

CONTRIBUTION FROM THE CONANT CHEMICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138**Porphyryns. VI. Extended Hückel Calculations on the Scandium Complex**

BY MICHAEL ZERNER AND MARTIN GOUTERMAN

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Extended Hückel calculations are performed on ScOH porphyrins to determine whether this unknown complex is inherently unstable. The calculations suggest that it should be stable, but should have an unusual visible-ultraviolet spectrum. It may be subject to photodissociation.

Introduction

In general, divalent metal porphyrin complexes not readily available as natural products can be prepared easily by direct reaction with metal salts, while higher valence states are most easily made through oxidation of the corresponding divalent complexes.

In contrast to the abundance of references in the literature on most of the first-row transition metal complexes of porphyrins, those of Sc and Ti have escaped our attention. (Cr porphyrin has just been synthesized.¹) Whether or not this is a manifestation of a failure to synthesize these complexes, or whether a reflection of lack of interest, is impossible to determine. Turning to the related phthalocyanine complexes, carefully investigated for their properties as stable dyes, of the first-row transition elements only Sc has not been reported as a complex.²

We describe here the results of extended Hückel calculations with ScOH replacing the H₂ of the free base porphyrin in an attempt to determine whether this complex is inherently unstable when examined by this molecular model.

The extended Hückel method which we use has been detailed elsewhere.^{3,4} A planar projection of the X-ray coordinates of Hamor, Hamor, and Hoard are used for the porphyrin moiety.⁵ An examination of the covalent radii of various transition metals and comparison with the known X-ray geometries of metal porphyrins⁶ indicates that even with the four porphyrin nitrogens extended 2.06 Å from the porphyrin center, the maximum suggested from information on the free base compound, the Sc atom will lie some 0.9 Å above the porphyrin plane. Assuming this geometry for the Sc atom, the Sc-O bond is set at 2.01 Å and the O-H bond at 0.984 Å.⁷ Our program constrains the H atom to lie on the z axis.

The atomic parameters which we use for Sc are given in Table I and are obtained in the same fashion as

described in previous work.³ All other considerations which enter into the normal execution of this model are as outlined in these previous works and will not be repeated here.

TABLE I
EXTENDED HÜCKEL PARAMETERS FOR Sc
Basis Set Exponentials

$$\zeta_{4s} = 1.230, \zeta_{2p} = 1.230, \zeta_{3d} = 2.030$$

Atomic Orbital Ionization Potentials

Sc \rightarrow Sc ⁺ + e	Sc ⁺ \rightarrow Sc ⁺² + e
d ⁿ⁻² s ² \rightarrow d ⁿ⁻² s + (s)	d ⁿ⁻² s \rightarrow d ⁿ⁻² + (s)
-6.64 eV	-12.82
d ⁿ⁻² sp \rightarrow d ⁿ⁻² s + (p)	d ⁿ⁻² p \rightarrow d ⁿ⁻² + (p)
-4.26 eV	-9.36
d ⁿ⁻² s ² \rightarrow d ⁿ⁻³ s ² + (d)	d ⁿ⁻² s \rightarrow d ⁿ⁻³ s + (d)
d ⁿ⁻¹ s \rightarrow d ⁿ⁻² s + (d)	d ⁿ⁻¹ \rightarrow d ⁿ⁻² + (d)
-6.33 eV	-13.90

Results

The top filled and lowest empty MO's obtained by this calculation are shown schematically in Figure 1, where they are compared with those of the known Ca and VO complexes similarly calculated.^{3,4} There are no apparent anomalies in this scheme that would suggest instability. A study of overlap population was made⁸ and indicates that the covalent bonding between the porphyrin nitrogens and Sc atom is as strong as or stronger than that calculated for the vanadyl complex. The ionic bonding, estimated by simple electrostatics using the results of a population analysis,⁸ is also nearly equal to the two complexes. The total bonding of these complexes is thus predicted to be nearly the same, and there is no obvious reason why the ground state of ScOH porphyrins should not be stable. The bonding in ScOH and VO porphyrins is, however, predicted to be quite different from that of the Ca complex which should have considerably stronger ionic bonding. However, the relatively higher energies of the Ca valence orbitals which gave rise to this increased ionic behavior have also led to a considerable reduction in the covalent strength by reducing the size of the orbital coefficients in occupied MO's.

The results of the population analysis are summarized in Figure 2. We find the net charges are Sc^{+0.41}. OH^{-0.10} with porphyrin -0.31, rather different from the classical Sc⁺³OH⁻. The electronic distribution of the Sc itself is, as shown in Table II, rather close to the s^{0.5}p^{0.5}dⁿ⁻¹ found in the other transition metal

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(2) F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds, Reinhold Publishing Corp., New York, N. Y., 1963.

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(4) M. Zerner, Ph.D. Thesis, Department of Chemistry, Harvard University, 1966.

(5) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Am. Chem. Soc.*, **85**, 2334 (1963).(6) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

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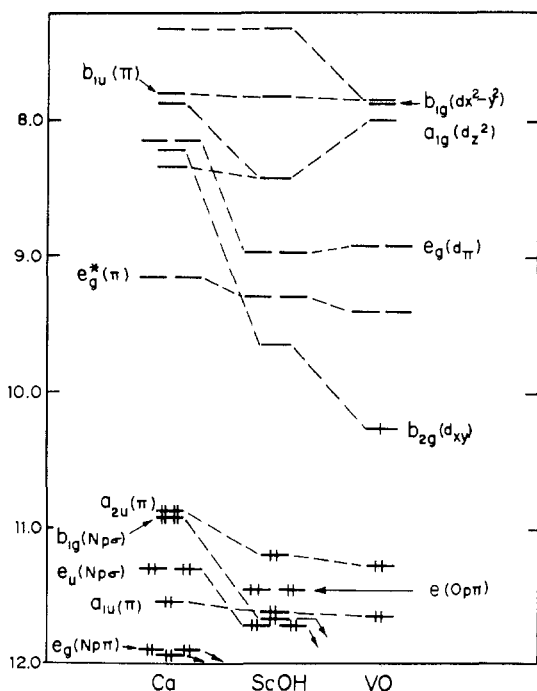


Figure 1.—Calculated energies for top filled and lowest empty orbitals. Ca assumed 1.36 Å above the plane; ScOH assumed 0.9 Å above the plane; VO assumed 0.74 Å above the plane.

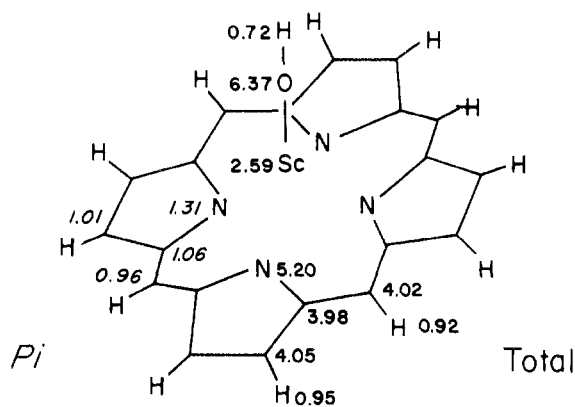


Figure 2.—Electronic population calculated for ScOH porphyrin.

not seem physical. If real, the unusually large porphyrin to metal coupling that has been calculated for this complex should manifest itself in a reduction of the intensity of the porphyrin $\pi \rightarrow \pi^*$ bands relative to other transition metal porphyrins.

The unoccupied $b_{2g}(d_{xy})$ ligand field orbital is calculated to be 98% pure metal $3d_{xy}$. Figure 1 indicates the possibility of allowed low-lying transitions to this orbital from the $e(O p_{\pi})$ MO's (83% OH $2p_{\pi}$ and 8% Sc $3d_{\pi}$) which have energies between those of the

TABLE II

ELECTRONIC STRUCTURE OF Sc (III) IN ScOH PORPHYRIN

4s	4p _x = 4p _y	4p _z	3d _{z²-y²}	3d _{xy}	3d _{yz} = 3d _{xz}	3d _{z²}	Total
0.27	0.12	0.17	0.65	0.03	0.40	0.42	2.58

porphyrin calculations.

A glance at Figure 1 suggests many possible electronic excitations. The main porphyrin bands are⁹ $a_{1u}(\pi) \rightarrow e_g^*(\pi)$ and $a_{2u}(\pi) \rightarrow e_g^*(\pi)$. For the ScOH complex their average is 2.06 eV as compared to 2.19 for the series Co to Zn tetraphenylporphyrin. However, the nature of these orbitals merits further discussion. The $a_{1u}(\pi)$, with nodes through both the porphyrin nitrogens and the methine bridges, is calculated from an investigation of orbital populations to be 100% on the $2p_z$ basis orbitals of porphyrin. The $a_{2u}(\pi)$ is calculated to be 93% porphyrin π , 1% metal $4p_z$, and 6% metal $3d_{z^2}$. This extension of the $a_{2u}(\pi)$ MO onto the $3d_{z^2}$ metal orbital is not unusual in our calculations for complexes in which the central metal atom is not in the porphyrin plane. The $e_g^*(\pi)$ MO's, however, although 93% of π symmetry, are calculated to be 22% Sc $3d_{\pi}$. Such a coupling between the porphyrin π system and the metal $3d_{\pi}$ orbitals occurred in our previous investigations of vanadyl porphyrins, but was easily removed by elevating the vanadium atom above the porphyrin plane. The result was a prediction of a normal vanadyl porphyrin $\pi \rightarrow \pi^*$ spectrum, as is observed. However, for this calculation the Sc atom is already 0.9 Å above the porphyrin plane and further elevation to 1.2 Å does not help much. Greater nonplanarity than this does

(9) As in ref 3 we use D_{4h} group labels for orbitals that correlate to orbitals in metal porphyrins with full symmetry and C_{4v} labels for orbitals localized in the ScOH fragment.

porphyrin $a_{2u}(\pi)$ and $a_{1u}(\pi)$ MO's.

These transitions should be weak because of the relatively local nature of the MO's involved. They are estimated by the model to lie in the near-red to visible region. Such a (x,y) polarized transition in the visible might not disturb the normal porphyrin $\pi \rightarrow \pi^*$ spectrum since the two transitions are of a quite different nature (small configuration interaction). Transitions from the $e_u(N p_{\sigma})$ to the $b_{2g}(d_{xy})$ are also indicated in Figure 1. Again, because of the charge-transfer nature of such an excitation, the transition should be weak and should not much interfere with the normal porphyrin visible spectrum near which energy it is estimated to occur.

Of considerable interest is the calculated location of the $e_g(d_{\pi})$ ligand field orbitals, resting slightly above the porphyrin $e_g^*(\pi)$'s. This orbital is estimated to be 56% metal $3d_{\pi}$, 8% OH $2p_{\pi}$, and as much as 31% porphyrin π . Although Figure 1 suggests that transitions $a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow e_g(d_{\pi})$ lie to the blue of the main porphyrin $\pi \rightarrow \pi^*$ transitions, exchange terms might shift them. Should they fall near any of the normal $\pi \rightarrow \pi^*$ excited states, a strong interaction can be expected. ScOH porphyrin is thus expected to have extra bands in the visible-ultraviolet region.

It is interesting to note that the $e_g(d_{\pi})$ MO's are strongly Sc to N antibonding, and any transition to these orbitals should greatly weaken the porphyrin to

ScOH bonding. Especially in this category fall transitions from the strongly bonding $e_u(Np_\sigma)$ and $b_{1g}(Np_\sigma)$, the latter gaining intensity as the complex goes from D_{4h} to C_{4v} symmetry. Both these possibilities not only destroy approximately 25% of the nitrogen-to-metal 3d overlap population, weakening the covalent bond, but also represent electronic charge transfer which results in excited states with a net negative charge on both the Sc atom and its neighboring nitrogen atoms. The analogous transitions in the vanadyl complex are predicted much to the blue and, because of the more local nature of the $e_g(d_\pi)$ ligand field orbitals, are predicted considerably weaker. As the $e_g(d_\pi)$ orbitals in VO porphyrin are calculated mostly on the vanadyl group, such transitions are not strongly metal-porphyrin antibonding. The implication is that ScOH porphyrins, if made, could photodissociate even if the vanadyl complex which we are using for comparison does not. Although the nature of the $e_g(d_\pi)$ MO's is somewhat sensitive to the assumed geometric relation between the Sc atom and the porphyrin plane, no significant change in this analysis is indicated when this distance is varied from 0.5 to 1.2 Å.

Although the metal character of the $e_g(d_\pi)$ MO's is somewhat sensitive to the location of the Sc atom, its position above the $b_{2g}(d_{xy})$ orbital appears not to be so dependent. For distances between the Sc atom and the porphyrin plane varying from 1.2 to 0.5 Å this orbital energy difference is 0.66 ± 0.03 eV. Likewise the energy gap between the principal $a_{1g}(d_{z^2})$ and $b_{2g}(d_{xy})$

ligand field orbital is rather insensitive to such geometry changes. In contrast to these, the energy of the $b_{1g}(d_{x^2-y^2})$ above that of the $b_{2g}(d_{xy})$ is strongly dependent on the location of the Sc atom above the plane. A similar result was found for VO complexes.³ For the 0.9 Å calculation, the orbital energy difference between the two is estimated at 2.35 eV and is calculated to change ~ 0.2 eV/0.1 Å for distances of 0.9 ± 0.3 Å.

Conclusions

Extended Hückel calculations on ScOH porphyrin have failed to indicate any inherent instability of the molecular ground state. However, these calculations do indicate that the ScOH complex could deviate from the "normal" transition metal porphyrin picture created by the extended Hückel model.³ Foremost among the unusual results noted is that $e_g^*(\pi)$, normally pure porphyrin π , has large $3d_\pi$ character, while $e_g(d_\pi)$ extends considerably into the porphyrin π system. Electronic transitions to these MO's could both alter the normal $\pi \rightarrow \pi^*$ porphyrin spectrum and lead to excited states in which the Sc to porphyrin bonds are greatly weakened.

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CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT

Phosponitrilic Compounds. VI.¹ High Molecular Weight Poly(alkoxy- and aryloxyphosphazenes)²

By H. R. ALLCOCK,³ R. L. KUGEL, AND K. J. VALAN

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The synthesis and characterization of the first fully substituted, high molecular weight, uncross-linked poly-(organophosphazenes) is described. Polymers of structure $(NPR_2)_n$ were prepared in which R was OCH_3 , OC_2H_5 , OCH_2CF_3 , and OC_6H_5 , by nucleophilic replacement of chlorine in uncross-linked $(NPCI_2)_n$ with alkoxide or aryloxy ions. Infrared, ultraviolet, nmr, glass transition, and X-ray diffraction data are considered in relation to previous structural interpretations of the polyphosphazene system. The marked depolymerization tendency and the nature of phosphorus-nitrogen bonding in these compounds are also discussed.

Introduction

The possibility that high molecular weight, open-chain polymers, comparable in structure and stability

(1) Part V: H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(2) For a preliminary account of parts of this work see H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965). The nomenclature used in this paper conforms to the "phosphazene"-based system used previously.¹

(3) To whom correspondence and reprint requests should be addressed at the Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802.

to silicones, might be derived from the phosphazene (phosponitrile) skeleton has intrigued many investigators in recent years. The fact that the phosphorus-nitrogen bond in cyclic trimeric and tetrameric organophosphazenes, $(NPR_2)_3$ and 4 , showed evidence of high thermal and chemical stability provided encouragement for this view. It was also apparent that, if polymers of this type (I) could be synthesized, with a