presence of some ligand–metal charge-transfer bands which may be obscured by the higher intensity intraligand transitions. Corresponding bands in the other complexes were less well-defined and of lower intensity. These may be due to similar intraligand or ligand–metal electron transfer.

Porphyrins. V. Extended Hückel Calculations on Vanadyl (VO²⁺) and Vanadium(II) Complexes

BY MICHAEL ZERNER AND MARTIN GOUTERMAN

The extended Hückel model is applied to VO^{2+} and V^{2+} porphins. VO is predicted to be out of plane; energies for d → d transitions are given. V is calculated to be stable, but subject to ready oxidation by O_2.

Introduction

Vanadyl porphyrins, in which VO replaces the H_2 of the free base, are widely distributed in nature in a variety of natural bitumens[1] and have become of theoretical interest, especially since epr studies have begun to shed light on the electronic structure of the vanadium orbitals.[2-6] There are, in addition, several other interesting phenomena which a quantum mechanical study of vanadium porphyrins might attempt to explain. Foremost among these is the apparent chemical instability of vanadium(II) porphyrins, *i.e.*, compounds where V alone replaces H_2 in the free base. We report in this work the results of a study of vanadyl and vanadium porphins using the extended Hückel model.[7-10] A previous investigation of vanadyl compounds by Ballhausen and Gray[11] has already gone a good way in explaining the quantum mechanical nature of VO in complexes in which V is penta- or hexacoordinated. Included in their calculations are the 3d, 4s, 4p orbitals of V, the valence orbitals of oxygen, and the sp^2 hybrids and p_π orbitals of the chelating atoms of the ligand groups. Their calculation is of the extended Hückel type, with provision made for atomic charge consistency. Our calculations are similar, but include all the valence orbitals of all the atoms in the porphin system.

Method

We seek solutions to the eigenvalue equation

$$H_{eff}\phi_j = w_j\phi_j$$

where H_{eff} is an effective one-electron Hamiltonian for the molecule. The molecular orbitals (MO) ϕ_j are expanded on a minimal basis set of atomic orbitals (AO), χ_p

$$\phi_j = \sum_p \chi_p c_{pj}$$

This leads to a secular equation

$$\det|H_{pq} - wS_{pq}| = 0$$

in which

$$S_{pq} = \int dv\, \chi_p\chi_q$$

$$H_{pq} = \int dv\, \chi_p H_{eff}\chi_q$$

In the extended Hückel model the latter are approximated by

$$H_{pq} = \frac{1}{2}S_{pq}(H_{pp} + H_{qq})[\kappa - (\kappa - 1)\delta_{pq}]$$

In the above κ is a pure parameter and H_{pp} are determined from atomic ionization processes. The methods of determining H_{pp} are described in more detail elsewhere and values for H, C, and N have been given in calculations reported on other metal porphyrin systems.[9] The values for V and O are given in Table I and were obtained by the same methods.[9,10,12,13]

Since ionization processes are highly dependent on net atomic charge, a self-consistent charge procedure was employed as in previous work.[9] A first calculation using H_{pp} for neutral atoms is carried out. Then H_{pp} are readjusted to be more in accord with the net charge on atom p calculated by a Mulliken population analysis.[14] A second calculation follows. Iterations continue until the calculated and assumed atomic charges agree to within 0.05 electron. This procedure greatly moderates charge buildup.

The AO basis set we use is

$$\chi(n,l,m) = Nr^{n-1}\exp(-\zeta r)Y_l^m(\theta,\Phi)$$

(1) A. Treibs, *Ann.*, **509**, 103 (1934).
(2) H. R. Gersmon and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).
(3) D. E. O'Reilly, *ibid.*, **29**, 1188 (1958); erratum, *ibid.*, **30**, 591 (1959).
(4) E. M. Roberts and W. S. Koski, *ibid.*, **34**, 591 (1961).
(5) D. Kivelson and S. Lee, *ibid.*, **41**, 1896 (1964).
(6) J. M. Assour, *ibid.*, **43**, 2477 (1965).
(7) M. Wolfsberg and L. Helmholtz, *ibid.*, **20**, 837 (1952).
(8) R. Hoffmann, *ibid.*, **39**, 1937 (1963); **40**, 2047 (1964); **40**, 2474 (1964); **40**, 2480 (1964); **40**, 2745 (1964).
(9) Paper IV: M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).
(10) M. Zerner, Ph.D. Thesis, Department of Chemistry, Harvard University, 1966.
(11) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(12) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).
(13) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(14) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955); *ibid.*, **23**, 1841 (1955).

TABLE I
ATOMIC IONIZATION PROCESSES[a]

$A^- \rightarrow A + e$	$A \rightarrow A^+ + e$	$A^+ \rightarrow A^{+2} + e$
O^b $s^2x^2y^2z \rightarrow sx^2y^2z + (s)$ -19.240	$s^2x^2yz \rightarrow sx^2yz + (s)$ -32.367	$s^2xyz \rightarrow sxyz + (s)$ -47.840
$s^2x^2y^2z \rightarrow s^2x^2yz + (p)$ -1.933	$s^2x^2yz \rightarrow s^2xyz + (p)$ -15.863	$s^2xyz \rightarrow s^2xy + (p)$ -33.630
V^c	$\left.\begin{array}{l} d^4s \rightarrow d^4 + (s) \\ d^3s^2 \rightarrow d^3s + (s) \end{array}\right\}$ -7.26	$d^3s \rightarrow d^3 + (s)$ -13.15
	$\left.\begin{array}{l} d^4p \rightarrow d^4 + (p) \\ d^3sp \rightarrow d^3s + (p) \end{array}\right\}$ -4.45	$d^3p \rightarrow d^3 + (p)$ -9.95
	$\left.\begin{array}{l} d^4 \rightarrow d^4 + (d) \\ d^3s^2 \rightarrow d^2s^2 + (d) \end{array}\right\}$ -7.40	$d^4 \rightarrow d^3 + (d)$ -13.30

[a] See also ref 9, Table V.   [b] Reference 12.   [c] Reference 10.

where N is a normalizing factor. The orbital exponents, ζ, for C, N, and O are those of Clementi, and Raimondi.[15] As pointed out previously,[9,15,16] such single exponential functions are rather poor representations of the correct atomic Hartree–Fock orbitals and are particularly bad for calculating the metal–nitrogen overlap integrals on which the extended Hückel calculations so critically depend. As in our previous calculations,[9] we have used for the 3d and for the 4s orbitals that value of ζ (see Table II) which best re-

TABLE II
BASIS SET EXPONENTIALS[a]

	s	p	d
O^b	2.2458	2.2266	
V^c	1.3000	1.3000	2.3300

[a] See also ref 9, Table 3.   [b] Reference 15.   [c] Reference 10.

produces the overlap between the metal Hartree–Fock orbitals of Watson[17] and nitrogen single exponential functions; the metal–nitrogen overlap integrals are reproduced within 5%. For the reasons given before, the ζ value for 4p is taken as identical with that of 4s. Unfortunately this method overestimates by some 20% the overlap between a Hartree–Fock $V(3d_{z^2})$ and $O(2p_z)$, although all other V–O overlaps are reproduced to within 4%. This can lead to an overestimation of the $3d_{z^2} - 3d_{xy}$ ligand field splitting in these calculations, a point which must be kept in mind in the later discussion. As in previous work,[9] we have used a single value of $\kappa = 1.89$ such that the calculated average of the two lowest lying porphyrin transitions, $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ and $a_{1u}(\pi) \rightarrow e_g^*(\pi)$, obtained by subtracting orbital energies equals the average of the observed transition energies of the two lowest energy $\pi \rightarrow \pi^*$ transitions, both singlets and triplets. This procedure is recommended by a correct treatment of two-electron terms in a configuration interaction refinement which indicates that these two lowest transitions are intimately mixed.[18] The same κ value has been used for all our porphyrin calculations to date.

By averaging the singlets and triplets in our adjustment of κ we wish to associate calculated orbital energy gaps with transitions from the ground state to an average of the terms arising from the excited configuration. With this association we have a reasonable scheme for estimating other transitions. Thus ligand field d → d transitions in a $(d)^1$ system are estimated by simple orbital energy differences, as each excited electronic configuration gives rise to but one doublet.

The locations of charge-transfer transitions are expected to be an interesting prediction of these calculations. Metal-to-porphin charge-transfer excitations, again doublet → doublet, will be estimated by orbital energy gaps. Porphin-to-metal charge transfers, however, may generate two doublets and a quartet for each excited configuration. As the corresponding transition energies will differ by exchange terms between ligand field orbitals, not always small, the calculated orbital energy gaps should be corrected to give meaningful estimates of transition energies for each of the spin states.

A planar projection of the "average" tetraphenylporphyrin coordinates of Hoard, Hamor, and Hamor[19] is used, with radial displacements of the chelating porphyrin nitrogen atoms to maintain a constant V–N bond length of 2.12 A for all geometries with V out of the porphin plane. This bond length is suggested by a comparison of covalent radii with known metal nitrogen bond lengths in other metalloporphyrins.[20] For those cases in which we assume the V is in the plane of the porphin the V–N bond is set at 2.06 A. It is difficult to conceive of a greater porphin distortion since the free base, with H_2 in the center, shows a center-to-nitrogen distance of only 2.054 A.[19,21] The V–O bond length is taken as 1.59 A from an X-ray study of vanadyl bisacetylacetonate.[22] The resulting coordinates are given in Table III. The V–O bond is assumed along the z axis, perpendicular to the porphin plane, as shown in Figure 1. The only remaining question is the actual location of the vana-

(15) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
(16) E. Clementi, *ibid.*, **41**, 303 (1964).
(17) R. E. Watson, *Phys. Rev.*, **119**, 1934 (1960).
(18) Paper III: C. Weiss, M. Gouterman, and H. Kobayashi, *J. Mol. Spectry.*, **16**, 415 (1965).
(19) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Am. Chem. Soc.*, **85**, 2334 (1963).
(20) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).
(21) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, **87**, 2305 (1965).
(22) P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965).

TABLE III

COORDINATES OF V AND VO PORPHIN (x, y, z) IN ANGSTROM UNITS[a]

All Cases

H(1)	(1.3250, 5.0840, 0.0000)	C(5)	(2.4440, 2.4440, 0.0000)
C(2)	(0.6810, 4.2170, 0.0000)	C(6)	(2.8393, 1.0980, 0.0000)
C(3)	(1.0980, 2.8393, 0.0000)	C(7)	(4.2170, 0.6810, 0.0000)
H(4)	(3.2080, 3.2080, 0.0000)	H(8)	(5.0840, 1.3250, 0.0000)

Case I		Case II	
N(9)	(2.0600, 0.0000, 0.0000)	N(9)	(2.0600, 0.0000, 0.0000)
N(10)	(0.0000, 2.0600, 0.0000)	N(10)	(0.0000, 2.6000, 0.0000)
V(11)	(0.0000, 0.0000, 0.0000)	V(11)	(0.0000, 0.0000, 0.4920)
O(12)	(0.0000, 0.0000, 1.5900)	O(12)	(0.0000, 0.0000, 2.0820)

Case III		Case IV	
N(9)	(1.9866, 0.0000, 0.0000)	N(9)	(2.0600, 0.0000, 0.0000)
N(10)	(0.0000, 1.9866, 0.0000)	N(10)	(0.0000, 2.0600, 0.0000)
V(11)	(0.0000, 0.0000, 0.7400)	V(11)	(0.0000, 0.0000, 0.0000)
O(12)	(0.0000, 0.0000, 2.3300)		

Case V	
N(9)	(2.0600, 0.0000, 0.0000)
N(10)	(0.0000, 2.0600, 0.0000)
V(11)	(0.0000, 0.0000, 0.4920)

[a] The geometry of the porphin moiety is taken from a planar projection of the X-ray coordinates of Hoard, Hamor, and Hamor, ref 19. Special attention was devoted to preserving bond lengths. The hydrogens are placed 1.08 A from the carbons.

dium nucleus with respect to the porphin plane, a question which appears partially answered by these calculations.

Results

(1) **Geometry.**—Initially the vanadium atom of VO was assumed to be in the porphin plane (case I). A calculation using this geometry led to a heavy mixing of
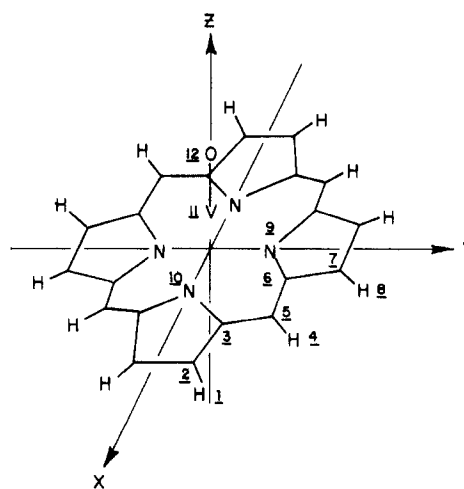

Figure 1.—Labeling of vanadyl porphin.

this calculation, which predicts quite an unusual visible and near-ultraviolet spectrum (see Figure 2), cannot be correct. Accordingly, calculations were performed with the VO group raised to two positions above the porphin plane: one 0.492 A above the plane (case II), suggested by the X-ray work of Hoard, Hamor, Hamor, and Caughey on ferric porphyrins,[27] and one 0.74 A above the plane (case III), suggested by the geometry of vanadyl bisacetylacetonate.[22] The third geometry reduces the $V(3d_\pi)$ mixing to about that found in other metalloporphyrin calculations (Table IV). We infer that case III may be nearest to the truth and choose to examine it most closely.

(2) **Ligand Field.**—Of primary interest is the re-

TABLE IV

PRINCIPAL LIGAND FIELD ORBITAL COEFFICIENTS[a]

Case	$3d_{x^2-y^2}$	$b_{1g}(d_{x^2-y^2})$ N(2s)	N(2p$_\sigma$)	N(2p$_\pi$)	$3d_{z^2}$	4s	$a_{1g}(d_{z^2})$[b] 4p$_z$	O(2p$_z$)	N(2p$_\pi$)
I	0.902	−0.127	0.364	0.000	0.749	0.203	−0.499	0.493	0.130
II	0.819	−0.110	0.321	0.075	0.813	0.005	−0.401	0.507	0.143
III	0.786	−0.114	0.296	0.072	0.824	−0.090	−0.349	0.508	0.156
IV	0.911	−0.125	0.359	0.000	0.911	0.000	0.000	...	...
V	0.819	−0.106	0.310	0.090	0.941	0.233	0.079	...	0.088

Case	$3d_{xz}$	$e_{gx}(d_\pi)$[c] O(2p$_x$)	N(2p$_\sigma$)	D(2p$_\pi$)	$b_{2g}(d_{xy})$ $3d_{xy}$	$e^*_{gx}(\pi)$[c] $3d_{xz}$
I	0.640 (0.359)	−0.341	−0.051	−0.266	0.987	0.612 (0.344)
II	0.745 (0.497)	−0.445	−0.121	−0.211	0.991	0.472 (0.204)
III	0.834 (0.615)	−0.514	−0.153	−0.155	0.991	0.301 (0.083)
IV	0.897 (0.800)	...	0.000	−0.008	0.989	0.375 (0.128)
V	0.909 (0.821)	...	−0.089	0.018	0.993	0.348 (0.112)

[a] Only the principal coefficients are given. The phases of the AO's are taken with all atomic coordinate axes parallel to the molecular axes of Figure 2. The nitrogen atom examined is N(10), Figure 1.   [b] The $a_{1g}(d_{z^2})$ orbital demonstrates one of the most striking breakdowns of the D_{4h} labeling scheme; see text.   [c] Numbers in parentheses are orbital populations.

$V(3d_\pi)$ with the empty porphin $e_g^*(\pi)$ responsible for the characteristic $\pi \rightarrow \pi^*$ spectra.[23-25] Such strong mixing is unique among all the metalloporphyrin calculations which we have performed. Judging from the apparently normal π spectra of vanadyl porphyrins,[26]

(23) The symmetry of VO porphin is probably C$_{4v}$, but it will prove more convenient to use D$_{4h}$ labels for those orbitals with analogs in D$_{4h}$ compounds.

(24) Paper I: M. Gouterman, *J. Mol. Spectry.*, **6**, 138 (1961).

(25) Paper II: M. Gouterman, G. Wagniere, and L. C. Snyder, *ibid.*, **11**, 108 (1963).

sulting ligand field given in Figure 2, which shows the MO energies for the top filled and lowest empty orbitals, and Table IV, which gives the coefficients for orbitals largely V(3d) in character as well as for the lowest empty porphin orbital $e_g^*(\pi)$. The highest occupied orbital is $b_{2g}(d_{xy})$, which is singly occupied and is rela-

(26) See, for example, W. S. Caughey, R. M. Deal, C. Weiss, and M. Gouterman, *ibid.*, **16**, 451 (1965).

(27) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).
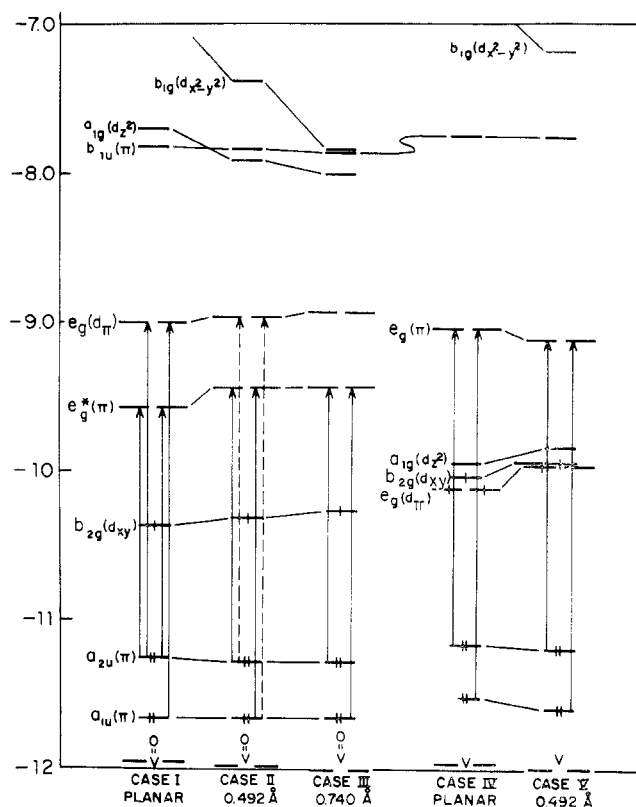
Figure 2.—Calculated energies for the top filled and lowest empty orbitals of vanadyl and vanadium porphyrins in different geometries.

tively pure $V(3d_{xy})$, in agreement with deductions from epr studies.[5,6] Above this in energy comes the empty porphin $e_g*(\pi)$ and then $e_g(d_\pi)$, which, in case III, is only about 60% $V(3d_\pi)$ in character and is strongly VO antibonding. At rather higher energies come a_{1g} (d_{z^2}) and $b_{1g}(d_{x^2-y^2})$; both are highly delocalized and the energy of the latter depends strongly on the geometry.

The calculation predicts the following d → d transitions: $^2B_{2g} \rightarrow {}^2E_g$ at about 11,000 cm^{-1}[11] (case III), $^2B_{2g} \rightarrow {}^2A_{1g}$ at about 18,300 cm^{-1} (case III), and $^2B_{2g} \rightarrow {}^2B_{1g}$ between 33,200 cm^{-1} (case I) and 19,500 cm^{-1} (case III). Only this last is strongly geometry sensitive. The transition $^2B_{2g} \rightarrow {}^2E_g$ is estimated to lie between 11,000 and 13,000 cm^{-1} in other vanadyl compounds.[11,28] The $^2B_{2g} \rightarrow {}^2B_{1g}$ is believed to be at 16,000–18,000 cm^{-1} in similar vanadyl compounds[11,28] and was assumed to be at 20,000 cm^{-1} for the epr analysis of vanadyl tetraphenylporphyrin.[6] These results tend to confirm the geometry of case III.

A rather interesting discrepancy arises from Ballhausen and Gray's[11] prediction that the forbidden $^2B_{2g} \rightarrow {}^2A_{1g}$ transition lies at ~30,000 cm^{-1}, or ~10,000 cm^{-1} above the $^2B_{2g} \rightarrow {}^2B_{1g}$ transition. This order of ligand field orbitals is in contradiction to all three of our VO calculations. To test whether a sixth coordinating ligand would affect these gaps, we recalculated case III with a water molecule added 2.0 A below the porphin plane; in this situation the calculated energy

(28) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

of the $^2B_{2g} \rightarrow {}^2A_{1g}$ rises only 600 cm^{-1}, coming into near degeneracy with the $^2B_{2g} \rightarrow {}^2B_{1g}$. It is also to be noted here, in considering transitions to the $a_{1g}(d_{z^2})$ orbital, that these transitions are probably upper limits. As discussed above, we have overestimated the $b_{2g}(d_{xy})-a_{1g}(d_{z^2})$ orbital energy split somewhat by overestimating the overlap of vanadium $3d_{z^2}$ and oxygen $2p_z$. This consideration firmly plants our b_{1g} $(d_{x^2-y^2})$ orbital above the $a_{1g}(d_{z^2})$ in these porphin calculations.

This apparent contradiction between the two calculations can be best explained by an examination of the nature of the atoms chelating to the vanadyl group. In porphins these atoms are nitrogens; for Ballhausen and Gray's considerations they are oxygens. Since the oxygen of the vanadyl group is most important in determining the positions of the $e_g(d_\pi)$ and $a_{1g}(d_{z^2})$ orbitals relative to the $b_{2g}(d_{xy})$, these orbitals should remain much the same in both series of complexes as long as the VO bond length remains reasonably constant.[22] However, the position of the $b_{1g}(d_{x^2-y^2})$ ligand field orbital is highly dependent on the nature of the four additional chelating atoms. Since ligands which contain oxygen as the chelating atom are seldom as strong a perturbation on the metal orbitals as those which contain nitrogen,[29] it is not surprising that the $b_{1g}(d_{x^2-y^2})$ orbital is considerably lowered upon going from vanadyl porphins to vanadyl complexes in which all the chelating atoms are oxygen.

Careful paramagnetic resonance investigations have been performed on vanadyl tetraphenylporphyrin[5,6] and on vanadyl etioporphyrins.[3,4] These investigations have yielded the g values presented in Table V.

Compound	$g \perp$	$g \parallel$	$\langle g \rangle$	Ref
Etioporphyrin I castor oil	1.987	1.948	1.974	3
Etioporphyrin II petroleum oil	1.988	1.947	1.974	4
Tetraphenylporphyrin CHCl$_3$	1.985	1.966	1.979	6
Tetraphenylporphyrin CS$_2$	1.990	1.965	1.982	6
Tetraphenylporphyrin H$_2$TPP	1.985	1.966	1.979	6
Tetraphenylporphyrin THF	1.987	1.962	1.979	5
Av	1.987	1.960	1.978	
Calcd	1.985	1.970	1.980	

As the calculation of g values is sensitive to ligand field transition energies, additional verification of the ligand field picture provided by these calculation can be obtained. In the MO description of (d)^1 complexes the formulas for the g values become[5,11]

$$g_\perp = 2 - 2\sum_{^2E_g} \frac{(c(b_{2g})c(e_g))^2\xi}{\Delta E(^2B_{2g} \longrightarrow {}^2E_g)}$$

(29) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, especially Chapter 7.

<div align="center">TABLE VI</div>
<div align="center">ELECTRONIC TRANSITIONS (CM^{-1})</div>

-Transition	Prediction	Polarization D$_{4h}$	Polarization C$_{4v}$	Comments
Normal Porphyrin $\pi \rightarrow \pi^*$ Spectrum				
$^1A_{1g}$ $\begin{vmatrix} a_{2u}(\pi) \rightarrow e_g^*(\pi) \\ a_{1u}(\pi) \rightarrow e_g^*(\pi) \end{vmatrix} \begin{matrix} ^1E_u \\ ^3E_u \end{matrix}$	Av 16,940	x, y $\cdots$	x, y $\cdots$	^3E_u 14,095[a] $^3E_u \sim$15,000, est from ref 18
		x, y	x, y	$^1Q_{0 \rightarrow 0}$ 16,800, $^1Q_{0 \rightarrow 1}$ 18,180[b]
^1E_u				
^3E_u		$\cdots$	$\cdots$	$^1B_{0 \rightarrow 0}$ 23,260, $^1B_{0 \rightarrow 1}$ 24,540[b] Av 17,290
$^1A_{1g}$ $\begin{vmatrix} b_{2u}(\pi) \rightarrow e_g^*(\pi) \\ a'_{2u}(\pi) \rightarrow e_g^*(\pi) \end{vmatrix} \begin{vmatrix} ^1E_u, \, ^3E_u \\ ^1E_u, \, ^3E_u \end{vmatrix}$	Av 24,040	x, y x, y	x, y x, y	^1N 31,250 ^1L >40,000, ref 26 for VO deuteroporphyrin
d $\rightarrow$ d Ligand Field Transitions				
$^2B_{2g}$ $b_{2g}(d_{xy}) \rightarrow e_g(d_\pi)$ ^2E_g	10,850	f	x, y	$\sim$11,000, est from ref 29 <19,500 from esr, ref 6
$^2B_{2g}$ $b_{2g}(d_{xy}) \rightarrow a_{1g}(d_{z^2})$ $^2A_{1g}$	18,330	f	f	See text
$^2B_{2g}$ $b_{2g}(d_{xy}) \rightarrow b_{1g}(d_{x^2-y^2})$ $^2B_{1g}$	19,490	f	f	16,000–18,000, ref 29 $\sim$20,000 from esr, ref 6
VO Transitions				
$^2B_2$ $e(Op_\pi) \rightarrow e_g(d_\pi)$ $\begin{vmatrix} ^4A_1, \, ^4A_2, \, ^4B_1, \, ^4B_2 \\ 2^2A_1, 2^2A_2, 2^2B_1, 2^2B_2 \end{vmatrix}$	$^2B_2$ 40,000–45,000	$\cdots$	z	$\sim$42,000, ref 11
$^2B_2$ $a_1(Op_z) \rightarrow a_{1g}(d_{z^2})$ $^2B_2, \, ^2B_2, \, ^4B_2$	$^2B_2$ 48,000–53,000	$\cdots$	z	$\sim$50,000, ref 11
Charge-Transfer Transitions				
$^2B_{2g}$ $a_{1u}(\pi) \rightarrow b_{2g}(d_{xy})$ $^2A_{1u}$	11,210	f	f	
$^2B_{2g}$ $b_{2g}(d_{xy}) \rightarrow b_{1u}(\pi)$ $^2B_{1u}$	19,520	z	z	
$^2B_{2g}$ $a_{2u}(\pi) \rightarrow e_g(d_\pi)$ $^4E_u, \, ^2E_u, \, ^2E_u'$	Av 19,024	x, y	x, y	*Predicted* ^2E_u 16,500, $^2E_u'$ 24,070
$^2B_{2g}$ $a_{1u}(\pi) \rightarrow e_g(d_\pi)$ $^4E_u, \, ^2E_u, \, ^2E_u'$	Av 22,064	x, y	x, y	*Predicted* ^2E_u 19,540, $^2E_u'$ 27,110
$^2B_{2g}$ $b_{2u}(\pi) \rightarrow e_g(d_\pi)$ $^4E_u, \, ^2E_u, \, ^2E_u'$	Av 27,683	x, y	x, y	*Predicted* ^2E_u 25,170, $^2E_u'$ 32,730
$^2B_{2g}$ $a_{2u}'(\pi) \rightarrow e_g(d_\pi)$ $^4E_u, \, ^2E_u, \, ^2E_u'$	Av 28,408	x, y	x, y	*Predicted* ^2E_u 25,890, $^2E_u'$ 33,450
$^2B_{2g}$ $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ $^4B_{1u}, \, ^2B_{1u}, \, ^2B_{1u}$	Av 26,500	z	z	
$^2B_{2g}$ $a_{2u}'(\pi) \rightarrow a_{1g}(d_{z^2})$ $^4B_{1u}, \, ^2B_{1u}, \, ^2B_{1u}$	Av 35,890	z	z	
$^2B_{2g}$ $b_{2u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$ $^4B_{1u}, \, ^2B_{1u}, \, ^2B_{1u}$	Av $\sim$44,380	z	z	

[a] J. B. Allison and R. S. Becker, *J. Phys. Chem.*, **67**, 2669 (1963), for vanadyl mesoporphyrin IX.   [b] Courtesy of D. Eastwood, for vanadyl etioporphyrin I.

$$g_{||} = 2 - 2\sum_{^2B_{1g}} \frac{(c(b_{2g})c(b_{1g}))^2 4\xi}{\Delta E(^2B_{2g} \longrightarrow {}^2B_{1g})}$$

if we ignore all but the single-centered vanadium terms. The spin–orbit coupling constant ξ is estimated as 115 cm^{-1} for $V^{+0.5}$ (d^x) from a linear extrapolation between the neutral value and that of the cation.[30] To obtain a first-order estimate we consider only the single principal ligand field transition indicated in each sum. This is a good approximation only in case III, where the ligand field orbitals are most pure. For this case, $g_\perp = 1.985$, $g_{||} = 1.970$, and $\langle g \rangle = \frac{1}{3}(2g_\perp + g_{||}) = 1.980$, in fair agreement with experiment. The larger experimental fluctuation in the value of $g_{||}$ can be explained by small changes in the geometry of the vanadium atom affecting the $b_{2g}(d_{xy}) \rightarrow b_{1g}(d_{x^2-y^2})$ transition. A much more complete investigation of magnetic parameters using these calculations is in progress.[31]

(3) Electronic Spectrum.—The electronic spectrum predicted by this model is summarized in Table VI for the case III complex. In the porphin moiety, the calculated $\pi \rightarrow \pi^*$ transitions are from the ground-state singlet to the average of the excited singlet and triplet terms stemming from the same excited electronic configuration. The very local nature of the single $b_{2g}(d_{xy})$ electron calculated for this complex ensures the normal porphyrin electronic structure and justifies our isolation of the porphin π manifold from the paramagnetic perturbations of the metal. The four lowest lying $\pi \rightarrow \pi^*$ transitions are paired

$$a_{2u}(\pi) \longrightarrow e_g^*(\pi)$$
$$a_{1u}(\pi) \longrightarrow e_g^*(\pi)$$

and

$$b_{2u}(\pi) \longrightarrow e_g^*(\pi)$$
$$a_{2u}'(\pi) \longrightarrow e_g^*(\pi)$$

as the near degeneracies of these pure transitions have been shown to lead to heavy pairwise mixing of the corresponding excited states.[18] The first pair of transitions, leading to the normal visible and near-ultraviolet porphyrin spectrum, is calculated to average $\sim$17,000 cm^{-1}, compared to the 17,500-cm^{-1} average calculated for the series Mn(II)–Zn(II) and to an experimental estimate of $\sim$17,300 cm^{-1}.[32] Good results are expected here as the interaction parameter κ was chosen to fit this average transition. The higher

(32) The "average tetraphenylporphin" spectrum is obtained from the observed Q_{0-0} (visible) and B (ultraviolet) bands of vanadyl etioporphyrin I, assuming a reasonable shift for the tetraphenyl case, from the emission (phosphorescence) of vanadyl mesoporphyrin IX, assumed to give the lowest triplet, and from a second triplet calculated in ref 18 to lie $\sim$0.1 ev above the lowest triplet; see Table VIII.

(30) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).
(31) R. Ake, in preparation.

energy pair, stemming from the second two $\pi \rightarrow \pi^*$ transitions, has a calculated average of $\sim$24,000 cm^{-1}. The experimental average is not known owing to a lack of knowledge of the corresponding porphyrin triplets.

An examination is made in Table VII of the MO's most responsible for the characteristic visible and ultraviolet spectrum of porphin. This table clearly demonstrates that reduction from D_{4h} symmetry to C_{4v} does not much alter the porphin π character of these orbitals. This is especially noted for our case III geometry, in which the $e_g^*(\pi)$ MO is localized mainly on the porphin basis orbitals of $2p_\pi$ symmetry (Table IV).

TABLE VII
TOTAL ELECTRONIC POPULATION IN π SYMMETRY AO's FOR IMPORTANT MO's

	$a_{1u}(\pi)$	$a_{2u}(\pi)$	$e_g^*(\pi)^a$	$O(2p_x)$	$e_g(d_\pi)^a$	$O(2p_x)$
Case I	1.00	0.99	0.82	0.17	0.91	0.09
Case II	1.00	0.99	0.89	0.10	0.82	0.15
Case III	1.00	0.98	0.95	0.05	0.76	0.20
Case IV	1.00	1.00	1.00	...	1.00	...
Case V	1.00	0.95	1.00	...	0.97	...

^{a} Includes all porphin $2p_z$ AO's and $V(3d_{xz})$.

where we have dropped exchange terms between porphin and metal orbitals. Considering the ligand field orbitals as pure metal orbitals of a +0.5 V atom, we can evaluate the exchange terms from atomic Slater–Condon factors extrapolated between the neutral and positive ion values. Using, for example, the factors obtained by Hinze and Jaffé[33] from their analysis of atomic spectra, $K(d_{xy}, d_{yz}) = K(d_{xy}, d_{xz}) = 3782$ cm^{-1}, $K(d_{xy}, d_{z^2}) = 4331$ cm^{-1}, and $K(d_{xy}, d_{x^2-y^2}) = 2135$ cm^{-1}, we obtain the predictions given in Table VI.[10]

In addition to the charge-transfer excitations, these calculations clearly indicate two allowed z-polarized transitions characteristic of the VO group. These are $e(Op_\pi) \rightarrow e_g(d_\pi)$ and $a_1(Op_z) \rightarrow a_{1g}(d_{z^2})$. (By e (Op_π) we refer to the π-bonding VO orbital whose major component is $O(2p_\pi)$; by $a_1(Op_z)$ we refer to the σ-bonding VO orbital whose major component is $O(2p_z)$. We use C_{4v} group labels as these orbitals have no D_{4h} analogs.) The first transition gives rise to four quartets and eight doublets; the second, to one quartet and two doublets. Estimates of the exchange integrals place the allowed doublet of the first transition between

TABLE VIII
METAL ELECTRONIC DISTRIBUTION^a

	4s	$4p_x = 4p_y$	$4p_z$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz} = 3d_{yz}$	$3d_{z^2}$	Total
Cases I, II, III	0.33	0.20	0.23	0.72	1.02	0.58	0.64	4.50
Cases IV, V	0.28	0.16	0.17	0.70	1.01	0.93	0.18	4.52

^{a} The largest deviation of an individual case from these average values was within ± 0.03.

Several low-lying charge-transfer bands are predicted for this complex, as demonstrated in Table VI. Assuming that orbital energy differences correspond to transition energies from the ground state to an average spin manifold of an excited configuration, we can estimate the energy of these charge-transfer states. Calculating the energy of each of the three spin states arising from a porphin to metal electronic excitation, we get for the two doublets (D,D') and the quartet (Q)

$$E^*(D) = W + (K_{ab}^2 + K_{ap}^2 + K_{bp}^2 - K_{ab}K_{ap} - K_{ab}K_{bp} - K_{ap}K_{bp})^{1/2}$$

$$E^*(D') = W - (K_{ab}^2 + K_{ap}^2 + K_{bp}^2 - K_{ab}K_{ap} - K_{ab}K_{bp} - K_{ap}K_{bp})^{1/2}$$

$$E^*(Q) = W - K_{ab} - K_{ap} - K_{bp}$$

in which W includes all the terms common to each spin state, K_{ij} is the exchange between i and j, and subscripts a, p, and b refer to the $b_{2g}(d_{xy})$ orbital, the porphin MO which has lost an electron, and the metal orbital which has gained one electron, respectively. Wishing to make the correspondence between calculated orbital energy gaps and an average transition we derive from

$$\bar{E}^* - E(\text{Grd}) = w_b - w_p$$

$$E^*(D) - E(\text{Grd}) = w_b - w_p + {}^4\!/_3 K_{ab}$$

$$E^*(D') - E(\text{Grd}) = w_b - w_p - {}^2\!/_3 K_{ab}$$

$$E^*(Q) - E(\text{Grd}) = w_b - w_p - {}^2\!/_3 K_{ab}$$

40,000 and 45,000 cm^{-1} and the second between 48,000 and 53,000 cm^{-1}. Both these transitions appear invariant to changes in the VO group relative to the porphin plane. The $\sim$8000 cm^{-1} difference between these two transitions makes them tempting candidates for the two bands seen in most vanadyl complexes at $\sim$42,000 and 50,000 cm^{-1}.[11,34]

We have in no way exhausted all the low-lying electronic transitions which are possible. In addition to the many charge-transfer possibilities, there are a number of porphin $\rightarrow$ porphin transitions which gain intensity as the molecular symmetry falls from D_{4h} to C_{4v}.

One thought underlies all these considerations and must be reemphasized. We have adjusted κ to fit the characteristic $\pi \rightarrow \pi^*$ spectrum of porphin. Other

(33) J. Hinze and H. H. Jaffé, *Can. J. Chem.*, **41**, 1315 (1963).

(34) The first transition is represented by a rather complex expression which reduces to

$$\Delta w - \frac{1}{6}[K_{arx} + K_{arx}*] + \frac{1}{3}[K_{rxry} - K_{rxry}*] + \frac{4}{3}K_{rxrx}* - \frac{3}{2}[(rxry^*|ryrx^*) - (rxry^*|rx^*ry)]$$

assuming $K_{arx} = K_{arx}*$; the second by

$$\Delta w + \frac{1}{3}[K_{ap} + K_{ap}* + K_{pp}*] \pm [K_{ap}^2 + K_{ap}*^2 + K_{pp}*^2 - K_{ap}K_{ap}* - K_{ap}K_{pp}* - K_{ap}K_{pp}*]$$

a is the $b_{2g}(d_{xy})$ orbital, rx $\approx$ N[$O(2p_x)$ + $\lambda V(3d_{xz})$], rx* $\approx$ N*[λ*$O(2p_x)$ − $V(3d_{xz})$], p $\approx$ N'[$O(2p_z)$ + $\lambda' V(3d_{z^2})$], and p* $\approx$ N'*[λ'*$O(2p_z)$ − $V(3d_{z^2})$]. In the second case the higher energy transition has most of the intensity.

transitions, notably the d → d and charge-transfer transitions, may or may not be well predicted. As no such transitions have been unambiguously identified in porphyrins, the present calculations are predictive and call for experimental testing.

(4) **Electronic Population.**—The electronic population, although not a direct measurable, is of considerable interest.

The neutral vanadium atom has a $3d^3 4s^2$ ground state. In vanadyl complexes the V atom is formally assigned a $+4$ charge and generally assumed to be $3d^1$; the vanadyl group as an entity is considered a dication. Many of the features of this classical analysis are maintained by these MO calculations; others are clearly not. The actual removal of four electrons from netural V requires some 99 v, clearly impractical.[35]

Table VIII summarizes how this model assigns electrons to the valance orbitals of the vanadyl group. The net charge on the vanadium atom is $+0.5$; the suggested configuration, $s^{0.35}p^{0.65}d^{3.50}$. The net charge on VO is $+0.18$. These results are relatively insensitive to the VO geometry. The net charge on V, when compared with the net metal charges of the other metal porphin calculations of ref 9, again falls in the order of chemical half-cell potentials as suggested in that paper: Mg > V > Zn > Co > Ni > Cu.

An analysis of the π-electron and total electron population about each atom is made in Table IX.

TABLE IX
ELECTRONIC POPULATION[a]

Atom	Cases, I, II, III π electron	Cases, I, II, III Total electron	Cases IV, V π electron	Cases IV, V Total electron
H(1) = H(8)	...	0.94	...	0.95
C(2) = C(7)	1.00	4.05	1.02	4.06
C(3) = C(6)	1.05	3.98	1.06	4.00
H(4)	...	0.92	...	0.93
C(5)	0.96	4.03	0.96	4.02
N(9) = N(10)	1.37	5.17	1.35	5.17
V	1.40[b]	4.50	2.03[b]	4.52
O	...	6.30	...	...

[a] The largest deviation of an individual case from these average values was within ±0.015. [b] Includes both $3d_\pi$ and $4p_\pi$.

The electronic distribution appears to be relatively insensitive to the details of the vanadyl bonding. The isolated porphin dianion should have 26 electrons in π-symmetry orbitals and has thus only lost 0.25–0.32 electron to vanadyl, or to the porphin σ system, upon reduction to C_{4v} symmetry.

(5) **Bonding.**—In vanadyl porphin the VO bond consists of MO's of $a_1(\sigma)$ symmetry and $e(\pi)$ symmetry. If we assume that the covalent strength of a bond is proportional to the electronic population in the region between two bonded atoms r and s, the so-called overlap population[14]

$$\rho_{rs} = 2\sum_j n(j) c_{jr} c_{js} S_{rs}$$

(35) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Circular 467, Vol. I, Government Printing Office, Washington, D. C., 1948–1952.
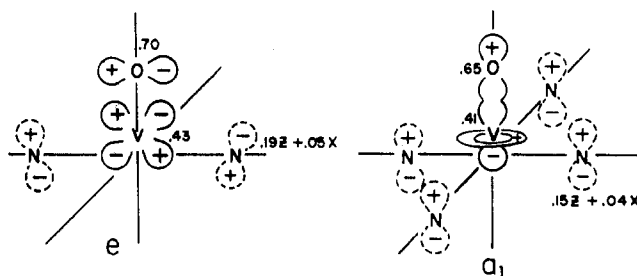

Figure 3.—VO bonding MO's.

where the sum is over all occupied MO's j with occupancy $n(j)$, then we conclude that the 4s,4p orbitals of V contribute as much as 27% of the total covalent bond stability. The inference that π bonding is important in VO is borne out by these calculations.[28,36] Fully 47% of the total overlap population is due to π bonding. It is interesting to note that, although many MO's contribute to the total bonding, one MO of a_1 symmetry and a pair of e symmetry, pictured in Figure 3, account for over 50% of the total overlap population.

The bond orders presented in Table X are Mulliken's normalized bond orders[14]

$$p_{rs} = (1 + S_{rs}) \sum_j n(j) c_{jr} c_{js}$$

which gives a π-bond order of 1.0 for ethylene, etc. Noteworthy is the large value of the bond order for each of the $V(3d_\pi)$–$O(2p_\pi)$ bonds.

Each of the V–N bonds have considerably less overlap population than the V–O bond, 0.411 as compared to 1.100. In view of the bond lengths this is not a very surprising result. Table X gives a breakdown of the overlap population for the V–N bond. Interactions involving the 4s and 4p metal orbitals account for 68% of this overlap population.

TABLE X
BONDING
(A) V–O Bond

Type	Interaction	Case III overlap population	Case III partial bond order
σ	$V(3d_{z^2})$–$O(2p_z)$	0.248	0.464
π	$V(3d_\pi)$–$O(2p_\pi)$	0.198 each	0.797 each
σ	$V(3d_{z^2})$–$O(2s)$	0.048	0.126
σ	$V(4p_z)$–$O(2s)$	0.172	0.264
σ	$V(4s)$–$O(2s)$	0.116	0.236
π	$V(4p_\pi)$–$O(2p_\pi)$	0.060 each	0.201 each
	Total	1.100	

(B) V–N Bond

Type	Interaction	Overlap population Case III	Overlap population Case V
σ,π	$V(3d)$–$N(2s,2p)$	0.132	0.132
σ,π	$V(4s,4p)$–$N(2s,2p)$	0.281	0.284
	Total	0.413	0.416

The oxygen of the vanadyl group has essentially no overlap population with the nitrogens of the porphin owing to the small atomic orbital overlaps. All told, it amounts to 0.001 for each N–O bond.

(36) J. G. Erdman, V. G. Ramsey, N. W. Kalenda, and W. E. Hanson, *J. Am. Chem. Soc.*, **78**, 5844 (1956).

(6) **Vanadium Porphin.**—In an attempt to understand the apparent chemical instability of V porphyrins, systems with V in the plane of the porphin (case IV) and 0.492 A above the plane (case V) were investigated. The details of these calculations are presented in Figure 2 and the various tables.

As shown in Figure 2 the calculations ascribe very different ligand field splittings to V and VO. In the former, the orbitals $e_g(d_\pi)$, $b_{2g}(d_{xy})$, and $a_{1g}(d_{z^2})$ lie within 1500 cm^{-1} of each other in both cases IV and V and are fairly pure metal orbitals; the $b_{1g}(d_{x^2-y^2})$ behaves similarly to that of the VO case and varies from 80 to 65% V($3d_{z^2-y^2}$) in the two geometries.

Since vanadium porphin is not known, we have, of course, no criterion for choosing the best geometry as was present in the case of the vanadyl complex. It seems, however, unlikely that the vanadium atom should be in the porphin plane in view of the relatively large effective radius of V and the steric contraints previously considered for the porphin cavity. We will thus more closely examine the calculation with V 0.492 A above the porphin plane (case V).

Of interest is the electronic population about the vanadium atom. It is seen from Table IX that the net charge about the vanadium atom in vanadium porphin and in vanadyl porphin, formally quite different, is essentially the same for all five calculations, and, indeed, is the same for cases III and V.

The detailed charge distribution is only somewhat different for V and VO in porphin. A population analysis of the former species suggests an $s^{0.30}p^{0.45}d^{3.75}$ V($+0.5$) configuration, to be compared with $s^{0.35}p^{0.65}d^{3.50}$ V($+0.5$) for the latter species.

The average of the lowest lying $\pi \rightarrow \pi^*$ transition is predicted in case V to lie at 18,000 cm^{-1}, or blue shifted 1000 cm^{-1} from the 17,000 cm^{-1} value predicted in case III. Both these values bracket the all-porphin average of 17,500 cm^{-1} and again tend to verify the conclusion reached in ref 9; no simple metal or ligand that leaves the porphin moiety intact shifts this transition average more than 1000 cm^{-1} from the all-porphin average, in agreement with experience.[24]

We can discover no reason why V porphyrins should not be stable. Table X shows that the covalent V–N (porphin) bond strength, as measured by the overlap population, is, strangely enough, the same, although individual contributions may vary.[37] Since the net charge on the vanadium atom in both cases is the same, and the net charge on the neighboring nitrogens varies only slightly, ionic contributions to the bond strength should be nearly the same. As previously discussed, the O of the very strong VO bond appears not to bond to any appreciable extent with the nitrogens of the

porphin. The orbital energy scheme of vanadium porphin in Figure 2 seems reasonable.

We can, however, suggest many reasons why this compound should be labile, especially in the presence of O_2, readily forming the strong V–O bond.

In this case, for example, we align the O_2 molecule perpendicular to the porphin plane and 2.0 A above the V atom. The electronic structure of the O_2 ground state is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^2$. The half-filled $1\pi_g$ diatomic orbitals mix slightly with the half-filled $e_g(d_\pi)$ orbitals of the V porphin and occur considerably lower in orbital energy. Having such low energy MO's only half-filled is not reasonable, and we can assume that at least one of the $e_g(d_\pi)$ electrons falls into the $1\pi_g$ orbital. This orbital is, of course, strongly O–O antibonding as well as V–O bonding, and we have a plausible "MO mechanism" for the formation of the VO bond.

Conclusions

Despite the many limitations of the extended Hückel model, which were detailed in paper IV,[9] it has proved very useful for the understanding of large molecules. The present paper applies this theory to V and VO porphin systems, and comparison of the calculations with the experimental spectra leads to the prediction that the vandyl group is located 0.5–0.8 A above the porphin plane. The ligand field picture deduced is in good agreement with information available from epr interpretations. A possible exception is the location of the $3d_{z^2}$ ligand field orbital, which is calculated by this model to lie below the $3d_{x^2-y^2}$ orbital, contrary to its order in the case of four chelating oxygens.

The calculated charge on the vanadium atom in both vanadium and vanadyl porphins is $+0.5$ even though formally these two species are quite different, that is, d^3 and d^1, respectively. This result is found to be independent of moderate geometry changes.

The strength of the VO bond has been examined, and it is found that the V($3d_\pi$)–O($2p_\pi$) interaction is important. Vanadyl oxygen to porphin nitrogen bonding is found to be negligible.

An examination of the calculations of V porphin showed no reason why this compound should be unstable, and we must infer that it could be made. Arguments are put forward, however, which would indicate that this compound would be very labile, especially in the presence of O_2.

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(37) We have simply added overlap populations as a measure of bonding. A more elaborate treatment would not seem justified at the present level of theoretical development.