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]

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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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four nitrogen atoms could scarcely be large enough to give the zinc ion significantly more room, much less to give it a quasi-regular tetrahedral array of complexing bonds. Thus in either the anhydrous or the hydrated species it would seem probable that the zinc ion lies out of plane from the nitrogens to give a coordination group of 4 mm-C_{4v} symmetry. In these terms a six-coordinate C_{4v}-octahedral $(H_2O)_2$ZnTPP is quite likely to lose the weakly complexed water molecule to give a stable five-coordinate, square-pyramidal H_2OZnTPP.

The foregoing considerations carry just enough weight to make one examine carefully the reported[3] X-ray analysis of structure for tetragonal crystals of an aquozinc(II) tetraphenylporphine to which Fleischer, *et al.*,[3] assign the composition $(H_2O)_2$ZnTPP and a molecular symmetry of 4/m-C_{4h}; this assignment requires a planar porphine skeleton, centers the zinc atom among the four nitrogen atoms at the point of intersection of the fourfold axis with the mirror plane, and places the two water molecules above and below the zinc atom equidistant from it. Hoard, *et al.*,[7] have questioned both this chemical formulation and the structure determination[8] on the basis of experimental evidence residing within the original paper.[3] This evidence includes the following points. The observed density of 1.30 g/cc is much closer to the 1.315 g/cc calculated for $n = 1$ than to the still larger 1.35 g/cc calculated for $n = 2$. The extraordinarily long Zn–OH_2 distances of 2.45 A correspond to such weak complexing as to provide little or no reason for the retention of the water molecules. The ostensible thermal parameter of the zinc atom for motion parallel to *c*, given as 7.3 A^2, is more than twice as large as the corresponding parameter of the porphine nitrogen atoms to which the zinc atom is complexed. Furthermore, the reported thermal parameters for the water molecules have such implausibly large values, $B_x = 20.5$ A^2 and $B_z = 11.4$ A^2, as to suggest that the water content of the crystals has been grossly overestimated.

We now report a reanalysis of the published experimental data that leads to the following conclusions: the crystal studied was not an ordered arrangement of nonpolar (C_{4h}) molecules of $(H_2O)_2$ZnTPP, but was instead a partially disordered arrangement of polar (C_4, but $\sim C_{4v}$) molecules of H_2OZnTPP with equal probabilities for parallel and antiparallel orientations of the polar axis with respect to the unique tetragonal *c* axis of the crystal. The disordered structure utilizes the space group I4/m-C_{4h} and, indeed, is otherwise closely akin to that described for ClFeTPP in the preceding paper.[6] In the statistically averaged molecule, all the atoms of the porphine skeleton, the four phenyl carbons 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 perpendicular to the symmetry plane. The half-atoms of zinc and of oxygen lie on the *c* axis at $\pm z$ and $\pm z'$, respectively.

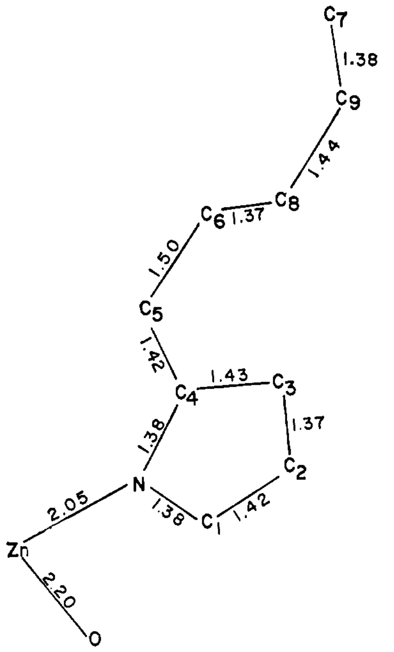

Figure 1. The asymmetric unit of the H_2OZnTPP molecule.

Isotropic least-squares refinement[10] of the disordered structure yields 0.092 for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. A variable occupancy factor for oxygen, put in at a value corresponding to $n = 2$, refined in the first cycle to a value corresponding to $n = 1$, *i.e.*, to the monoaquo complex. The zinc and oxygen have thermal parameters of $B = 2.3$ and 9.3 A^2, respectively, of which the latter value is large even though $n = 1$.

A model utilizing anisotropic thermal parameters was derived with $R = 0.078$ as compared with $R = 0.080$ in the original study.[3] However, the very factors that allow the ordered model to fit the data so well preclude the meaningful use and refinement of anisotropic thermal parameters with either model. The data, apparently taken about only one axis, require separate scale factors for each value of *l*; this leads to an observed correlation in the attempted refinement of essentially 1.0 between the scale factors and β_{33} of the zinc, in agreement with the discussion of Lingafelter and Donahue.[11] Of even greater concern is the asymmetric sampling of reciprocal space represented by the data. The maximum value of *l* reported was only 6, for which 19 reflections were observed. This corresponds to a *d* spacing of 1.6 A, whereas the maximum value (15) for *h* corresponds to $d = 1.1$ A. Such a distribution lends further credence to a disorder along *c* and, in conjunction with the overlap of zinc half-atoms, precludes the simultaneous refinement of *z* and β_{33} for zinc. We thus report[12] the parameters, bond lengths, and angles based on the isotropic refinement in Tables I and II, and in Figure 1.

The isotropic least-squares analysis places the zinc(II) half-atom 0.19 A from the porphyrin plane. The true displacement, however, is not known with a high

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(8) Webb and Fleischer[9] have subsequently reaffirmed their confidence in the Fleischer, *et al.*,[3] analysis.

(9) L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 43, 3100 (1965).

(10) The lattice constants used were, as reported:[3] $a = 13.440$ A and $c = 9.715$ A. The full-matrix, least-squares refinement employed the 569 data of Fleischer, *et al.*, which were obtained from ADI Document 7869; the data were weighted according to the multiplicity of each plane. Programs used in this work included the Wisconsin versions of the Busing–Martin–Levy ORFLS and ORRFE least-squares and function-error programs. The scattering curves of D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965), were used.

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(12) Tables of structure amplitudes have been deposited as Document No. 9395 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 remitting in advance $1.25 for photoprints or $1.25 for 35-mm film by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Table I. Atomic Parameters for $H_2OZnTPP^a$

	x	y	z	B
Zn	0	0	0.0191 (15)	2.35 (7)
O	0	0	0.2461 (57)	9.32 (176)
N	0.1477 (5)	−0.0355 (5)	0	2.45 (17)
C_1	0.1884 (7)	−0.1294 (7)	0	2.89 (20)
C_2	0.2942 (7)	−0.1239 (7)	0	2.83 (20)
C_3	0.3192 (7)	−0.0250 (7)	0	2.98 (20)
C_4	0.2280 (7)	0.0291 (7)	0	2.78 (19)
C_5	0.2192 (7)	0.1340 (7)	0	3.01 (20)
C_6	0.3150 (7)	0.1907 (7)	0	2.58 (18)
C_7	0.4924 (8)	0.2979 (8)	0	3.80 (23)
C_8	0.3583 (7)	0.2168 (7)	0.1222 (14)	5.13 (23)
C_9	0.4512 (7)	0.2699 (7)	0.1226 (14)	5.60 (24)

[a] Estimated standard deviations of the last figures are given in parentheses.

Table II. Intramolecular Bond Lengths and Angles for $H_2OZnTPP^a$

Bond Lengths, A		Angles, deg	
Zn–O	2.20 ± 0.06	$ZnNC_1$	126.8 ± 0.6
Zn–N	2.05 ± 0.01	$ZnNC_4$	127.5 ± 0.6
C_1–N	1.38 ± 0.01	NC_1C_2	110.5 ± 0.8
C_4–N	1.38 ± 0.01	NC_4C_3	110.5 ± 0.8
C_2–C_2	1.42 ± 0.01	$C_1C_2C_3$	107.1 ± 0.8
C_3–C_4	1.43 ± 0.01	$C_4C_3C_2$	106.5 ± 0.8
C_2–C_3	1.37 ± 0.01	C_1NC_4	105.4 ± 0.7
C_4–C_5	1.42 ± 0.01	$C_3C_4C_5$	125.5 ± 0.9
C_1''–C_5	1.41 ± 0.01	NC_4C_5	124.4 ± 0.9
C_5–C_6	1.50 ± 0.01	$C_4C_5C_6$	115.8 ± 0.8
C_6–C_8	1.37 ± 0.01	$C_6C_8C_9$	119.9 ± 1.1
C_8–C_9	1.44 ± 0.01	$C_8C_9C_7$	119.1 ± 1.2
C_9–C_7	1.37 ± 0.01	$C_9C_7C_9'$	120.4 ± 1.2
Ct–Zn^b	0.19 ± 0.02	$C_8C_6C_8'$	121.3 ± 1.3
Ct–O	2.39 ± 0.06		
Ct–N	2.04 ± 0.01		
Ct–C_5	3.45 ± 0.01		

[a] The primed (′) and double-primed(″) atoms correspond to atoms related by the mirror plane and fourfold axis, respectively, to the original atoms. The numbering corresponds to that of Fleischer *et al.*,[3] and is shown in Figure 1. [b] Ct represents the center of the porphine skeleton.

degree of accuracy as a result of the aformentioned lack of resolving power in the z direction and the overlap between the two zinc(II) half-atoms in the statistical model. The resulting Zn–OH_2 distance of 2.20 A then corresponds to a real, but still weak, bond. We suggest that the out-of-plane displacement of 0.19 A for the zinc atom represents a minimum value, and that the true value corresponds to a shorter, stronger Zn–OH_2 complexing bond.

The nonbonded repulsions between the apical H_2O and the four basal nitrogen atoms in this square-pyramidal arrangement necessarily cause some displacement of the zinc atom toward the apical water. The magnitude of the out-of-plane zinc displacement, even if somewhat underestimated, could be accounted for by these repulsions. A structural investigation of a Zn(II) derivative of α,β,γ,δ-tetra(*p*-pyridinyl)porphine is therefore underway to determine whether in fact an out-of-plane displacement is present in a four-coordinate zinc(II) complex.

Webb and Fleischer[9] have discussed at some length the question of whether the porphine skeleton in an isolated porphyrin molecule should be planar. They characterize present opinion on this matter as divided between two opposing theories, and they cite their structure determinations for $(H_2O)_2ZnTPP$ and porphine as providing critical examples of planar porphine skeletons.

We first direct attention to the probable source of the highly deformable character observed experimentally for the porphine skeleton. (1) A planar configuration for the porphine skeleton, unlike the case of a benzenoid hydrocarbon, cannot be expected to minimize angular strains in the pattern of σ bonding—certainly not for a series of metal derivatives which demands a series of internal adjustments. (2) The delocalized π bonding that favors a planar configuration is largely confined in the porphine skeleton to a 16-membered ring of in-and-out contour comprising the methine carbon atoms, the α-carbon atoms of pyrrole rings, and the nitrogen atoms; the capacity of π bonding to enforce planarity is surely much more limited than in the benzene series. Whether the equilibrium configuration of the free molecule is or is not planar depends upon the relative importance of (1) and (2), *i.e.*,on the respective potential curves (considered as separable) for reflection of configuration. Thus, rather than a dichotomy of theory, there is only the question of whether the preferred pattern of σ bonding or that of π bonding dominates. The thermal parameters found from the reinterpretation of X-ray data for $H_2OZnTPP$ indicate no major deviations from planarity, but the disorder prevents the identification of small deviations. In the structure of crystalline porphine,[9] there are deviations from planarity which, though almost trivially small in appearance, are significant in terms of the reported standard deviations and are of the same nature as the quasi-S_4 ruffling found in nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester.[13] It is therefore clear that neither of these structures may be used as evidence for a planar configuration in an isolated porphyrin molecule. Indeed, no unambiguous answer to this question is obtainable from studies of crystals.

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