact less than most other metal porphyrins.

In contrast to the $a_{2u}(\pi)$ orbital, as shown in Fig. 2 and Table 5, the energy and composition of $b_{1g}(\mathrm{N}p_\sigma)$ shows little variation. Since the Np_σ electrons cannot combine with the *s* and *p* electrons of the metal, it is not surprising that this orbital is quite independent of the metal-nitrogen bond distance. The fact that the b_{1g} orbital in Sn(II) porphin only has 0.1% $d_{x^2-y^2}$ character reinforces the contention that the *d* electrons in Group IV porphyrins are not involved in bonding. The $b_{1g} \rightarrow e_g^*(\pi)$ transition (x, y polarized) is no longer forbidden in the out of plane porphyrins, although the very local nature of the b_{1g} orbital makes an appreciable intensity for this transition unlikely. However, this transition may still affect the emission properties of these compounds.

From Fig. 2 one would predict an electronic absorption band in the infrared due to the transition $a_1(p_z) \rightarrow e_g^*(\pi)$. It must be pointed out, however, that the EH model has been chosen to fit the $\pi \rightarrow \pi^*$ transitions of porphyrins, and may not be a good guide for locating other types of transitions. For example, extended Hückel calculations on Zn porphin suggests the presence of a low lying forbidden charge transfer transition $b_{1g}(\sigma) \rightarrow e_g^*(\pi)$. Yet, the normal luminescence of Zn porphyrins indicates that this charge transfer state is considerably to the blue from the calculated value. We believe that this is generally true of charge transfer transitions calculated by our EH method. Nevertheless, the $a_1(p_z) \rightarrow e_g^*(\pi)$ transition probability should be large enough to have an experimentally measured intensity, for increasing the metal-nitrogen bond distance tends to make the $a_1(p_z)$ MO more delocalized by giving it appreciable porphin π character (see Table 5).

Table 6. *Electronic population of divalent Group IV porphins*[a]

	Ge[c] (0.36 Å out of plane)		Ge[d] (planar)		Sn[c] (0.91 Å out of plane)		Sn[c] (planar)		Pb[e] (0.95 Å out of plane)	
	Total	π	Total	π	Total	π	Total	π	Total	π
H(1)[b]	0.94		0.96		0.95		0.95		0.94	
C(2)	4.04	1.01	4.07	1.06	4.05	1.01	4.05	1.01	4.05	1.01
C(3)	3.97	1.07	3.99	1.11	3.98	1.07	3.97	1.07	3.97	1.06
H(4)	0.92		0.94		0.92		0.92		0.92	
C(5)	4.02	0.98	4.05	1.03	4.02	0.98	4.03	0.98	4.02	0.97
N(9)	5.18	1.39	5.12	1.40	5.19	1.34	5.17	1.37	5.18	1.35
Metal	13.86	1.73	13.46	0.95	13.71	1.35	13.75	1.93	3.73	1.39
Net Metal	+0.14		+0.54		+0.29		+0.25		+0.27	

[a] Mulliken population analysis, Ref. [23].
[b] Numbering of atoms given in Fig. 1.
[c] Results are for an $(a_1)^2$ ground state.
[d] Results are for an $(e_g)^2$ ground state.
[e] Calculations do not include the 5*d* electrons of Pb.

The results of a Mulliken population analysis (Table 6) for Ge(II), Sn(II), and Pb(II) porphins are very similar to those obtained for other metalloporphyrins. Although the total atomic charge density is not very geometry dependent, the individual orbital contributions to the charge density change appreciably with geometry (e.g. the planar and non-planar Sn). The net positive metal charge increases slightly as the distance from the porphin plane increases. If one assumes that the overlap population is a measure of the amount of covalent bonding, then covalent bonding dominates in the divalent Group IV porphyrins. This is generally true of Pb and Sn compounds.

B. *Tetravalent Species*

The energies of the top filled and lowest empty MO's of tetravalent Group IV porphins are given in Fig. 3. Except for the appearance of ligand MO's a_{1g}, e_u, e_g, the compounds of D_{4h} symmetry show the usual porphin pattern. The energy level pattern with the Sn out of plane and the Cl ligands above the porphin nitrogens (Fig. 3(a)) is drastically different from that of the D_{4h} complexes. Consequently, the electronic spectrum of such a compound would differ substantially from other porphyrins. With the Cl atoms above the bridged carbon (Fig. 3(b)), there is less mixing of the porphin and ligand AO's. However, even in this configuration the $e_g(\pi)$ MO is split by about 700 cm^{-1}; e.g., the calculation predicts the *Q* and *B* bands of this compound should each be split by about 700 cm^{-1}. Since the visible and *uv* spectra of Sn(IV) porphyrins are not unusual, these compounds are most probably octahedral.

The $a_{1u}(\pi)\rightarrow e_g^*(\pi)$ and $a_{2u}(\pi)\rightarrow e_g^*(\pi)$ averages for Si(OH)$_2$. Ge(OH)$_2$, GeCl$_2$ and SnCl$_2$ (D_{4h}) are 2.00, 2.09, 1.99 and 2.03 eV respectively. Thus, the EH model predicts a red shift for the two main electronic bands of these compounds. These

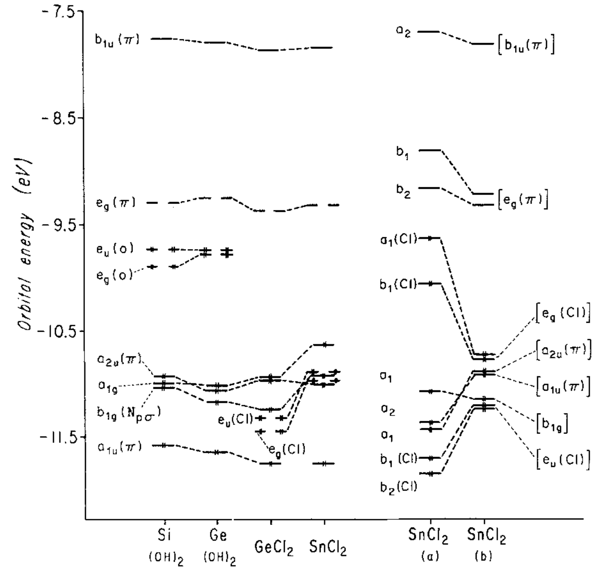

Fig. 3. Top filled and lowest empty MO's of tetravalent Group IV metal porphins: D_{4h} symmetry except for (a) and (b) which are C_{2v} symmetry as specified in text. Bond distances in Table 2

values are essentially geometry independent, for changing the Si–N bond distance to 1.95 Å and the Ge–N band distance to 2.04 Å does not change these numbers by more than 0.01 eV.

It can be seen from Fig. 3 that in addition to the usual porphin allowed transitions, $a_{1u}(\pi) \rightarrow e_g^*(\pi)$ and $a_{2u}(\pi) \rightarrow e_g^*(\pi)$, the chlorine and hydroxy ligand introduce another allowed low lying transition, $e_u \rightarrow e_g^*(\pi)$. Since the ligand AO's mix fairly strongly with those on the porphin nitrogen (Table 7), this band should have some intensity. Although this transition is predicted to be in the infrared for –OH and in the visible for –Cl, one should again be reminded that the EH model poorly predicts the energy of charge transfer bands. Spectra of $SnCl_2Pc$ contain a weak band at 480 mμ which is not present in Sn(II)Pc [4]. This band, which is strongly solvent dependent, may be due to this $e_u(Cl) \rightarrow e_g^*(\pi)$ transition. Boylan and Calvin [24] report a normal visible spectra for $Si(OH)_2$ porphyrins. However, no systematic study of the electronic absorption of Si and Ge porphyrins has been made, while the work on Sn(IV) porphyrins has suffered from insufficient knowledge about the exact ligands present [5].

Because of the mixing of the ligand orbitals with the porphyrin $e_g(\pi)$, the intensity of the Q and B bands may be somewhat less in these tetravalent compounds than in other porphyrins. Although the transitions $b_{1g} \rightarrow e_g(\pi)$ and $a_{1g} \rightarrow e_g^*(\pi)$ are forbidden in D_{4h} symmetry, a reduction of the full symmetry by non-planarity of the ring might give intensity to these low lying charge transfer transitions.

Table 8 summarizes the results of a Mulliken population analysis on these compounds. As expected, the positive charge on the metal has increased in going from the divalent to the tetravalent compound. For the dichloro compounds

Table 7. *Percent composition of* MO's *of tetravalent porphins*[a]

	a_{2u}		b_{1g}	a_{1g}			e_u (ligand)		e_g (ligand)		$e_g(\pi)$	
	porphin π	ligand p_z	Np_σ	ligand p_z	H1s	Np_σ	ligand	Np_σ	ligand	porphin π	ligand	porphin π
$Si(OH)_2$	82	13	79	58	9	20	96	3	97	3	26	74
$Ge(OH)_2$	89	8	78	62	14	18	97	2	96	4	36	64
$GeCl_2$	77	22	80	78	—	19	93	5	92	8	3	97
$SnCl_2$	59	39	80	83	—	15	95	4	99	1	2	98

[a] Composition of $a_{1u}(\pi)$ is 100% porphin π.

Table 8. *Total electronic population of tetravalent Group IV porphins*[a]

	$Si(OH)_2$		Ge(OH)		$GeCl_2$		$SnCl_2$	
	Total	π	Total	π	Total	π	Total	π
H(1)	0.95		0.95		0.94		0.94	
C(2)	4.05	1.01	4.05	1.03	4.04	1.00	4.05	1.01
C(3)	3.97	1.08	3.97	1.08	3.96	1.07	3.96	1.06
H(4)	0.92		0.92		0.92		0.92	
C(5)	4.03	0.98	4.04	1.01	4.02	0.96	4.02	0.97
N(9)	5.18	1.42	5.16	1.41	5.17	1.39	5.16	1.37
Net Porphin	−0.26		−0.25		+0.01		+0.10	
Metal[b,c]	+0.69	0.68	+0.65	0.69	+0.61	0.79	+0.64	
Ligand	O/6.44 H/0.78	1.22	O/6.42 H/0.78	1.16	Cl/7.31	1.63	Cl/7.37	1.65
Net Ligand	−0.43		−0.40		−0.62		−0.74	

[a] Symmetry of all these molecules D_{4h} (geometries given in Table 2).

[b] Under "total" we give net charge on metal.

[c] Under "π", only np_z population is given.

the charge on the porphin ring has become positive while all the negative charge is now concentrated on the chlorine atoms. This result is in agreement with the relative electronegativities of hydroxy and chloro ligands. Thus, the increased ionic bonding in the tetravalent compounds is not between the metal and the porphyrin moeity.

Generally, when the organic group is large as in porphyrins, dihydroxides rather than oxides will be the ligands [25]. Nevertheless, calculations were made on PbO and SnO porphins. Since all attempts to make Pb(IV)Pc have been unsuccessful [25], it was not surprising that our calculation on PbO did not converge. This often happens for an unrealistic molecule. Although the calculation on SnO was more approximate than those on other tetravalent compounds, it did indicate the following low lying allowed transitions: $e_u(\sigma) \rightarrow e_g^*(\pi)$ and $a_{2u}(p_z) \rightarrow e_g^*(\pi)$. The $a_{2u}(p_z)$ orbital of the oxygen is now quite high since the oxygen is no longer bonded to a hydrogen. Unfortunately, the electronic absorption spectra of this compound is not known.

Conclusions

Although EH calculations on large molecules usually do not give much information about geometry, some conclusions have been reached about Group IV porphyrins. For example, it is extremely likely that divalent Sn and Pb porphyrins are non-planar. In the latter case, this is substantiated by the great reactivity of Pb porphyrins. We also conclude that tetravalent Group IV porphyrins have the metal in the porphyrin plane since calculations with the metal out of plane give results incompatible with experimental spectra.

These calculations predict a charge transfer (C.T.) band for the divalent metal porphyrins. Evidence for its existence is obtained from the electronic absorption spectra of Sn(II) and Pb(II)TPP. The latter spectrum is well known [3] and shows three bands at 656, 459 and 347 mμ. The first two resemble (except for a red shift) the *Q* and *B* bands of a normal porphyrin. The third is a unique, broad, moderately intense band that we assign as C.T. The red shift of the *Q*, *B* bands can then be attributed to configuration interaction with the C.T. band. We assume with Edwards *et al.* [5] that the spectrum they obtained on reduction of Sn(II)TPP is that of Sn(*II*)TPP, although the species responsible for the spectrum has not been fully characterized. It shows three bands at 680, 489, and 387 mμ. On intensity grounds the band at 387 mμ is clearly the *B* band. Thus the bands at 680 and 489 mμ must be assigned as C.T. and *Q* or as *Q* and C.T. The two states are expected to mix by configuration interaction and a unique assignment may be impossible. The situation might be clarified by studying the spectra in various solvents. These assignments require that the C.T. band be at higher energy than that predicted by the EH model. The model does predict an appreciable intensity for the PbTPP C.T. band, as is observed, due to delocalization of $a_1(p_z)$. The red shift of the C.T. band in Sn(II)TPP relative to PbTPP is also consistent with the results of our calculations.

Although calculations were not made on Group IV phthalocyanines, we would not expect the results to be vastly different from porphyrins [26]; i.e., the divalent metal complex would show a low lying $a_1(p_z) \rightarrow e_g^*(\pi)$ transition. A normal phthalocyanine has two main peaks at around 680 and 330 mμ. Edwards *et al.* [4] found a third band in spectra of PbPc at ~450 mμ, which they attributed to a $\sigma \rightarrow \pi$ transition. However, it now seems likely that this band is due to the $a_1(p_z) \rightarrow e_g^*(\pi)$ charge transfer transition. Spectra of SnPc show no extra bands, although experimental information is not available on wavelengths greater than 700 mμ.

Calculations on tetravalent Group IV porphins indicate the possibility of ligand to porphyrin charge transfer bands, which would be considerably lower in energy for –OH as compared to –Cl. So far, the only experimental evidence for such transitions is the weak absorption around 480 mμ observed in $SnCl_2Pc$ [5]. However, no studies of the effect of counterions on the spectra, such as those performed by L. Boucher on Mn(III) porphyrins [27], have been carried out. Such low energy transitions would greatly influence the emission properties of these compounds. To clarify these matters, a detailed experimental study of the absorption and emission spectra of Group IV porphyrins is being undertaken at our laboratory.

Acknowledgements. This research was supported in part by Public Health Research Grant GM-14292 from the Institute of General Medical Sciences. We had helpful discussions with Dr. Lawrence Edwards.

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