and E_a in branched polyethylene would be useful.

The enhancement of $J_e°$ remains entirely without explanation. Although Γ_2, like Γ_1, correlates satisfactorily with $\varphi^{5/6}(\varphi M/fM_c)$ for polyisoprene stars,[6] its concentration dependence in general is clearly more complicated.[30] The influence of deformation history on the flow properties of certain branched polymers is similarly unexplained. Are such effects associated with crystallizability, or do they reflect an extremely slow relaxation process merely related to viscosity enhancement, perhaps involving only the largest, most structurally complex molecules in a polydisperse system?

A detailed understanding of commercial branched polymers may remain beyond reach for some time. The most highly branched molecules in a polydisperse system appear in the high molecular weight tail of the distribution and are extremely difficult to detect and characterize by conventional dilute solution methods. Flow properties on the other hand, especially those associated with elastic response,[43] are most sensitive to these same molecules. On the other hand, the qualitative features of branched polymer behavior—increased η_0, increased $J_e°$, reduced macromolecular mobility, and increased shear rate dependence of viscosity—will probably appear even in the most complex systems.

I am grateful to Professor A. J. Kovacs and Dr. C. P. Thomas for permission to quote results prior to publication. This work was supported by the National Science Foundation (ENG75-15683).

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Trends in Metalloporphyrin Stereochemistry

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Metalloporphyrins are a class of tetrapyrrolic compounds derived from the nucleus of porphine, **1**. Metalloporphyrins are (usually) easily prepared by the substitution of the two central protons of the macrocycle with a metal ion. Various ring substituents of **1** lead to the commonly studied porphyrins: protoporphyrin IX, **2**; octaethylporphyrin, **3**; and tetraphenylporphyrin, **4**. These porphyrins will be abbreviated as H_2Proto IX, H_2OEP, and H_2TPP and their metal derivatives as MProto IX, MOEP, and MTPP.[1]

Initial interest in the stereochemistry of metalloporphyrins stems from the occurrence of these species and closely related substances in biological processes. Photosynthetic processes utilize chlorophyll or bacteriochlorophyll which are magnesium porphyrin derivatives related to protoporphyrin IX but which have a fifth isocyclic ring and one or two reduced pyrrole rings. Iron protoporphyrin IX or a closely related derivative serves as the prosthetic group in the several classes of heme proteins, including hemoglobin, myoglobin, catalase, peroxidase, and the cytochromes. The properties of the heme proteins have been studied by the variation of axial ligands (see General Considerations) and by the substitution of other metal ions for iron. Thus the study of metalloporphyrins other than the iron derivatives is of interest for the detailed understanding of the function of the heme proteins.

Moreover, the stereochemistry of metalloporphyrins is interesting in its own right. The principal theme of this Account is a detailing of structural trends observed by us and others for several groups of metalloporphyrin complexes. These trends are discussed in terms which we believe illuminate the primary structural principles of this interesting class of compounds.

General Considerations

The porphinato ligand, which loses the two pyrrolic protons on complexation of the metal ion, is a dianion. With very few exceptions, the porphinato dianion acts as a tetradentate ligand with metal ions. Thus the usual minimum coordination number of the metal ion in a metalloporphyrin is four. The extensive electronic delocalization which occurs in the porphinato ligand leads to a substantial planarity of the macrocycle and an essentially square-planar environment for the metal ion in the four-coordinate complexes. Coordination numbers greater than four result from the addition of other ligands, either neutral or anionic, and metalloporphyrins in which the metal ion has a coordination number of five, six, seven, or eight have been characterized. The five-coordinate complexes have a square-pyramidal geometry with the single axial ligand occupying the apex of the square pyramid. The two axial ligands of the six-coordinate metalloporphyrins are found on opposite sides of the porphinato plane, yielding complexes with tetragonal geometries. In principle, the two axial donor atoms could be placed on the same side of the porphinato plane, but such complexes have not been characterized.[2] The seven-

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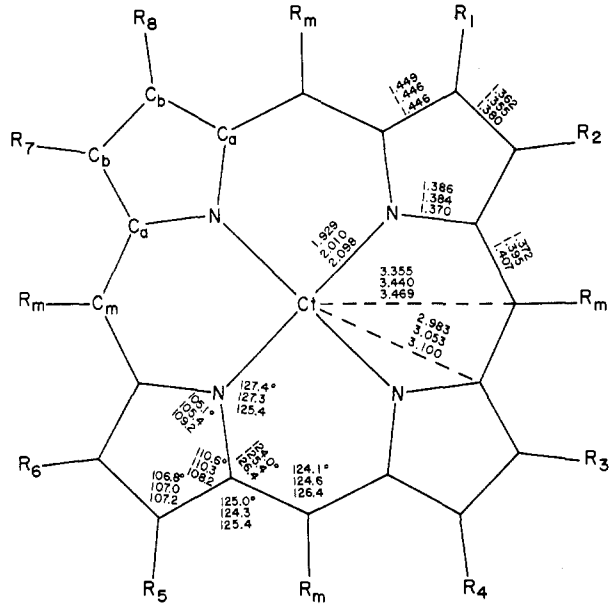
(1) The general form for the abbreviation of metalloporphyrin derivatives will be the metal symbol, followed by the abbreviation for the porphinato ligand, and then by the symbol(s) for the axial ligand(s). Thus chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) will be abbreviated as FeTPP(Cl). Ligand abbreviations: Pip, piperidine; 4-MePip, 4-methylpiperidine; Im, imidazole; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; Py, pyridine.



1 $R_1 \cdots R_8$, $R_m = -H$

2 $R_1, R_3, R_5, R_8 = -CH_3$, $R_2, R_4 = -CH=CH_2$, $R_6, R_7 = -CH_2CH_2CO_2H$, $R_m = -H$

3 $R_1 \cdots R_8 = -CH_2CH_3$, $R_m = -H$

4 $R_1 \cdots R_8 = -H$, $R_m = -C_6H_5$

Figure 1. A formal diagram of the porphinato skeleton of a metalloporphyrin. The metal is centered at Ct. Values of principal radii (Å), bond lengths (Å), and bond angles are entered. The data, ordered from top to bottom, are from the tetragonal crystal form of NiOEP,[4] a reference porphyrin of least strain,[5] and $SnTPP(Cl)_2$.[6] This multipurpose diagram also illustrates common peripheral substituents of the porphine nucleus, which has two hydrogen atoms bonded to opposite pyrrole nitrogen atoms.

and eight-coordinate derivatives, however, do have three or four axial donor groups bonded to the metal ion on the same side of the porphinato plane.

For coordination complexes, a stereochemical parameter of prime interest is the metal–ligand bond length. The $M-N_p$[3] bond lengths in metalloporphyrins are restricted by the constraints of the macrocyclic ring, which limits the radial expansion or contraction of the core. However, a relatively large range of $M-N_p$ bond distances are possible, with observed $M-N_p$ bond lengths varying from 1.928 to 2.098 Å. In addition to the radial expansion or contraction, the porphinato core has been observed to undergo substantial deformations normal to the mean plane. Thus the term "quasi-rigid" has been used to emphasize the fact that the porphinato core possesses some flexibility and variability in size. A convenient descriptor of the size of the porphinato ligand is the "radius of the central hole" or $Ct \cdots N_p$ distance where Ct denotes the center of the ring.

It is obvious that structural changes in the porphinato core must occur with variations in the size of the central hole. Figure 1 illustrates the structural parameters for three cores with differing $Ct \cdots N_p$ distances; each carries the unique parameters for a structure averaged in accord with effective D_{4h} symmetry. Examination of Figure 1 shows that there is no single "best" set of values appropriate for the bond lengths and angles of the core of an arbitrarily chosen metalloporphyrin. Note that averaging the chemically equivalent bond parameters in agreement with D_{4h} symmetry represents a procedure that allows for minor variation in bond distances or angles resulting from packing constraints or the like; the averaged result still reflects the objective significance of the experimental data. It should be further noted that, within the accuracy of the experimental structural results, there are, at most, small differences in structural parameters resulting from differing substituents on the periphery of the porphine core.

Four-Coordinate Metalloporphyrins

With no axial ligands, the four-coordinate metalloporphyrins represent the simplest series of derivatives. Within the first transition series, all divalent members from chromium(II) to zinc(II) have been prepared and structurally characterized.

The structures of the several nickel(II) derivatives illustrate important stereochemical features of metalloporphyrins. The observed $Ni-N_p$ bond distances range from 1.928 Å to 1.960 Å.[4,7] Although these distances represent the shortest $M-N_p$ distances observed for metalloporphyrins, they are substantially longer than the ~1.85 Å Ni–N bond distance usually found in square-planar complexes.[8] Thus the macrocyclic constraints of the porphinato core lead to substantially stretched $Ni-N_p$ bond lengths. It might be expected that a disruption of the π delocalization within the porphinato macrocycle would lead to greater flexibility and shorter $Ni-N_p$ distances for the nickel(II) complexes. This has been observed for two different systems, porphodimethenes[9a] ($Ni-N_p$ = 1.908 (9) Å) and homoporphyrins ($Ni-N_p$ = 1.905 Å[9b] and 1.880 (6) Å[9c]). The respective authors[9a,c] have also discussed the correlation of the observed bond parameters of the core with limiting Kekulé formulas.

The differing $Ni-N_p$ distances in the nickel(II) porphyrins correlate well with the conformation of the core. The triclinic modification of NiOEP[7c] has a planar conformation and $Ni-N_p$ = 1.958 (2) Å; the tetragonal crystalline modification of NiOEP[4] has an S_4 ruffled conformation[10] and $Ni-N_p$ = 1.929 (3) Å. Hoard[11] has

(2) The recently characterized $TiOEP(O_2)$ which has a symmetrically coordinated peroxo ligand might be considered an exception to this generalization: R. Guilard, M. Fontesse, P. Fournari, C. Lecomte, and J. Protas, *J. Chem. Soc., Chem. Commun.*, 161 (1976).

(3) The symbol $M-N_p$ will always represent the metal–porphinato nitrogen bond. Except where specifically noted, the value quoted is the averaged value of this parameter. The number in parentheses is the estimated standard deviation of the average value.

(4) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **28**, 2162 (1972).

(5) D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3761 (1970).

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(7) (a) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963); (b) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, **87**, 2305 (1965); (c) D. L. Cullen and E. F. Meyer, *ibid.*, **96**, 2095 (1974); (d) R. C. Pettersen, *ibid.*, **93**, 5629 (1971); (e) A. A. Sayler and J. L. Hoard, to be published.

(8) L. Sacconi, *Transition Met. Chem.*, **4**, 199 (1968).

(9) (a) P. N. Dwyer, J. W. Buchler, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 2789 (1974); (b) B. Chevrier and R. Weiss, *ibid.*, **97**, 1416 (1975); (c) B. Chevrier and R. Weiss, *Inorg. Chem.*, **15**, 770 (1976).

(10) The required symmetry is that of the point group S_4; the geometry approximates rather closely to the requirements of the point group D_{2d}. The required dihedral mirror planes pass through the methine carbon atoms, Cm on Figure 1, and the required equatorial twofold axes pass through the nitrogen atoms and the midpoint of the C_b-C_b bonds. In this arrangement, the methine carbon atoms are alternately displaced above and below the mean plane of the core. In NiOEP, the displacement is ±0.51 Å. The porphinato core also displays a geometry consistent with the D_{2d} point group in which the positions of the mirror planes and twofold axes are reversed. In this alternate D_{2d} conformation, a ruffling of the methine carbon atoms is not observed.

(11) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, **206**, 18 (1973).

Table I
Complexing Bond Lengths in a Sequence of Four-Coordinate Metallotetraphenylporphyrins

Metal ion	M–N_p distances, Å[a]	Spin state, S	Symmetry[b]	Ref
d^4 Cr	2.033	2	C_i	18
d^5 Mn	>2.082	$^5/_2$	C_i	13
d^6 Fe	1.972	1	S_4	14
d^7 Co	1.949	$^1/_2$	S_4	15
d^8 Ni	1.928	0	S_4	7e
d^9 Cu	1.981	$^1/_2$	S_4	12b
d^{10} Zn	2.036	0	C_i	16

[a] For all derivatives except MnTPP, M–N_p ≡ Ct· · ·N_p.
[b] Symmetry required of the molecule in the crystal.

shown that this type of D_{2d} ruffling of the core is geometrically conducive to a significant shortening of the complexing bonds relative to those expected with a planar core. The question of whether the planar conformation or the ruffled conformation is energetically favored for the unconstrained molecule has not been unambiguously answered. However, packing calculations for the two crystalline modifications of NiOEP suggest a lower energy for the ruffled form in the solid state.[7c]

A similar correlation of porphinato core conformation and the M–N bond length has been observed for two copper(II) derivatives. $\alpha,\beta,\gamma,\delta$-Tetra-*n*-propylporphinatocopper(II)[12a] has a planar conformation and Cu–N_p = 2.000 (5) Å, while CuTPP[12b] has an S_4 ruffled core and Cu–N_p = 1.981 (7) Å. The tetragonal crystal form of CuTPP provides the pattern for the crystalline arrangement for the several metallotetraphenylporphyrins listed in Table I (ref 7e, 12b, 13–16) with S_4 symmetry. The M–N_p bond distances for the derivatives listed in Table I are correlated with the required presence of an electron in the $3d_{x^2-y^2}$ orbital of the d^9 copper(II) ion and the high-spin d^5 manganese(II) ion and the absence of a $3d_{x^2-y^2}$ electron in the intermediate-spin iron(II) ion and the low-spin cobalt(II) and nickel(II) ions. As the iron(II) through copper(II) derivatives of Table I form an isomorphous series, any solid-state effects on the stereochemistry are likely to be similar. Hence, the structural differences for these members can be regarded as purely electronic in origin.

The stereochemistry of the high-spin MnTPP[13] complex is particularly interesting. This complex was studied at room temperature and −175 °C. No effects of temperature were noted for parameters of the core, although the complex thermal motion of the peripheral phenyl groups was significantly damped at low temperatures (Figure 2). Despite a substantial expansion of the porphinato core (Ct···N_p = 2.082 Å), the manganese(II) ion appears to be too large to fit into the central hole of the macrocycle and is forced to take an out-of-plane position. The determination of exact parameters presents a problem in interpretation of the diffraction data; for complete details, the original publication[13b] should be consulted. The Mn–N_p distance is in the range 2.082–2.092 Å; the displacement of the Mn(II) ion out of plane is ~±0.18 Å. The zinc(II) ion might also be slightly too large to fit into the central hole of a porphinato ligand; indeed, an out-of-plane displacement of the metal ion has been suggested.[5] Our investigation of ZnTPP[16] shows, however, that the zinc(II) ion is centered in the macrocycle with Zn–N_p = 2.036 (6) Å.

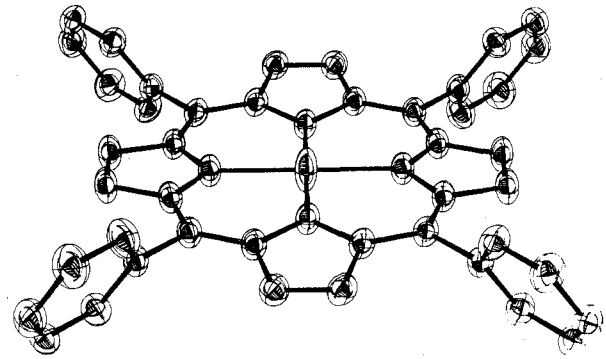

Figure 2. The MnTPP molecule. Atoms are represented by their vibrational ellipsoids contoured to enclose 50% of the electron density. Inner ellipsoids represent atoms at −175°, the outer ellipsoids represent the atoms at 20°. Data from ref 13b.

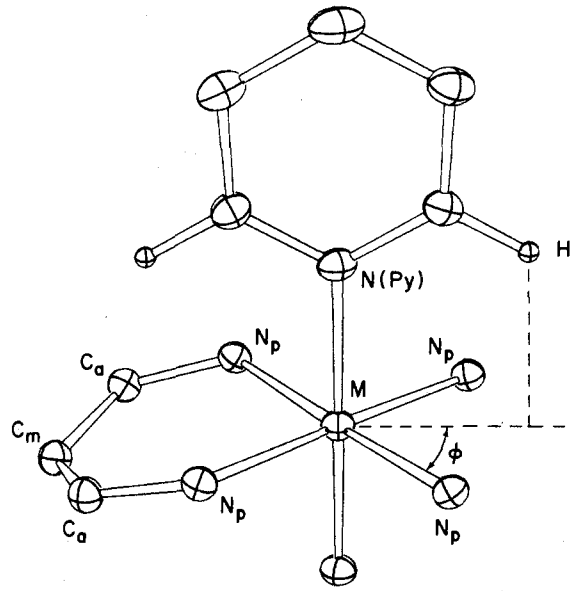

Figure 3. A diagram illustrating the steric interactions of an axial ligand of a metalloporphyrin with the porphinato core. The dihedral angle is between the plane of the ligand and the plane defining a coordinate plane, i.e., a porphinato nitrogen atom, the metal, and the ligand nitrogen atom N(Py).

The foregoing results suggest that a four-coordinate chromium(II) porphyrin, known to be high spin,[17] with the $3d_{x^2-y^2}$ orbital empty, would have substantially shorter M–N_p bonds than the Mn(II) derivative. Results from a structure determination of CrTPP[18] are in satisfactory agreement with Cr–N_p = 2.033 (1) Å.

Six-Coordinate Metalloporphyrins

The majority of six-coordinate metalloporphyrins of known structure are first-row transition-metal derivatives. Most have two equivalent axial ligands; the axial

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(14) J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676 (1975).
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(16) M. E. Kastner, K. Hatano, and W. R. Scheidt, to be submitted for publication.
(17) S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).
(18) W. R. Scheidt and C. A. Reed, to be submitted for publication.

ligands are commonly piperidine, pyridine, and imidazole, or substituted derivatives thereof. The detailed stereochemistry of the first-row transition-series derivatives depends on the electronic configuration of the metal ion. As with the four-coordinate complexes, an occupied $3d_{x^2-y^2}$ orbital leads to long equatorial $M-N_p$ bonds. Further, the occupancy of the $3d_{z^2}$ orbital leads to long axial bond lengths. Axial bond lengths are also influenced by steric interactions between the axial ligand atoms and atoms of the porphinato core. For planar atomatic ligands, the importance of the orientation of the ligand can be seen with the aid of Figure 3. We define an angle Φ, the dihedral angle between the plane of the ligand and a plane defined by N_p-M-N_b. For a fixed value of the M–N(Py) bond distance, steric interaction between pyridine hydrogen atoms and porphinato nitrogen atoms is maximized at $\Phi = 0°$ and minimized at $\Phi = \pm 45°$. Steric interactions can be diminished by a ruffling of the core, which is shown (somewhat exaggerated) on the left-hand side of Figure 3. Essentially all possible values of Φ have been observed.

The effects of the electronic configuration on the structure of the six-coordinate metalloporphyrins is most clearly seen for the cobalt(II), cobalt(III), and nickel(II) derivatives. The cobalt derivatives are all low-spin complexes; thus for the cobalt(III) complexes the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are unoccupied; the $3d_{z^2}$ orbital is singly occupied in the d^7 cobalt(II) derivatives. For the cobalt(III) derivatives, the equatorial $Co-N_p$ bond distances range from 1.958 to 1.982 Å;[19] the differences are attributable to differing porphinato core conformations. The axial Co–N bond distances in $CoTPP(Pip)_2^+$ is 2.060 (3) Å;[19a] for $CoTPP(NO_2)$(3,5-lutidine) the Co-N(3,5-lut) distance is 2.036 (4) Å.[19b] These distances are somewhat elongated from normal $Co^{III}-N$ bond distances owing to unfavorable nonbonded interactions between the ligand and porphinato core. In the absence of nonbonded interactions, the axial Co–N distances are normal. Thus, the $Co-N(NO_2)$ distance in $CoTPP(NO_2)$(3,5-lutidine) is 1.948 (4) Å and Co–N(Im) = 1.93 (3) Å in $CoTPP(Im)_2^+$.[19c,20]

The equatorial $Co-N_p$ distances for the two cobalt(II) derivatives of known structure are 1.987 (2) Å[21a] and 1.992 (2) Å,[21b] essentially the same as those observed for the cobalt(III) complexes. The axial bonds are substantially elongated, however, as a consequence of the populated $3d_{z^2}$ orbital. In $CoTPP(Pip)_2$,[21a] the axial Co–N bond distance increases 0.37 Å, relative to the analogous Co(III) derivative, to 2.436 (2) Å. Similarly long axial bonds were found for $CoOEP(3\text{-picoline})_2$,[21b] with $Co-N_{ax}$ = 2.386 (2) Å.

The d^8 nickel(II) ion in its six-coordinate porphinato derivatives is high spin, i.e., both the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are singly populated. The molecular stereochemistry of one such derivative, the bis(imidazole)-nickel(II) complex of tetra(4-*N*-methylpyridyl)-porphyrin, has been determined.[22] The equatorial $Ni-N_p$ bond distance is 2.038 Å; the axial Ni–N bond length is 2.160 (4) Å. The extension of the equatorial bond lengths from the 1.928–1.960 Å values observed for the low-spin four-coordinate derivatives clearly shows the effect of populating the $3d_{x^2-y^2}$ orbital. The fact that the extended equatorial bonds are not as long as the ~2.08-Å value expected for monodentate ligands in a paramagnetic NiN_6 coordination group reflects the constraints imposed by the porphinato ligand. The axial bond lengths, although considerably longer than the ~2.08-Å value, and in qualitative agreement with the low stability constant observed,[23] are ~0.2 Å shorter than the extended $Co-N_{ax}$ bonds in the Co(II) complexes where the $3d_{z^2}$ orbital is also singly populated. The shortening of the axial bonds in this nickel(II) complex may result, in part, from the electron-withdrawing properties of the positively charged *N*-methylpyridyl groups.

The stereochemical parameters of the six-coordinate iron(II) and iron(III) porphyrins are obviously of interest because of their biological significance. The d^5 and d^6 ions in these derivatives are low spin, and the iron atom is centered or nearly centered in the porphinato plane in all its complexes. We consider first the iron(II) derivatives.

The structures of the iron(II) and the isoelectronic cobalt(III) complexes should be quite similar; the major difference would be slightly shorter bond parameters for the cobalt(III) species owing to the increase of one charge unit on the central metal. The structures of two bis(amine) derivatives are known, $FeTPP(Pip)_2$[24a] and FeTPP(1-MeIm)$_2$.[24b] These derivatives have $Fe-N_p$ = 2.004 (4) and 1.997 (4) Å, respectively. The axial Fe–N distance in $FeTPP(Pip)_2$ is 2.127 (3) Å.[24a] The authors pointed out that this bond length is substantially longer than expected for low-spin iron(II) complexes and attributed this to unfavorable steric interactions between ligand hydrogen atoms and atoms of the porphinato core. Consistent with this conclusion, the observed axial Fe–N distance in FeTPP(1-MeIm)$_2$[24b] is 2.014 (5) Å and is a rational value for axial Fe–N bond distances in iron(II) porphyrins and heme proteins. Similar equatorial $Fe-N_p$ distances and an axial Fe–S distance of ~2.33 Å are observed in FeTPP(tetrahydrothiophene)$_2$.[24c]

Other iron(II) porphyrin structures, although less precisely determined than the foregoing, are of considerable interest. Two are derivatives of Collman's "picket fence" porphyrin[25a] or *meso*-tetra-α(*o*-pivalamidophenyl)porphyrin, in which the axial ligand pairs are (O_2)(1-MeIm)[25b] and (CO)(1-MeIm).[25c] The first provides evidence that the coordination group of the heme proteins which carry dioxygen contain coordi-

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(20) The steric requirements of imidazole are substantially less demanding than are those of pyridine, the consequence of the differing internal angles of five- and six-membered rings.

(21) (a) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974); (b) R. G. Little and J. A. Ibers, *ibid.*, **96**, 4440 (1974).

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(25) (a) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975); (b) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 1326 (1974); (c) J. P. Collman, R. R. Gagne, T. R. Halbert, J. L. Hoard, C. A. Reed, and A. A. Sayler, unpublished study, quoted by J. L. Hoard in "The Porphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 8; (d) S.-M. Peng and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 8032 (1976).

nated dioxygen with a bent Fe–O–O bond system, the second that the Fe–C–O bond system is linear. This coordination geometry for the CO ligand is confirmed by the structure determination of FeTPP(CO)(Py).[25d]

The structural parameters of the iron(III) porphyrins are similar to those of the iron(II) complexes, displaying slightly shorter bond lengths because of the increased charge on the central metal atom. Data are available for four complexes.[26] In the $FeTPP(Im)_2^+$ cation,[26a] $Fe–N_p$ = 1.989 (4) Å. The two axial Fe–N(Im) distances are 1.957 (4) and 1.991 (5) Å. The inequivalence appears to be a consequence of the differing orientations of the two ligands. The ligand with the shortest $Fe–N_{ax}$ distance has a more favorable orientation (ϕ = 39°); the other ligand has ϕ = 18°. Furthermore, the iron atom is displaced by 0.009 Å toward the farther ligand. $FeTPP(N_3)(Py)$,[26d] the only iron(III) complex with inequivalent axial ligands, has $Fe–N_p$ = 1.990 (6) Å. The linear azide ion coordinates with an FeNN angle of 125.8 (6)°, $Fe–N(N_3)$ = 1.926 (6) Å and Fe–N(Py) = 2.085 (6) Å. That the Fe–N(Py) distance is much longer than the corresponding Co–N(Py) bond in $CoTPP(NO_2)$(3,5-lutidine) reflects a possibly weaker bond and also the 0.03-Å displacement of the iron atom toward the azide ligand.

The structure of high-spin d^4 manganese(III) complexes ($3d_{z^2}$ singly occupied) would be expected to differ from the iron(III) complexes primarily by substantial extensions of the axial bonds. Two complexes have been examined, MnTPP(Cl)(Py)[27a] and $MnTPP(N_3)(CH_3OH)$.[27b] The $Mn–N_p$ distances are 2.009 (3) and 2.031 (7) Å, respectively, with differing core conformations responsible for the differing bond lengths. The axial bond parameters in MnTPP(Cl)(Py)[27a] are Mn–Cl = 2.468 (1) Å and Mn–N(Py) = 2.444 (4) Å. Both axial bonds are weak, although the Mn–N(Py) linkage is the weaker. The Mn–Cl bond distance increases by 0.095 Å relative to the distance observed in five-coordinate MnTPP(Cl). An unusual feature is the relatively large displacement (0.12 Å) of the Mn atom from the porphinato nitrogen plane toward the chloride ligand. This displacement plus the stretch in the Mn–Cl bond yields a $Cl···N_p$ nonbonded distance of ~3.3 Å, slightly less than the sum of the van der Waals radii of chlorine and aromatic nitrogen, the same as observed in the five-coordinate complex. Similar displacements of the Mn atom and stretch of the axial $Mn–N(N_3)$ bond are observed in $MnTPP(N_3)(CH_3OH)$.[27b] The axial $Mn–N(N_3)$ bond is 2.176 (9) Å. The Mn–O bond distance is 2.329 (8) Å, surprisingly shorter than the Mn–N(Py) distance in MnTPP(Cl)(Py).

The importance of the electronic configuration is again demonstrated by the structure of $CrTPP(Py)_2$.[28] The d^4 ion in this derivative is low spin, whereas the isoelectronic manganese(III) derivative are high spin. The axial Cr–N(Py) bonds (=2.131 (14) Å) are considerably shorter than in the Mn(III) complexes. The equatorial $Cr–N_p$ bonds are 2.027 (8) Å.

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Table II
Structural Parameters for Six-Coordinate Metalloporphyrins[a]

Metal	Spin state, S	$M–N_p$ distance, Å	M–Ax[b]
d^4 Cr	1	2.03	N
d^4 Mn	2	2.01–2.03	L
d^5 Fe	$^1/_2$	1.99	N
d^6 Fe	0	2.00	N
d^6 Co	0	1.95–1.98	N
d^7 Co	$^1/_2$	1.99	L
d^8 Ni	1	2.04	L

[a] See text for specific examples. [b] Metal-axial ligand bond distance; L denotes that this distance can be expected to be long and N denotes that this distance can be expected to be normal, or near normal.

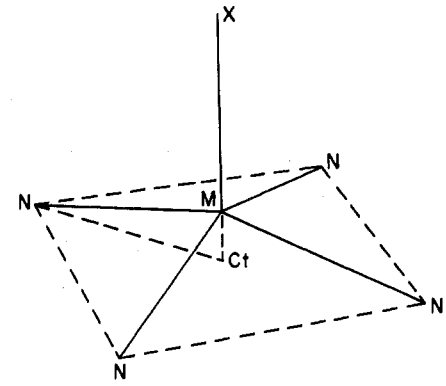

Figure 4. A diagram of the square-pyramidal coordination group for five-coordinate metalloporphyrins.

Table II summarizes the observed structural parameters of the various six-coordinate first-row transition-metal porphyrin derivatives. Two absences from this table merit comment, the high-spin d^5 Mn and d^9 Cu derivatives. From our prior discussion, we see that the axial bonds for these complexes would be expected to be quite long, with attendent low stability constants for the addition of the axial ligands.[29] Stable Mn(II) derivatives must be low spin, and no axial ligands (except NO; vide infra) appear able to force the transition.[13a]

Five-Coordinate Metalloporphyrins

The stereochemical parameters of importance for the square-pyramidal coordination group are illustrated in Figure 4. In addition to the metal–ligand bond lengths, the displacement of the metal atom out of the porphinato plane, denoted here as M···Ct, is an important characteristic of this class of compounds. A displacement of the metal atom out-of-plane allows relatively large $M–N_p$ bond distances without requiring large, energetically demanding, radial expansion of the porphinato core. The magnitude of the metal atom displacements, with some modulating contribution from radial expansion of the core, are correlated with the "size" of the metal atom with respect to forming metal–nitrogen bonds. Almost all characterized five-coordinate metalloporphyrins are first-row transition-element derivatives. All are neutral species, i.e., the axial ligand bears a charge which is just that needed to balance the residual charge on the metal ion. Nu-

(29) The known equilibrium constants are quite small. Data for cobalt(II) complexes: F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1154 (1973); data for nickel(II) complexes: F. A. Walker, E. Hui, and J. M. Walker, *ibid.*, **97**, 2390 (1975), and ref 23.

Table III
Stereochemical Parameters of Five-Coordinate Metalloporphyrins

Metalloporphyrin	Distances, Å				Spin state, S	Ref
	M–N_p	Ct· · ·N_p	M· · ·Ct	M–L (ax)		
$MgTPP(OH_2)$	2.072 (7)	2.054	0.27	2.099	0	30
ZnTPyP(Py)	2.073 (3)	2.047 (3)	0.33	2.143 (4)	0	5
$TiOEPMe_2(O)$[a]	2.110 (3)	2.031 (3)	0.58	1.619 (4)	0	32a
MnTPP(Cl)[b]	2.008	1.990	0.27	2.373	2	34
$MnTPP(N_3)$	2.005 (3)	1.992	0.23	2.045 (4)	2	35
FePorp(X)[c]	2.067	2.015	0.45		$^5/_2$	36a,b
MnTPP(1-MeIm)	2.128 (7)	2.065	0.56	2.192 (2)	$^5/_2$	37
FeTPP(2-MeIm)	2.086 (4)	2.044	0.42	2.161 (5)	2	38b
$CoTPP(\text{-}CH_2C(O)CH_3)$	1.948 (4)	1.945	0.11	2.028 (3)	0	39
CoTPP(1-MeIm)	1.977 (6)	1.973	0.13	2.157 (3)	$^1/_2$	40a
CoTPP(1,2-DiMeIm)[d]	1.985 (2)	1.979	0.15	2.216 (2)	$^1/_2$	40d
TIOEP(Cl)	2.212 (6)	2.10	0.69	2.452 (3)	0	41

[a] $OEPMe_2$ is the dianion of α,γ-dimethyl-α,γ-dihydrooctaethylporphyrin. [b] Average of two determinations. [c] Average values from the structures of ref 36a and b. [d] 1,2-DiMeIm is 1,2-dimethylimidazole.

meric details for selected examples of this class are given in Table III.

We consider first the d^0 Mg(II) and d^{10} Zn(II) derivatives. Disorder in crystalline $MgTPP(OH_2)$[30] and in the isomorphous $ZnTPP(OH_2)$[31a] derivative, particularly, leads to underestimates of the metal atom displacement and to overestimates for the axial bond lengths. The principal parameters of ZnTPyP(Py)[5] and ZnOEP(Py)[31b] are similar except for Zn–N(Py) which are 2.134 (4) and 2.200 (3) Å, respectively. This difference results from a relatively unfavorable orientation of the pyridine ligand in ZnOEP(Py). In the radical $ZnTPP(ClO_4)$ species,[31c] the axially coordinated perchlorate balances the charge resulting from the loss of an electron from the highest filled molecular orbital of the porphinato ligand; the Zn–O distance is 2.079 (8) Å. Other parameters differ insignificantly from ZnTPyP(Py).

Early members of the transition-metal class include titanium(IV) and vanadium(IV) derivatives with a strongly bound oxo ligand. Parameters for the oxotitanium(IV) derivative of α,γ-dimethyl-α,γ-dihydrooctaethylporphyrin[32] are given in Table III. The structure of TiOEP(O),[32b] based on a minimal data set, is similar except for Ti–O = 1.67 (1) Å. $TiOEP(O_2)$,[2] with its symmetrically bound peroxo ligand, can be considered a five-coordinate complex. The Ti–O distances are 1.829 (6) and 1.822 (8) Å; other parameters are the same as the other Ti(IV) derivatives. Two vanadyl (VO^{2+}) porphyrins have been examined.[33] The parameters are similar to those of the oxotitanium derivatives.

Five-coordinate manganese, iron, and cobalt porphyrin derivatives have been rather intensively studied. The d^4 Mn(III) derivatives are high spin, the d^5 Mn(II) and Fe(III) species are all high spin, the d^6 Fe(II) and Co(III) derivatives are high spin and low spin, respectively, and the d^7 Co(II) complexes are low spin. The presence of an unpaired electron in the $3d_{x^2-y^2}$ orbital of the high-spin d^5 and d^6 complexes is responsible for the substantial displacement of the metal atom from the porphinato plane.

Averaged values for two different solvates of MnTPP(Cl)[34,35] are given in Table III. The out-of-plane displacement of 0.27 Å is surprisingly large in view of the short Mn–N_p bonds. The Ct···Cl separation of 2.64 Å appears to result from the tight Cl···N_p contacts of ~3.30 Å (~0.2 Å less than the sum of the van der Waals radii) but does not explain the quantitative division of Ct···Cl into the Mn···Ct and Mn–Cl components.

A large number of iron(III) porphyrins have been examined.[36] The specific compounds studied and details concerning axial ligation are given in ref 36. With the possible exception of the thiolate complex,[36f] the axial bond lengths are quite short for high-spin iron(III) complexes. An isoelectronic manganese(II) complex, MnTPP(1-MeIm),[13a,37] has substantially large values for all parameters of the coordination group. For both the Mn(II) and Fe(III) derivatives, the M–N_p bond distances are quite short relative to the values observed when the high-spin metal atom is coordinated to either monodentate or multidentate nitrogen ligands.

A d^6 iron(II) derivative analogous to MnTPP(1-MeIm) requires the use of 2-methylimidazole as the axial ligand in order to prevent the formation of a six-coordinate species.[38a] An unusual feature of the FeTPP(2-MeIm)[38b] molecule is the significant amount of "doming"; the mean porphinato core is displaced by 0.13 Å from the mean plane of the four porphinato nitrogen atoms away from the axial ligand. The usual

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Table IV
Nitrosylmetalloporphyrins

Metalloporphyrin	Distances, Å				MNO angle, deg	ν(NO), cm^{-1}	Ref
	M–N$_p$	M–N (NO)	M· · ·Ct[a]	M–N (ax)			
CoTPP(NO)	1.978 (4)	1.833 (53)	0.094		≤128.5	1689	42a
FeTPP(NO)	2.001 (3)	1.717 (7)	0.211		149.2 (6)	1670	42b
MnTPP(4-MePip)(NO)	2.027 (4)	1.644 (5)	0.10	2.206 (5)	176.2 (5)	1740	42c
FeTPP(1-MeIm)(NO)	2.008 (12)	1.743 (4)	0.07	2.180 (4)	142.1 (6)	1625	42d
FeTPP(4-MePip)(NO)	2.004 (10)	1.721 (10)	0.09	2.328 (10)	139 (1)	1640	42e
FeTPP(4-MePip)(NO)	1.999 (10)	1.740 (7)	0.11	2.463 (7)	143.7 (6)	1653-56	42e

[a] All metal atom displacements are towards the axial NO ligand.

value of this displacement in five-coordinate metalloporphyrins is ≤0.05 Å.

The absence of a $3d_{x^2-y^2}$ electron in the low-spin cobalt(III)[39] and cobalt(II)[40,41] derivatives leads to quite small displacements of the cobalt atom (0.11 to 0.15 Å). Average Co–N$_p$ in the cobalt(II) porphyrins range from 1.977 (6) to 2.000 (4) Å. Unlike the six-coordinate Co(II) derivatives, the single axial Co–N bond lengths to sterically unhindered ligands are not exceptionally long. In CoTPP(1-MeIm),[40a] the axial bond distance is 2.157 (3) Å. Similar axial bond distances are observed in CoOEP(1-MeIm)[40b] and CoTPP(3,5-lutidine).[40c] The latter compound demonstrates that pyridine and imidazole derivatives display nearly identical behavior as complexing agents in forming five-coordinate cobalt(II) porphyrin derivatives. The preparation and structure determination of CoTPP(1,2-DiMeIm)[40d] demonstrate a stretch in the axial bond resulting from the sterically active 2-methyl substituent of 1,2-dimethylimidazole. The Co-N(1,2-DiMeIm) bond distance is 2.216 (2) Å, an increase of 0.06 Å compared to the 1-methylimidazole complexes.

Nitrosylmetalloporphyrins

A series of Mn(II), Fe(II) and Co(II) porphyrins with nitric oxide as an axial ligand have been synthesized and characterized.[42] The structural examination of this series has allowed the evaluation of the changes in stereochemistry caused by the removal or addition of a 3d electron or the coordination of a second axial ligand. Stereochemical parameters are summarized in Table IV. Two points are to be emphasized. The M–N(NO) distances and M–N–O angles suggest the ordering Mn > Fe > Co for π interaction in the axial NO bonding system. For the six-coordinate iron(II) derivatives, the correlation between the Fe–N(ax) bond length and ν(NO) is remarkable. Further details are found in the original publications.[42]

Binuclear Metalloporphyrins with Bridging Ligands

Most examples of this class utilize oxo ligands as the bridging ligand; we briefly note two particularly interesting pairs of complexes. The binuclear Nb(V) and Mo(V) complexes have the same molecular formula, $M_2(TPP)_2(O)_3$, but radically differing structures;[43] the two Mo(V) ions are bridged by a single oxo ligand while the two Nb(V) ions are bridged by all three oxo ligands.

The μ-oxo bridged iron(III) porphyrins are the best known examples of binuclear metalloporphyrins. Parameters of the coordination group of $(FeTPP)_2O$[44] are similar to those characteristic of the monomeric high-spin five-coordinate iron(III) porphyrins. However, $(FeTPP)_2N$, formally derived by the replacement of the bridging oxygen atom of $(FeTPP)_2O$ with a nitrogen atom, has coordination group parameters that resemble those of a low-spin iron(III) porphyrin. A complete comparison is given in ref 45.

Summary

This Account has attempted to survey trends in metalloporphyrin stereochemistry, especially those which can be qualitatively correlated with position in the periodic table or electronic configuration. It is hoped that the results presented here illustrate not only the diversity of metalloporphyrin stereochemistry but will be useful in anticipating structure for other metallomacrocycles and additional metalloporphyrin derivatives.

I gratefully acknowledge the assistance of my co-workers and collaborators whose names appear in the references. The support of the National Institutes of Health and the Research Corporation is also gratefully acknowledged.

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