The Stereochemistry of the Coordination Group in an Iron(III) Derivative of Tetraphenylporphine[1,2]

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Abstract: The X-ray data reported by Fleischer, *et al.*,[4] for tetragonal crystals assumed to be the aquohydroxyiron(III) derivative of tetraphenylporphine ($H_2OFeOHTPP$) are reanalyzed to take account of (1) the probability that the material studied was in fact the chloroiron(III) derivative of tetraphenylporphine (ClFeTPP) and (2) orientational disorder of the molecules in the crystal that, on either chemical formulation, is of major importance in interpreting the experimental data. Chemical analysis of the original preparation prior to recrystallization supports, but does not establish, the ClFeTPP composition. The structural model for each formulation assigns equal probabilities for parallel and antiparallel orientation of the polar coordination group along *c*; independent refinement of these models yields a pair of statistically averaged molecules that have objectively indistinguishable geometries. The ClFeTPP formulation provides a rational accounting for every aspect of the experimental data and the derived results, whereas the $H_2OFeOHTPP$ formulation requires several detailed interpretations that are rather unconvincing. The square-pyramidal coordination group in the ClFeTPP molecule, with Fe–N = 2.049 ± 0.009 A and Fe–Cl = 2.192 ± 0.012 A, closely resembles that in chlorohemin. The iron atom is displaced out-of-plane from the nitrogen atoms by 0.383 ± 0.005 A.

The rather unorthodox coordination geometry displayed by the iron porphyrins containing either quintet Fe(II) or sextet Fe(III) would appear to play an essential role in the mechanism of hemoprotein function.[5,6] Thus it has been pointed out that marked conformational alterations in the coordination group should accompany the transition of an iron porphyrin from the spectroscopic state of highest multiplicity to the low-spin state in which the number of unpaired electrons is minimized.[6] One important aspect of the coordination geometry of high-spin iron porphyrins is brought out in the statement that, for any realizable coordination number, a substantial displacement (>0.30 A) of the iron atom from the mean plane of the four porphine nitrogen atoms is the normal expectation. The single apparent exception to this principle, that provided by an earlier X-ray diffraction study[4] of a crystalline material presumed to be the aquohydroxyiron(III) derivative of tetraphenylporphine (written hereafter as $H_2OFeOHTPP$), was questioned[5] on the grounds that the failure of the investigators to consider convincing evidence for a simple type of orientational disorder of the molecules in the crystal had vitiated the stereochemical description of the coordination group given by the structure analysis. Furthermore, it has subsequently become clear that reinterpretation of the X-ray data[4] must take into account both this orientational disorder and the probability, recently developed from consultation with Dr. E. B. Fleischer, that the crystal employed for recording the data was largely or wholly the chloroiron(III) derivative of tetraphenylporphine (written as ClFeTPP) rather than the reported $H_2OFeOHTPP$. Such reanalysis of structure is the subject of this paper.

We shall postpone discussion of the suggestive, but certainly not definitive, chemical analysis of the original preparation pending investigation of the relative merits of the two limiting formulations, $H_2OFeOHTPP$ and ClFeTPP, as alternative compositions for the interpretation of the X-ray and other physical data.

The body-centered tetragonal unit of structure in the crystal,[4] with a = 13.53 and c = 9.82 A, contains two porphyrin molecules; agreement between the measured and the calculated densities at 1.31 g/cc is obtained with either ClFeTPP or $H_2OFeOHTPP$ as the assigned composition. The space groups requiring consideration are I4, $I\bar{4}$, and I4/m.

The structure proposed for the assumed $H_2OFeOHTPP$ by Fleischer, *et al.*,[4] is based upon the space group, I4-C_4^5 and involves no positional disorder;[7] it does, on the other hand, lead to such large apparent thermal motions parallel to the unique c axis for the iron atoms as to preclude altogether the use of anisotropic thermal parameters during refinement of the structural model. That the iron atoms, in particular, should be in extraordinarily anisotropic movement is objectively incompatible with the fact that the 399 independent nonzero reflections distribute satisfactorily through a quasi-spherical region of reciprocal space (levels with l = 0, ±1, . ., ±10 are included).

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[1] This investigation was supported by Public Health Service Research Grant No. 5-ROI-GM09370 from the National Institutes of Health, General Medical Sciences, by National Science Foundation Grant G-23470, and by the Advanced Research Projects Agency.

[2] Presented in preliminary form at the Symposium on Biologically Significant Coordination Compounds, 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 22–31, 1966, Abstract H31, and at the Johnson Research Foundation Colloquium, Philadelphia, Pa., April 16–17, 1966. The conclusions now presented supersede those reported earlier.

[3] Fellow of the John Simon Guggenheim Memorial Foundation, 1966–1967.

[4] E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964); these X-ray data (and those of several other compounds) are on deposit as Document No. 7869 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $6.25 for photoprints, or $2.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[5] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, 87, 2312 (1965).

[6] J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., in press.

[7] The positioning of a water molecule on the fourfold axis seems unobjectionable; it would appear that the water molecule should have an orientational mobility approximating in a practical sense to free rotation about the fourfold axis.

Consequently, it is not surprising that by isotropic refinement of their model Fleischer, *et al.*, were able to reduce $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ only to 0.17, and were left with correspondingly large values for the estimated standard deviations in bond parameters.

Assuming the $H_2OFeOHTPP$ formulation as reported,[4] it is seen that the unique axis of the six-coordination group in the molecule is, as the sequence, H_2O–Fe–OH, indicates, necessarily polar. In the reported structure these polar axes (or polar coordination groups) are all aligned parallel to the *c* axis. Excepting other atoms within the coordination group, the nearest neighbors of H_2O and OH are distant hydrogen atoms of phenyl groups. Thus it is evident that there is no dimensional restriction on the use of a mixture of parallel and antiparallel orientations of the polar groups; it is further evident that a statistically random (1:1) mixture is conducive to kinetic simplicity during crystallization and to a stabilizing entropy of disordering (or mixing). We are then led to a disordered structure based upon the space group $I4/m\text{-}C_{4h}^5$ that, following refinement as outlined later, differs from the Fleischer, *et al.*, model in several notable respects.

This disordered crystalline arrangement is sufficiently characterized by describing the *statistically averaged* molecule of $4/m\text{-}C_{4h}$ symmetry that is centered at the origin of the cell (and at every other lattice point). What is to be described is in principle the averaged result of the antiparallel superposition of two enantiomorphic molecules of $4\text{-}C_4$ symmetry that derive from one another through reflection in a plane ($z = 0$) perpendicular to the *c* axis. It turns out in fact that, to the best approximation derivable from the X-ray data, it is only the averaged result of reflecting the coordination group through the plane of the four nitrogen atoms that makes the statistically averaged molecule differ in any objectively significant regard from either individual enantiomorph. Thus all atoms of the porphine skeleton, the four phenyl carbon atoms attached to methine carbons, and the four terminal carbon atoms of phenyl groups lie in the symmetry plane at $z = 0$, and the planes of the phenyl groups are parallel to the *c* axis. Half-atoms of iron lie on the *c* axis at $\pm z$ and two sets of half-atoms of oxygen at $\pm z'$ and $\pm z''$.

At this point we anticipate the later refinement of the disordered crystalline model corresponding to the $H_2OFeOHTPP$ formulation to remark that half-atoms of oxygen from H_2O and OH groups lying on the same side of a half-atom of iron turn out not to be resolvable from one another; indeed, the refinement suggests exact superposition or, otherwise put, that $z'' \equiv z'$. A model for this simplified version of the statistically averaged molecule, with half-atoms of iron at $\pm z$ and (full) atoms of oxygen at $\pm z'$, is quite like that illustrated in Figure 1 for the case of ClFeTPP (*vide infra*).

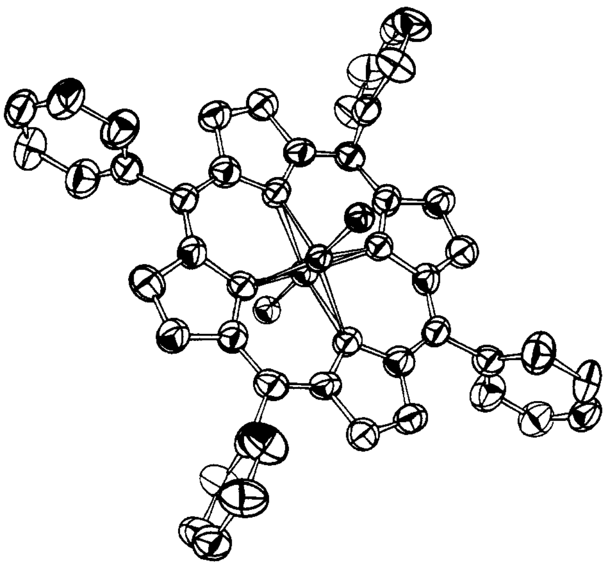

Figure 1. Model of the statistically averaged molecule of ClFeTPP. The ellipsoids represent the apparent thermal motions of the atoms as derived from the anisotropic thermal parameters.

In the alternative ClFeTPP formulation, the disordered crystalline arrangement utilizes the polar five-coordination groups in a statistically random (1:1) mixture of parallel and antiparallel orientations with respect to the *c* axis. The statistically averaged molecule (Figure 1) has half-atoms of iron and half-atoms of chlorine on the *c* axis at $\pm z$ and $\pm z'$, respectively; thus it carries the same formal description, with appropriately altered numerical values of the axial parameters, as the simplified version of the statistically averaged molecule of $H_2OFeOHTPP$.

Use of the Fleischer, *et al.*, X-ray data in full-matrix least-squares refinement[8] of the partially disordered structure based upon the $H_2OFeOHTPP$ formulation leads to $R = 0.100$ in the isotropic case, to $R = 0.073$ when anisotropic thermal parameters are employed. There are, however, no significant differences in bond parameters from the two refinements. Both least-squares refinements check out most satisfactorily against final difference syntheses.

As a solution of the purely crystallographic problem, the refined crystalline arrangement is eminently convincing except in regard to the composite oxygen atom. It proves to be difficult, if not impossible, to find a quite satisfactory stereochemical basis for either the apparently exact coincidence of the Fourier peaks representing half-atoms of oxygen from H_2O and OH or the numerical value for the *z* coordinate of this composite peak. Furthermore, the apparent thermal parameters for the composite oxygen atom are unduly small, especially the B_z of 2.3 A^2 for motion along *z*; the B_z values for nitrogen and iron are, respectively, 4.4 and 4.9 A^2, and those of all other atoms are still larger.

The foregoing reanalysis of structure is that briefly reported elsewhere[2] when we had no reason to suspect that the crystal used for recording the X-ray data was other than $H_2OFeOHTPP$. Upon learning of the possibility that the crystal was in fact largely or wholly ClFeTPP,[9] we recognized that our disordered structure, as refined for the assumed $H_2OFeOHTPP$ composition, should fit in quantitative detail every stereochemi-

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(8) The function minimized in the least-squares refinement was $\Sigma w(F_o - F_c)^2$, where the weights *w* reflect the multiplicity of each plane. The atomic scattering factors of D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965), were used. Major programs for the CDC 1604 used in this work were local modifications of the Wisconsin versions of the Busing–Martin–Levy ORFLS least-squares program and ORFFE function and error program, and the Blount–Fourier program.

(9) The probability of marked chloride contamination of the original preparation was mentioned by Dr. E. B. Fleischer during a conversation in Sept 1966. The chemical analysis discussed in the text comes from his letter of Dec 10, 1966. We thank Dr. Fleischer for his cooperation in this matter.

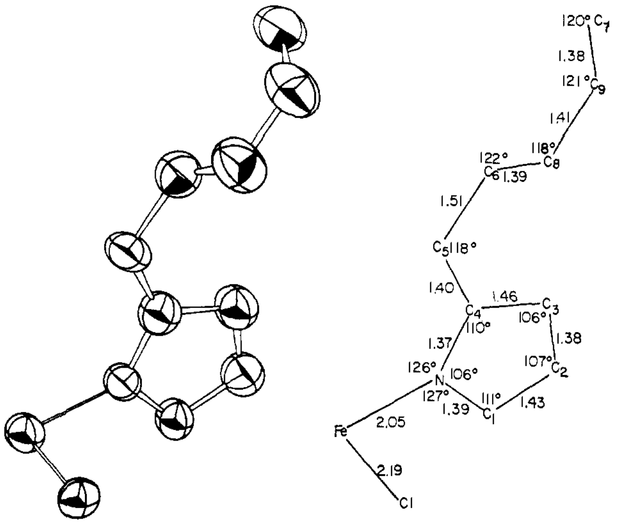

Figure 2. The asymmetric unit of ClFeTPP. On the left is an enlargement from Figure 1 in which one can see the apparent torsional motion of C_8 and C_9. On the right are shown the intramolecular bond lengths and angles.

Table I. Atomic Parameters from Anisotropic Refinement of ClFeTPP

	Positional parameters[a]			Thermal parameters[b]		
	10^4x	10^4y	10^4z	B_x, A^2	B_y, A^2	B_z, A^2
Fe	0	0	0390 (5)	3.2	3.2	4.8
Cl	0	0	2623 (10)	4.2	6.7	4.0
N	1436 (6)	0384 (7)	0	3.3	3.3	4.5
C_1	2252 (9)	−0246 (9)	0	3.0	4.3	5.8
C_2	3154 (10)	0302 (10)	0	4.5	5.0	5.4
C_3	2899 (9)	1290 (10)	0	3.6	4.5	7.4
C_4	1819 (9)	1324 (10)	0	3.6	4.4	5.6
C_5	1272 (9)	2201 (9)	0	4.1	3.5	5.4
C_6	1839 (9)	3161 (9)	0	3.7	3.8	7.2
C_7	2913 (10)	4908 (10)	0	4.8	3.8	10.2
C_8	2099 (8)	3587 (8)	1240 (11)	7.2	6.0	5.3
C_9	2649 (8)	4471 (7)	1219 (12)	7.4	5.0	7.6

[a] Estimated standard deviations are given in parentheses. [b] The anisotropic thermal parameters were introduced in the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}\,kl)$; $B_x = 4\beta_{11}/a^{*2}$, etc. Among the off-diagonal terms, only $B_{xy} = 4\beta_{12}/a^*b^*$ for C_8 and C_9 (1.8 ± 0.5) differ significantly from zero. Estimated standard deviations of the above thermal parameters range from 10 to 20% of the values.

cal requirement of the ClFeTPP composition. This conclusion was warranted by the circumstance that, in the statistically disordered crystalline arrangement, the scattering of X-rays by a statistical half-atom of chlorine should be comparable with that by an oxygen atom.

While awaiting further information on the chemical composition of the original preparation,[9] the X-ray data have been employed in anisotropic, full-matrix, least-squares refinement of the disordered structure as based directly upon the ClFeTPP formulation.[10] Changes in *R*, in the atomic coordinates, and in interatomic distances from the earlier refinement of the $H_2OFeOHTPP$ model prove to be completely trivial; thus the formally computed shift in any bond length does not exceed an apparent 0.002 A and the average shift is less than 0.001 A. There is just one significant change in the description of the statistically averaged molecule: the apparent thermal parameters of the chlorine half-atom are realistically larger (Table I) than those obtained for the composite oxygen atom.

Atomic coordinates and thermal parameters from the ClFeTPP refinement[11] are listed in Table I and the bond lengths and angles derived therefrom in Table II. Figures 1 and 2 show the statistically averaged molecule, its apparent thermal motion, and the bond lengths and angles. Bond parameters within the porphine skeleton and the phenyl groups are in good agreement with the collected data from earlier porphyrin studies as critically discussed by Hamor, *et al.*[12] The corresponding parameters given by Fleischer, *et al.*,[4] are internally consistent in terms of the estimated standard deviations cited by them, but the new results represent a striking improvement. Thus the six phenyl C–C bond lengths from the earlier study range from 1.30 to 1.44 A, average to 1.385 A, and carry an average estimated standard deviation (esd) for an individual bond length of 0.06 A; the three independent phenyl C–C bond lengths from the study now reported range from 1.382 to 1.409 A, average to 1.395 A, and carry an average esd for an individual bond length of 0.012 A.

Table II. Stereochemical Parameters of the ClFeTPP Molecule

Distances, A		Angles, deg	
Fe–Cl	2.192 ± 0.012	$FeNC_1$	126.6 ± 0.8
Fe–N	2.049 ± 0.009	$FeNC_4$	126.3 ± 0.8
C_1-N	1.394 ± 0.014	NC_1C_2	111.1 ± 1.0
C_4-N	1.374 ± 0.015	NC_4C_3	110.3 ± 1.0
C_1–C_2	1.429 ± 0.017	$C_1C_2C_3$	106.8 ± 1.2
C_3–C_4	1.463 ± 0.017	$C_4C_3C_2$	106.3 ± 1.2
C_2–C_3	1.380 ± 0.017	C_1NC_4	105.6 ± 0.9
C_4–C_5	1.399 ± 0.016	$C_3C_4C_5$	123.8 ± 1.2
C_1–C_5'	1.391 ± 0.016	NC_4C_5	126.0 ± 1.1
C_5–C_6	1.508 ± 0.017	$C_4C_5C_6$	117.5 ± 1.1
C_6–C_8	1.393 ± 0.011	$C_6C_8C_9$	118.5 ± 1.1
C_8–C_9	1.409 ± 0.013	$C_8C_9C_7$	120.4 ± 1.2
C_9–C_7	1.382 ± 0.012	$C_9C_7C_9'$	120.4 ± 1.4
Ct–Fe[a]	0.383 ± 0.005	$C_8C_6C_8'$	121.9 ± 1.3
Ct–N	2.012 ± 0.009		
Ct–C_5	3.441 ± 0.012		

[a] Ct represents the center of the porphine skeleton.

The apparent thermal motions of atoms in the porphine skeleton of the statistically averaged molecule are not much larger parallel to the *c* axis than they are in the mirror plane perpendicular to *c*. This result suggests both that the simplified superposition pattern (*vide supra*) defining the statistically averaged molecule is a very good approximation and that any departure from planarity in the equilibrium configuration of the porphine skeleton of the individual molecule in the crystal must be small.

We next consider those stereochemical parameters of the coordination group in the statistically averaged molecule that do not depend on whether the chemical composition is taken as ClFeTPP or $H_2OFeOHTPP$

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(10) We are indebted to Mr. Victor Day for these computations.

(11) A table of the 399 calculated and observed structure factors has been deposited as Document No. 9396 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(12) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, 87, 2305 (1965).

(or any mixture thereof). Most important is the observation that the iron half-atoms are resolved from one another at 0.766 ± 0.011 A, thus putting the iron atom of an individual molecule some 0.38 A out-of-plane from the nitrogen atoms—in full agreement with the principle enunciated earlier.[5,6] Reported out-of-plane displacements of the iron atoms in two five-coordinate, high-spin porphyrins are 0.475 A in chlorohemin[13] and 0.455 A in methoxyiron(III) mesoporphyrin-IX dimethyl ester[5] (abbreviated as MeOFeMeso). The Fe–N bond lengths observed in chlorohemin (2.062 ± 0.010 A), in MeOFeMeso (2.073 ± 0.006 A), and in this study (2.049 ± 0.009 A) are in mutual agreement and are all much longer than the expected[6,14] low-spin value, 1.91 A.

Other stereochemical data from the chlorohemin and MeOFeMeso molecules can be used to suggest the probable chemical composition of the statistically averaged molecule of Figure 1 and Tables I and II. In the five-coordinate, square-pyramidal coordination groups of chlorohemin and MeOFeMeso, the bond lengths, Fe–Cl = 2.218 ± 0.006 A and Fe–O = 1.842 ± 0.004 A, along the unique axes of these high-spin complexes are, respectively, as short as or shorter than the values expected[6,14] for low-spin (octahedrally coordinated) Fe(III).[15] It is evident that a ClFeTPP molecule in which the square-pyramidal coordination group has an axial Fe–Cl bond at 2.192 ± 0.012 A, four Fe–N bonds at 2.049 ± 0.009 A, and an out-of-plane displacement of the iron atom of 0.383 ± 0.006 A meets the specifications of Table II and Figure 1, and, moreover, that this coordination group differs significantly from that in chlorohemin only in the magnitude of the out-of-plane displacement of the iron atom. This particular structural parameter is, of course, especially sensitive to the minor dimensional alterations in the core of the porphine skeleton and in the Fe–N bond length that are produced by variations in the environment and the thermal motions of the molecule.

No such convincing assignment of the axial bond-length data to a six-coordinate $H_2OFeOHTPP$ molecule is to be found. Fe–O distances (from refinement of the $H_2OFeOHTPP$ structural model) of 2.190 ± 0.012 and 2.959 ± 0.012 A are required in this chemical formulation. Noted for general reference is the fact that Fe–O distances below 2.05 A are normally expected for bonds from octahedrally coordinated Fe^{3+} to H_2O and, more especially, to OH^-; 2.05 A, indeed, is the averaged Fe–O bond length observed in each of the two different seven-coordinate amine polycarboxylate complexes of high-spin ferric iron wherein the mutual nonbonding repulsions of the ligands are much more serious than in an octahedral complex.[16,17]

Identification of the 2.95- and 2.19-A distances with the respective Fe^{3+}–OH_2 and Fe^{3+}–OH^- separations runs into numerous difficulties. The extraordinarily long 2.95-A distance corresponds to a very weak Fe^{3+}–OH_2 complexing interaction that can scarcely account for the stability of the crystal toward loss of water. The conjecture that this stability might be attributed to a highly efficient trapping of the water molecules within the crystalline framework finds no support in our accompanying report[18] on the closely related structure of the aquozinc(II) derivative of tetraphenylporphine. Discounting the role of the distant water molecule, the remainder of the coordination group is effectively a five-coordinate, square-pyramidal configuration in which the length of the bond to the apical OH^- must be put at 2.19 A, 0.35 A greater than the 1.84 A observed for the corresponding Fe–OMe bond in the MeOFeMeso molecule. Any rational expectation value for a bond in this category[15] is surely below 2.00 A.

Only slightly less implausible is the alternative fitting of axial bond lengths to the $H_2OFeOHTPP$ formulation that identifies the 2.19- and 2.95-A distances with the respective bonds to H_2O and OH^-. For if it is then true that each bond corresponds to a substantial stabilizing energy, it remains a matter of conjecture why both bonds should be so extraordinarily long.

The apparently exact superposition in the Fourier synthesis of pairs of half-atoms of oxygen from H_2O and OH and the small magnitude of the apparent thermal parameter for vibration parallel to c of these composite oxygen atoms are particularly difficult to understand in the $H_2OFeOHTPP$ formulation, but are extraneous to the ClFeTPP formulation. Nor, in this latter case, can the stability of the crystal toward loss of water be pertinent.

We conclude that the ClFeTPP formulation gives a rational accounting of all quantitative aspects of the molecular stereochemistry, including specifically those data that the $H_2OFeOHTPP$ formulation seems unable to handle satisfactorily.

We learn[9] that the crystal used in recording the X-ray data was obtained by recrystallization of a portion of the original preparation from a chloroform–ethanol mixture that had not been dried. The recent chemical analysis of the original preparation yields[9] Cl, 6.0%; H, 3.72%; C, 66.05%. The calculated values for ClFeTPP are Cl, 5.04%; H, 4.02%; C, 75.1%; those for $H_2OFeOHTPP$ are H, 4.44%; C, 75.1%. The quite impure nature of this material, prior to recrystallization, is evident. However, it is also clear that the chlorine–carbon and chlorine–hydrogen ratios in the preparation correspond, respectively, to 30 and 22% excess chlorine beyond that needed for pure ClFeTPP. Although these data are not definitive, they certainly are compatible with the ClFeTPP formulation of the material obtained by recrystallization. There is, by contrast, very little in the partial chemical analysis that suggests the H_2OFe-OHTPP formulation.

Consideration of all of the evidence leads us to conclude that the crystal used for recording the X-ray data was largely or wholly ClFeTPP. The sharp definition of the axial (chloride) ligands achieved during Fourier and least-squares refinements of structure and the near-perfection of the final difference synthesis suggest that

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(13) D. F. Koenig, *Acta Cryst.*, 18, 663 (1965).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 246, 248.

(15) These observations are readily interpretable in molecular orbital terms. The d_{z^2} orbital of Fe^{3+} can combine with the appropriate σ-type orbital of the axial ligand to give a strongly bonding orbital that holds a donor electron pair and a weakly antibonding orbital that accommodates the unpaired electron; the 4s and $4p_z$ orbitals of Fe^{3+} may also contribute to the bonding. Such matters are treated more fully in ref 6.

(16) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, 3, 34 (1964).

(17) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, 88, 3228 (1966).

(18) M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, 89, 1996 (1967).

the concentration of $H_2OFeOHTPP$ or other impurity held in solid solution could not have been large.

Chlorohemin, MeOFeMeso, and now ClFeTPP all exemplify the stabilization of a high-spin ferric porphyrin through the addition to the Fe^{3+} ion of a singly charged, strongly complexing axial ligand to yield a five-coordinate, square-pyramidal coordination group that is electrically neutral. The use of an uncharged (but strongly complexing) ligand, such as a nitrogen atom of a histidine residue, yields a similar geometry for the coordination group in a high-spin ferrous porphyrin, as exemplified in the heme of deoxymyoglobin,[19] or a derivative form of this coordination geometry in a high-spin ferric porphyrin, as in the heme of ferrimyoglobin.[20] In this latter case the residual field from the Fe^{3+} ion through the base of the coordination pyramid permits the attachment in the sixth position of a ligand such as H_2O or F^- that is incapable of triggering the transition from the high-spin to the low-spin state. The currently best estimate[21] of the out-of-plane displacement of the Fe^{3+} ion (away from the water molecule and toward the histidine nitrogen atom) in the heme of ferrimyoglobin is ~0.30 A. According to Zerner, *et al.*,[22] recent theoretical calculations lend their full support to the principle that an out-of-plane displacement of the iron atom is required for stability in high-spin iron porphyrins, whether the coordination number be four, five, or six.

It is quite generally observed that the complexing of the two axial ligands by a high-spin iron porphyrin may give a low-spin product, but apparently never one of intermediate spin. We suggest that the strong interaction needed for removal of the electron from the d_{z^2} orbital into one of the t_{2g} set requires the close approach of both ligands to the iron atoms, that this is feasible only if the iron and the four nitrogen atoms are virtually coplanar, and that such coplanarity is achieved only by the simultaneous clearance of the electron from the $d_{x^2-y^2}$ orbital into another within the t_{2g} set. The 2.06 ± 0.01 A Fe–N distance recorded above for three high-spin ferric porphyrins is some 0.15 A greater than the 1.91 A expected in the low-spin case.[6,15]

The conformational alterations within the heme that are concomitant with transition from the high-spin to the low-spin state are seen to be substantial, but they have not the gross character that permits of their certain identification by the direct determination of hemoprotein structure. Thus, for example, the Fe–N distances of ~1.9 A reported[23] for the high-spin ferrimyoglobin are suggestive, albeit roughly, of the low-spin state. Matters touched upon in these final paragraphs are discussed in detail elsewhere.[6]

(19) C. L. Nobbs, H. C. Watson, and J. C. Kendrew, *Nature*, **209**, 339 (1966).

(20) *Cf.* L. Stryer, J. C. Kendrew, and H. C. Watson, *J. Mol. Biol.*, **8**, 96 (1964).

(21) H. C. Watson, private communication, 1966.

(22) M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966).

(23) J. C. Kendrew, R. E. Dickerson, B. E. Strandberg, R. G. Hart, D. R. Davies, D. C. Phillips, and V. C. Shore, *Nature*, **185**, 422 (1960).

The Stereochemistry of the Coordination Group in Aquozinc(II) Tetraphenylporphine[1]

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Abstract: A reinterpretation of the X-ray data measured by Fleischer, *et al.*,[3] for a reported diaquozinc(II) tetraphenylporphine supports the reformulation of this complex as the monoaquo derivative. Evidence for crystalline disorder leads to a model in which the polar five-coordination group has equal probabilities for parallel and antiparallel orientation with respect to the tetragonal *c* axis. The zinc(II) ion in the square-pyramidal configuration is displaced ~0.20 A from the basal plane of the nitrogens toward the complexed water molecule at a distance of ~2.20 A.

Interest in the aquozinc(II) derivative or derivatives of tetraphenylporphine, to be written $(H_2O)_nZnTPP$ with n to be determined, is both chemical and stereochemical. Inasmuch as Zn^{2+} is an 18-shell cation with an effective ionic radius[4] nearly as large as that of high-spin Fe^{2+}, and monopyridinezinc(II) porphyrins are known to be quite reluctant to accept a second molecule of pyridine,[5] there is some reason to suspect that the zinc ion, like the high-spin iron cations,[6] is too large to be accommodated in the plane of the four porphine nitrogen atoms. That anhydrous ZnTPP does not crystallize isomorphously with CuTPP and PdTPP, but appears instead in low-density forms[3] (of undetermined structures), suggests that the planar array of complexing bonds found in the Cu(II) and Pd(II) derivatives is not accessible to the Zn(II) complex. A disphenoidal (S_4 or D_{2d}) distortion from planarity of the

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