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Porphyrins

X. Extended Hückel Calculations on Alkaline Earth Complexes*

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Extend Hückel calculations on Be, Mg, and Ca porphin indicate that these compounds should have much the same electronic structure as do the transition metal complexes. The possibility of $\sigma \rightarrow \pi^*$ electronic transitions in these complexes is noted, and the increased importance of ionic metal to porphin bonding demonstrated. A $(BeCl)_2$ porphin complex is examined and is shown by these calculations to be quite similar in electronic structure to the centrally symmetric metal complexes of the other alkaline earth porphins.

Rechnungen mit der erweiterten Hückel-Theorie an Be-, Mg- und Ca-Porphin ergeben, daß diese Verbindungen eine ähnliche Elektronenstruktur wie die Übergangsmetallkomplexe haben sollten. Auf die Möglichkeit von $\sigma \rightarrow \pi^*$-Übergängen in diesen Verbindungen wird hingewiesen, ebenso wie auf den zunehmenden Ionencharakter der Metall-Porphyrin-Bindung. Auch ein $(BeCl)_2$-Porphinkomplex hat im Rahmen dieser Rechnungen eine ähnliche Elektronenstruktur wie die Erdalkalikomplexe mit einem Zentralatom.

Des calculs en méthode de Hückel étendue sur les porphines de Be, Mg et Ca indiquent que ces composés devraient avoir à peu près la même structure électronique que les complexes des métaux de transition. On remarque la possibilité de transitions électroniques $\sigma \rightarrow \pi^*$ dans ces complexes et on démontre la plus grande importance de la liaison ionique du métal à la porphine. Un complexe $(BeCl)_2$ porphine est étudié et sa structure électronique se révèle au calcul assez semblable à celle des complexes métalliques à symétrie centrale des autres porphines alcalino-terreuses.

Introduction

Although the transition metal complexes of porphyrins are perhaps the best known and most often examined, alkaline earth complexes are also known and are of considerable interest, especially the Mg salt which is related to the biologically active chlorophylls. In this paper we report the results of calculations of Ca, Mg, and Be porphins using the extended Hückel method extensively developed in our previous investigations of transition metal porphins [*14, 15, 16, 17*]. The parameters which we use as characteristic of these alkaline earths are given in Tab. 1. All other considerations entering into the normal execution of this method are as outlined in these prior references.

Geometric Considerations

A planar projection of the X-ray coordinates of HOARD, HAMOR, and HAMOR [*7*] are used for the porphin moiety, with special attention paid to the preservation

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* For Paper IX, see Ref. [*4*].

Table 1. *Extended Hückel Parameters for* Be, Mg, Ca[a]

A. Basis Set Exponentials (Bohr radii)$^{-1}$

Be	$\zeta_{2s} = 0.9560$,	$\zeta_{2p} = 0.9560$	
Mg	$\zeta_{3s} = 1.1025$,	$\zeta_{3p} = 1.1025$	
Ca	$\zeta_{4s} = 1.210$,	$\zeta_{4p} = 1.210$,	$\zeta_{3d} = 1.850$

B. Ionization Potentials (eV)

	$M \to M^+ + (e)$	$M^+ \to M^{++} + (e)$
Be	$s^2 \to s + (s) - 9.32$	$s \to (s) - 18.21$
	$sp \to s + (p) - 5.96$	$p \to (p) - 15.49$
Mg	$s^2 \to s + (s) - 7.65$	$s \to (s) - 15.03$
	$sp \to s + (p) - 4.53$	$p \to (p) - 10.61$
Ca	$s^2 \to s + (s) - 6.11$	$s \to (s) - 11.87$
	$sp \to s + (p) - 3.96$	$p \to (p) - 8.73$
	$sd \to s + (d) - 3.54$	$d \to (d) - 10.17$

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[a] See also Tabs. 3 and 5, Ref. [*15*].

of bond length, Fig. 1. Examination of the covalent radius of Ca, comparison with the X-ray geometries of known metal porphyrins [*5*], and consideration of the bond lengths of such compounds as Ca_3N_2 [*12*] places the Ca atom considerably out of the porphin plane, even when the bonding nitrogens are displaced to allow the maximum reasonable area in the central porphin cavity. Using the stericly crowded free base compound in which the central metal is replaced by two hydrogens as an outer limit, we place the nitrogens 2.06 Å from the porphin center [*7*]. The suggested Ca–N bond length of 2.47 Å places the Ca atom 1.36 Å out of plane. Such a non-planarity seems too extreme in view of what is known of porphyrin complexes. If account is taken of the somewhat ionic results obtained from calculations of this non-planar geometry and extrapolation made between the covalent and ionic radii of Ca, the Ca atom must still remain ~0.36 Å above the porphin plane. Nevertheless we have carried out calculations for a planar geometry as this represents an extreme form useful for comparison. We believe the probable geometry has the Ca atom between 0.36 Å and 1.36 Å out of plane.

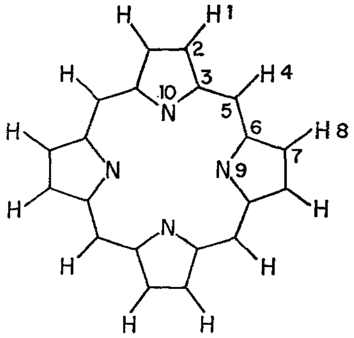

Fig. 1. Geometry and Labeling of D_{4h} Porphin

Mg is a somewhat smaller atom. Comparison of the covalent radii of Mg and Ca, and of Mg with transition elements for which the porphyrin geometry is known, suggests a Mg–N bond length of approximately 2.16 Å. This places the Mg atom 0.65 Å above the porphin plane with the nitrogen atoms 2.06 Å from the center. Consideration of the partial ionic character calculated for this geometry, suggests the Mg complex could be planar. We calculated both for planar and non-planar geometries and found our results rather independent of this variation.

Be is a relatively tiny atom and no reasonable porphin distortion will accomodate the suggested Be–N bond length of 1.7 Å implied by the covalent radius of Be and the X-ray coordinates of Be bis-acetylacetonate [*1*]. The shortest metal to nitrogen bond reported for porphyrins is that of 1.957 Å given for Ni etioporphyrin [*5*]. The Be atom is essentially lost in the porphin cavity. Nevertheless, for the completeness of these metal porphin calculations we consider the case of a centrally contained Be complex with the Be–N bond decreased to 1.90 Å. We obtain this geometry by drawing in the four pyrrole rings from their position in compounds where the nitrogens are 1.957 Å from the center, the shortest observed metal to porphyrin bond. We distort in this way so as not to extend the C–N bonds to unusual lengths. The resulting reduction in the methine bridge angles [i.e., *C*(5), Fig. 1], is 0.3°. A greater porphin distortion than this is unlikely.

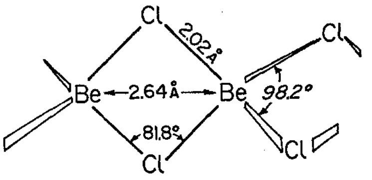

Fig. 2. Geometry of $(BeCl_2)_x$; Be is almost tetrahedral [*3*]

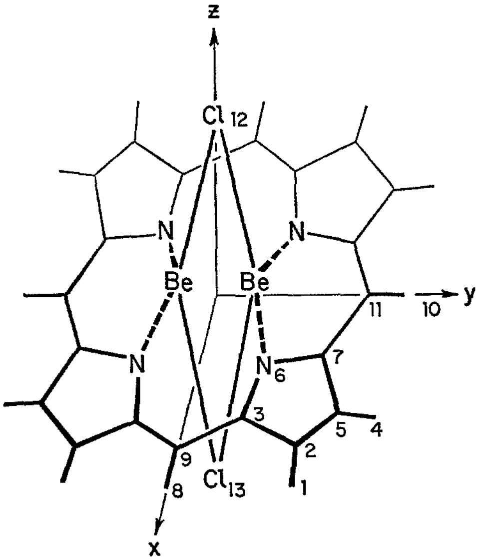

Fig. 3. Geometry and Labeling of $(BeCl)_2$ Porphin

More probable, however, is a complex in which the Be atom is no longer in the center but lies between two adjacent nitrogens. Such a geometry has too low a symmetry to be studied by our present computer programs. Moreover, the loss of symmetry might be expected to lead to a visible spectrum similar to that found for the free base [*6*]. Since compounds of Be of the form $[BeCl_2]_x$, as shown in Fig. 2, are well known [*3, 11*], we consider as distinct possibilities $(BeCl)_2$ complexes of porphin, in which the metal chloride group fits rather snugly into the porphin cavity. An examination of such complexes is especially tempting since BECKER and ALLISON [2] reported that attempts to isolate Be porphyrins led to complexes which, upon elemental analysis, showed an excess of Be salts. Attempting to preserve as much of the $(BeCl_2)_x$ and porphin geometry as possible, and setting the Be–N bond at 1.7 Å, the two Be atoms fit between adjacent nitrogens 0.55 Å above the porphin plane, as shown in Fig. 3. The Be–Be distance is decreased to 2.226 Å, the geometry of Be metal [10]. The distance between the two Be atoms above the porphin plane to the Cl below the plane is increased to maintain a van der Waal distance of 3.3 Å from the porphin nitrogens [9]. Since the results of this calculation are somewhat geometry dependent, we present them only as suggestive.

Results

The top filled and lowest empty orbitals are given schematically in Fig. 4. The group labels used for Be and $(BeCl)_2$ correspond to their respective symmetry of D_{4h} and C_{2v}, with the axes for the latter rotated by 45° as shown in Figs. 1 and 3. The non-planar Ca and Mg complexes have symmetry C_{4v}. We have used C_{4v} labels for orbitals located on the metal but have maintained D_{4h} labels for orbitals located on the ring. In Fig. 4 we omit the orbital energies for planar Mg as the level scheme is the same as for the non-planar case except that the a_1(Mg) orbital is raised considerably in energy.

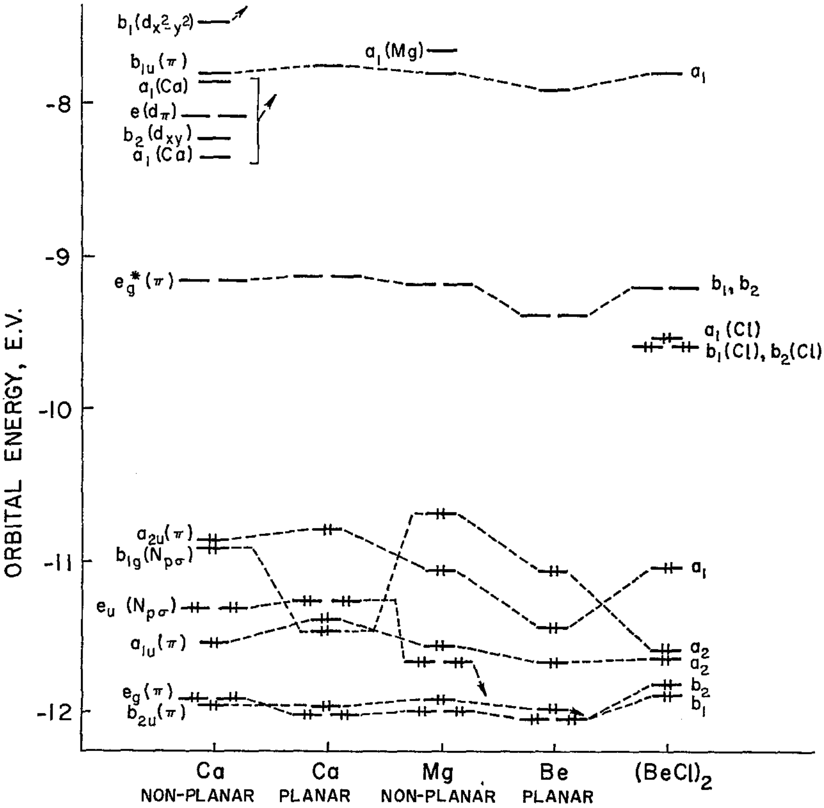

Fig. 4. Top Filled and Lowest Empty MO's of Alkaline Earth Porphins

The level pattern for Ca appears quite as it is for transition metal porphyrins [*15, 16*]. The average of the two lowest lying $\pi \rightarrow \pi^*$ transitions, $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ and $a_{1u}(\pi) \rightarrow e_g^*(\pi)$, is 2.06 eV for the non-planar geometry and 2.17 eV for the planar. This energy corresponds to the average of the transition energies to the two lowest excited singlets, that give rise to the characteristic visible and near UV porphyrin bands, and the two lowest triplets [*13, 15*]. The average value calculated for Co, Ni, Cu, Zn, for which the parameters were calibrated, is 2.19 eV [*15*]. Thus both Ca geometries suggest a red shift. ALLISON and BECKER [*2*] found that the Ca complex of mesoporphyrin IX dimethyl ester was red shifted 0.09 eV from the Co–Zn average. Unfortunately the extended Hückel model is too imprecise to allow determination of the Ca geometry from this observed spectral shift.

The orbitals involved in the electronic transitions of the Ca complex are calculated to remain fairly pure porphyrin π in character. We find for the non-planar geometry that $e_g^*(\pi)$ is 99%, $a_{2u}(\pi)$ is 95%, and $a_{1u}(\pi)$ is 100% porphin π based on a Mulliken population analysis [*8*]. Mixed into $a_{2u}(\pi)$ in the non-planar geometry is 2% Ca ($3d_{z^2}$), 1% Ca ($4s$), and 1% Ca ($4p_z$), a not unusual composition [*15*]. The composition and energy (s. Fig. 4) of the $b_{1g}(\mathrm{N}_{p\sigma})$ is more geometry dependent: its energy decreases in going from non-planar to planar geometry while the contribution of Ca ($3d_{x^2-y^2}$) is calculated to increase from 11%—17%. This may be contrasted with the Zn complex which is only 3% $d_{x^2-y^2}$ in character.

There are a group of orbitals localized largely on the Ca atom at energies above $e_g^*(\pi)$, as shown in Fig. 4. The lowest a_1 orbital is 50% Ca ($3d_{z^2}$), 29% Ca ($4p_z$), and 20% Ca ($2s$) in the non-planar geometry and becomes 85% Ca ($3d_{z^2}$) and 15% Ca ($4s$) in the planar case. The $b_2(d_{xy})$ remains nearly 99% Ca ($3d_{xy}$). The $e(d_\pi)$ change from 92% Ca ($3d_\pi$) in the non-planar case to 74% in the planar. The a_1 orbital above this is a mixture of Ca ($4p_z$), Ca ($4s$), and Ca ($3d_{z^2}$) in the non-planar geometry, going into nearly pure Ca ($4p_z$) in the planar. All these orbitals shift to higher energy on increasing planarity, as shown in Fig. 4. Although their energy is probably too high to give rise to observable charge transfer excitations, they may be important for complex formation.

The Mg porphin scheme appears quite normal. The highest filled MO is now the $b_{1g}(\mathrm{N}_{p\sigma})$. Unable to combine with the $3s$ and $3p$ valence orbitals of Mg, this MO is 75% $\mathrm{N}_{p\sigma}$ in character. The average of the two lowest lying $\pi \rightarrow \pi^*$ transitions is calculated to be 2.13 eV, again to the red of the Co–Zn average. The spectra of the Mg complex is observed to be slightly less red shifted than that of Ca [*2*].

The centrally symmetric Be complex appears to have much the same MO scheme as that of Mg. The average of the two lowest $\pi \rightarrow \pi^*$ transitions is estimated at 2.17 eV. The $(\mathrm{BeCl})_2$ porphin calculation is interesting in that it clearly shows how such a complex might maintain the normal porphin $\pi \rightarrow \pi^*$ absorbtion. The reduction from D_{4h} to C_{2v} symmetry has only split the porphin $b_1[e_g^*(\pi)]$ and $b_2[e_g^*(\pi)]$ MO's by 24 cm^{-1}. The $a_1[a_{2u}(\pi)]$ and $a_2[a_{1u}(\pi)]$ MO's are much the same as in the centrally symmetric system. The average $\pi \rightarrow \pi^*$ transition is estimated at 2.11 eV, or not far from the porphyrin average. The $a_1[a_{2u}(\pi)]$ is 95% porphin π; the $b_1[e_g^*(\pi)]$ and $b_2[e_g^*(\pi)]$, 92%. The $a_2[a_{1u}(\pi)]$ MO is 79% porphin π, the major impurity being 10% $\mathrm{N}(p\sigma)$. This loss of π character might be manifest in a decreased transition probability of the porphyrin $\pi \rightarrow \pi^*$ bands when compared with other porphyrin complexes, but the σ impurity is rapidly diminished upon lowering

Table 2. *Electronic Population*[a]

Fig. 1	Ca[b] (1.36 Å out-of-plane)		Mg[b] (0.65 Å out-of-plane)		Be		$(BeCl)_2$		
	Total	π	Total	π	Total	π	Total	π	Fig. 3[e]
H(1) = H(8)	0.95		0.95		0.94		0.95		H(1) = H(4)
C(2) = C(7)	4.06	1.02	4.06	1.02	4.05	1.00	4.06	1.02	C(2) = C(5)
C(3) = C(6)	3.99	1.07	3.98	1.07	3.97	1.07	3.96	1.07	C(3)
	(4.00)	(1.06)					3.98	1.07	C(7)
H(4)	0.92 (0.93)		0.92		0.91		0.93		H(8) = H(10)
C(5)	4.04	0.98	4.03	0.97	4.02	0.96	4.03	0.99	C(9)
							4.02	0.98	C(11)
N(9) = N(10)	5.22	1.27	5.21	1.27	5.21	1.31	5.17	1.34	N(6)
	(5.23)	(1.28)		(1.28)					
							7.01		Cl(12)
							7.46		Cl(13)
Metal	1.28	0.28[c]	1.41	0.27	1.74	0.38	1.61	0.51[d]	Be
	(1.11)	(0.25)	(1.42)	(0.30)					
Net Metal	+0.72 (0.89)		+0.59 (+0.58)		+0.26		+0.39		Net per Be

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[a] Mulliken population analysis, Ref. [*8*].

[b] Results for planar calculation, where different, shown in parenthesis.

[c] $4p_z$ and both $3d\pi$.

[d] $2p_z$ only.

[e] Note that the equalities in this case are *not* required by symmetry.

the two Be atoms more into the porphyrin plane. Similarly, the $a_2[b_{1g}(\sigma)]$ orbital just above the $a_2[a_{1u}(\pi)]$ has gained 36% porphyrin π character, and transitions from this orbital to the empty $b_1[e_g^*(\pi)]$ and $b_2[e_g^*(\pi)]$ might have intensity. If so, these new transitions

$$a_2[b_{1g}(\sigma)] \rightarrow b_1[e_{gx}^*(\pi)]\,, \quad b_2[e_{gy}^*(\pi)]$$

Table 3. Ca *Electronic Population*

	$4s$	$4p_x = 4p_y$	$4p_z$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{yx} = 3d_{xz}$	$3d_{z^2}$	Total
non-planar	0.3100	0.1469	0.1201	0.3285	0.0077	0.0816	0.0602	1.2836
planar	0.1880	0.0550	0.1530	0.4641	0.0242	0.0463	0.0705	1.1025

of (x, y) polarization could introduce new structure into the porphyrin π spectrum. However, increased planarity quickly reduces the π character of this orbital, and with it, the probability of transitions from this MO. The three filled orbitals occurring above the highest filled porphin MO's, of a_1, b_1, and b_2 symmetry, are nearly pure $3p$ AO's belonging to the chlorine below the porphin plane. Raising this chlorine atom closer to the two Be atoms leads to a large mixing of the Cl AO's with those of the porphin nitrogens. The result is a strongly antibonding combination, an expression of van der Waal repulsion. Transitions from these orbitals are allowed, but should be very weak because of their very local nature. However, the existence of these low lying excited states might affect emission. The Be complex is not observed to phosphoresce [*2*].

The results of a population analysis [*8*] on these complexes appears in Tab. 2 and are very similar to those obtained in our investigations of the transition metal compounds. The net charges on the nitrogen atoms of the $(BeCl)_2$ complex is somewhat less than that calculated for the other alkaline earth porphins, but is increased upon lowering the Be atoms more into the porphin plane.

An examination of this table indicates very little reduction of the four fold symmetry in the charge distribution of porphin upon chelation with $(BeCl)_2$. In this complex the Cl atom further from the two Be atoms is calculated to be considerably more negative than its closer counterpart and begins to appear much more as an isolated chloride ion.

The net charge calculated on Ca is found to be slightly geometry dependent; $+0.72$ when the Ca atom is 1.36 Å above the porphin plane and 2.47 Å from its four neighboring nitrogens, and $+0.89$ when the Ca atom is in the plane, 2.06 Å from the four nitrogens. The calculated net charge on the Mg atom, $+0.59$, appears to be almost independent of geometry throughout the range that we have considered. The positive charges calculated for the alkaline earth metals fall in the order suggested by their location in the periodic table.

The detailed electronic structure about the Ca atom is given in Tab. 3. It is seen that the $3d$ orbitals, vacant in the ground state of the atom, have gained 0.56 electrons for the non-planar geometry and 0.65 for the planar, and are quite important in determining the net charge of the Ca atoms.

Conclusions

Extended Hückel calculations on Ca and Mg porphins have indicated that these alkaline earth complexes should have much in common with their transition metal analogues. The characteristic porphin π structure should be preserved. The electronic distribution about the porphin moiety is essentially unchanged. The preservation of the normal porphin electronic structure by the more complicated $(BeCl)_2$ complex has also been demonstrated.

Interesting differences do, however, occur. The appearance of a $b_{1g}(\mathrm{N}_{p\sigma})$ MO among the top occupied MO's might lead to additional structure in the spectrum. Deviations from planarity, or reduction of full symmetry by additional ligands above and below the porphin plane, might give intensity to low lying $b_{1g}(\mathrm{N}_{p\sigma}) \rightarrow e_g^*(\pi)$ transitions. Also possible are $e_u(\mathrm{N}_{p\sigma}) \rightarrow e_g^*(\pi)$ transitions. Although formally allowed such transition should be weak because of the quite local nature of the $e_u(\mathrm{N}_{p\sigma})$. These latter transitions are predicted to lie in the visible to near *UV* region, or in the region of the normal porphin $\pi \rightarrow \pi^*$ bands. Excitations from the $b_{1g}(\mathrm{N}_{p\sigma})$ and $e_u(\mathrm{N}_{p\sigma})$ MO's are predicted at higher energies in the transition metal complexes as these orbitals have combined with available $3d$ or lower lying $4p$ metal AO's and have been lowered in energy.

If we use "overlap population" [*8*] as a measure of covalent bonding, these calculations indicate that ionic bonding between the central metal and the porphin ring is relatively more important in Ca and Mg porphins than in the transition metal complexes, where covalent bonding dominates. In this respect the Zn complex is more like those of the alkaline earths we examine. The relatively higher energies of the alkaline earth valence orbitals has given rise to only a small amount of mixing with filled MO's, resulting in large positive charges on the central metals and small overlap populations. In the Zn complex, the totally filled $3d$ orbitals give rise to an antibonding interaction with the porphin system. The net overlap population after consideration of the $4s$ and $4p$ valence orbitals of Zn, and the relatively large positive charge of $+0.40$ calculated for Zn atom, make this bonding scheme appear somewhat similar to that found in the alkaline earth complexes examined in this paper.

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