Table III. Complexing Bond Lengths in a Sequence of Four-Coordinate Metallotetraphenylporphyrins[a]

	Metal ion				
	d^6 Fe	d^7 Co	d^8 Ni	d^9 Cu	d^5 Mn
M–N, Å	1.972 (4)	1.949 (3)	1.928 (3)	1.981 (7)	2.082–2.092
Spin state, *S*	1	$^1/_2$	0	$^1/_2$	$^5/_2$
Ref	*b*	*c*	*d*	*e*	*f*

[a] The number in parentheses is the estimated standard deviation for the bond distance. [b] Reference 12. [c] This work. [d] Reference 13. [e] Reference 14. [f] Reference 25.

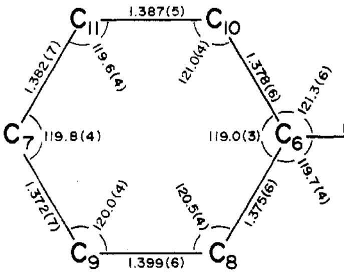

Figure 3. Diagram of a peripheral phenyl group displaying the numbering scheme used for the atoms and the values, with estimated standard deviations, of all bond parameters.

phyrin wherein the core was nearly planar would have Co–N bond distances of 1.97–1.98 Å.

The observed M(II)–N bond distances in a sequence of MTPP derivatives are given in Table III. The presence of an electron in the $3d_{x^2-y^2}$ orbital of the d^9 copper(II) atom and the high-spin d^5 manganese(II) atom is clearly correlated with the M–N bond lengths and, of course, the magnetic data. The absence of such an electron in the intermediate-spin iron(II) and the low-spin cobalt(II) and nickel(II) atoms also correlates with the M(II)–N bond distances. It should be pointed out that MnTPP is anomalous not only with respect to the very large difference in the M–N bond distances but also in porphyrin core conformation. The other members of the series listed in Table III have porphyrin cores ruffled in agreement with S_4–$\bar{4}$ symmetry; MnTPP has an expanded, nearly planar core.

The individually determined bond parameters of the peripheral phenyl group are given in Figure 3. The dihedral angle between the mean plane of the core and the phenyl ring is 80.0°. The C–C bonds of the phenyl ring that are foreshortened from the standard aromatic spacing are associated with the thermal motion of the rigid group; this phenomenom has been discussed previously.[25,26]

The packing relationships in crystalline CoTPP are quite similar to those found in the isomorphous crystals of H_2TPP; a complete description is given in Table VI of ref 22.

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Registry No. CoTPP, 14172-90-8.

Supplementary Material Available: Listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Use of Electron Spin Resonance Data to Assist in the Assignment of Vanadyl Optical Transitions

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In a review of oxovanadium(IV) chemistry Selbin[1] pointed out that more than ordering of optical assignments can fit a single set of ESR data. This is because there are two additional important variables in the appropriate equations.[2] They are the spin–orbit coupling constant ζ and the dipole parameter P. They have generally been considered as fixed parameters. However, it is known that they both are functions of the charge on the vanadium. Since the values of the molecular orbital coefficients are what determines the charge, it is possible to write a computer program which does an iterative charge self-consistent solution of the ESR equations, given the experimental ESR parameters and a set of optical assignments. Although this approach will not give a unique set of optical assignments for each compound, a comparison of the range of acceptable values for complexes of different covalent character should be useful in establishing the general behavior of the optical transitions.

Experimental Section

The experimental ESR values were related to the molecular orbital coefficients by[2]

$$g_{\|} = 2.0023 - \frac{8\zeta N_{\pi_2}{}^2 N_{\sigma_2}{}^2}{\Delta\pi_2 \rightarrow \sigma_2\ (\mathrm{I})}[1 - \frac{1}{2}(\lambda_{\pi_2}\lambda_{\sigma_2})T(n) - 3^{1/2}\lambda_{\sigma_2}S_{\mathbf{d},\sigma_2} - 2\lambda_{\pi_2}S_{\mathbf{d},\pi_2}] - \frac{8\zeta N_{\pi_2}{}^2(1 - N_{\sigma_2}{}^2)}{\Delta\pi_2 \rightarrow \sigma_2\ (\mathrm{II})} \quad (1)$$

Table I. Ranges of Values Which Resulted in Self-Consistent ESR Solutions[a]

Compd	Vanadium charge	$N_{\pi_2}^2$	$N_{\pi_1}^2$	$N_{\sigma_2}^2$	$\Delta E_{\pi_2 \to \pi_1}$[b]	$\Delta E_{\pi_2 \to \sigma_2}$[b]
$VO(CN)_5^{3-}$	0.72-1.94	0.80-1.01	0.61-1.08	0.44-1.00	5.5-14.0	6.5-30.0
	0.72-1.43	0.88-1.01	0.61-0.80	0.74-0.99	5.5-8.5	14.0-29.0
VO(porphyrin)	1.34-2.45	0.83-1.01	0.60-1.09	0.58-1.02	7.0-20.0	8.0-29.0
	1.34-1.68	0.95-1.01	0.60-0.80	0.89-1.02	7.0-12.0	21.0-29.0
VO(acac)en	1.58-2.58	0.85-1.01	0.66-1.09	0.68-1.03	7.0-16.0	10.5-27.5
	1.58-1.82	0.97-1.01	0.66-0.80	0.93-1.03	7.0-10.5	21.0-27.5
VOacac	1.53-2.54	0.85-1.01	0.71-1.08	0.57-1.01	7.0-15.5	7.5-20.5
	1.60-1.83	0.96-1.00	0.71-0.80	0.93-1.01	7.0-9.0	17.0-20.5
VOF_5^{3-}	1.76-2.72	0.86-1.01	0.72-1.08	0.78-1.03	6.5-12.0	9.5-20.0
	1.91-2.02	0.97-0.99	0.72-0.80	0.99-1.01	6.5-7.5	17.5-19.0

[a] The first row for each compound gives the total range of the values. The second row gives the range of values when $N_{\pi_1}^2$ is restricted to values less than 0.81. [b] In units of 1000 cm^{-1}.

$$g_\perp = 2.0023 - \frac{2\zeta N_{\pi_2}^2 N_{\pi_1}^2}{\Delta\pi_2 \to \pi_1\ (\mathrm{I})}[1 - (1/2)^{1/2}\lambda^e{}_{\pi_1}\lambda_{\pi_2} - 2S_{\mathrm{d},\pi_2}\lambda^e{}_{\pi_2} - (1/2)^{1/2}2S_{\mathrm{d},\pi_2}\lambda^e{}_{\pi_1} - S_{\mathrm{d},\pi_1}] - \frac{2\zeta N_{\pi_2}^2(1 - N_{\pi_1}^2)}{\Delta\pi_2 \to \pi_1\ (\mathrm{II})} \quad (2)$$

$$A_{\parallel} = -{}^4/_7 N_{\pi_2}^2 P + A + {}^2/_3 g_{\parallel} P - {}^5/_{21} g_\perp P - {}^6/_7 P \quad (3)$$

The molecular orbitals are of the form

$$\psi^*(xy) = N_{\pi_2}(\phi_{xy} - \lambda_{\pi_2}\phi_{\mathrm{ligand}}) \quad (4)$$

$$\psi^*(x^2 - y^2) = N_{\sigma_2}(\phi_{x^2-y^2} - \lambda_{\sigma_2}\phi_{\mathrm{ligand}}) \quad (5)$$

$$\psi^*(xz \text{ or } yz) = N_{\pi_1}(\phi_{xz\ \mathrm{or}\ yz} - \lambda^e{}_{\pi_1}\phi^e{}_{\mathrm{ligand}} - \lambda^a{}_{\pi_1}\phi^a{}_{\mathrm{ligand}}) \quad (6)$$

$T(n)$ is defined by Kivelson and Lee,[5] S_{d,π_2} is the metal d–ligand p_{π_2} atomic overlap integral, and $\lambda^e{}_{\pi_1}$ and $\lambda^a{}_{\pi_1}$ are the *xz*, *yz* molecular orbital coefficients for the equatorial and axial ligands, respectively. The spin–orbit coupling constant is positive if the transition is one where an unpaired electron goes from a half-filled orbital to an unoccupied orbital and is negative if the transition is from a filled orbital to a half-filled orbital. Transitions I and II are the d–d and the charge-transfer transitions, respectively.

The equation for the charge dependence of P (in units of cm^{-1}) that was used is

$$P = 8.57 \times 10^{-3} + 2.1385 \times 10^{-3} \times \text{charge} \quad (7)$$

The equation is based on the following values which were calculated by McGarvey:[3] V, 85.7 × 10^{-4} cm^{-1}; V^{2+}, 128 × 10^{-4} cm^{-1}; V^{3+}, 150 × 10^{-4} cm^{-1}; V^{4+}, 172 × 10^{-4} cm^{-1}. The equation for ζ is[4]

$$\zeta = 18\,200P - 56 \quad (8)$$

In the program the d–d transition energies were varied from 5000 to 30 000 cm^{-1} in steps of 500 and the charge-transfer transitions were varied from 20 000 to 50 000 cm^{-1} in steps of 10 000 by the use of four nested DO loops.[10] For each combination of the four optical transitions, the computer attempted an iterative self-consistent solution.

Discussion

The ranges of values which resulted in self-consistent solutions are given in Table I. Also included in Table I are the ranges which resulted in values for $N_{\pi_1}^2$ of 0.80 or less. $N_{\pi_1}^2$ reflects the π bonding in the vanadium–vanadyl oxygen bond. Hopefully, one can say that if there is general agreement on any aspect of bonding in vanadyl complexes, it is on the point that the V–O bond has considerable π-bond character.

The calculated charge behavior is consistent with the expected behavior. The largest (most positive) charge is found on the vanadium bonded to the electron-withdrawing fluorines and the lowest positive charge is found on the vanadium bonded to the covalent cyanides. As expected the $N_{\pi_2}^2$ values indicate that the in-plane π bonding is appreciably ionic. For VOF_5^{3-} one can obtain an independent estimate of $N_{\pi_2}^2$ (0.92) from the anisotropic fluorine hyperfine splitting data of Manoharan and Rogers.[6]

The $N_{\sigma_2}^2$ values obtained without the $N_{\pi_1}^2 \leq 0.80$ restriction cover such a wide range that very little information can be obtained from them. With the $N_{\pi_1}^2$ restriction all of the $N_{\sigma_2}^2$ ranges, except for $VO(CN)_5^{3-}$, indicate relatively ionic σ bonds. For $VO(CN)_5^{3-}$, the $N_{\sigma_2}^2$ range is from moderately covalent to ionic. Since the isotropic ^{13}C ESR hyperfine splitting, 11.3 G,[7] is of the same magnitude as the ^{13}C splittings reported[8,9] for $Cr(CN)_6^{3-}$ and $Cr(CN)_5NO^{3-}$, similar covalent σ-bond character is expected for the three.

Of particular interest are the predicted optical transition ranges. The ranges determined without the $N_{\pi_1}^2$ restriction are of limited usefulness due to the considerable overlap of the ranges of the two transitions. However, when the $N_{\pi_1}^2$ range is restricted, a clear separation of the two ranges occurs. Thus, support is given to those literature assignments which place the $\pi_2 \to \sigma_2$ transition above the $\pi_2 \to \pi_1$ transitions for complexes with similar ligands. The actual magnitudes of the predicted ranges are, of course, dependent upon the choice of numerical parameters in eq 7 and 8 and the approximations involved in eq 1–3. However, one would expect that the relative magnitudes are significant.

Registry No. $VO(CN)_5^{3-}$, 26062-62-4; VO(porphyrin), 15654-19-0; VO(acac)en, 60490-50-8; VOacac, 31447-14-0; VOF_5^{3-}, 22657-37-0.

Supplementary Material Available: A listing of the Fortran computer program that was used (4 pages). Ordering information is given on any current masthead page.

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