The Crystal Structure and Molecular Stereochemistry of μ-Oxo-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III)][1]

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Abstract: Crystals of μ-oxo-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III)] observe the space group symmetry of $C2ca$-C_{2v}^{17}; the unit cell has a = 15.197 (5), b = 25.077 (12), and c = 18.074 (6) Å, and contains four oligomeric molecules, O(FeTPP)$_2$; the respective calculated and experimental densities are 1.30 and 1.28 g cm^{-3}. Determination and least-squares refinement of structure utilized some 3501 independent, counter-measured, intensity data (Mo Kα radiation) retained as observed from θ–2θ scans for $(\sin \theta)/\lambda \lesssim 0.65$ Å^{-1}. The binuclear $N_4FeOFeN_4$ coordination group of the oligomer approximates D_{4d}-$\bar{8}2m$ symmetry with an Fe–O bond length of 1.763 (1) Å, an averaged Fe–N distance of 2.087 (3) Å, and an FeOFe angle of 174.5 (1)°. The square-pyramidal five coordination around each iron atom is entirely typical for a high-spin ferric porphyrin, the strong antiferromagnetic interaction of the ferric ions through the Fe–O–Fe linkage notwithstanding. Thus the ferric ion is displaced 0.50 Å from the mean plane of the porphinato nitrogen atoms toward the axial oxo ligand. As is usual in crystalline porphyrins, the porphine skeleton departs significantly from planarity. Bond lengths in the skeleton are in good agreement with those in other iron porphyrins.

X-Ray analyses of crystalline structure for the high-spin iron(III) porphyrins, chlorohemin,[5] the methoxyiron(III) derivative of mesoporphyrin IX dimethyl ester[6] (written as MeOFeMeso), and monochloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III)[7] (written ClFeTPP),[8] show that in every such molecule the high-spin ferric ion is in square-pyramidal five-coordination with rather long bonds (2.07 Å) to porphinato nitrogen atoms, but a very short bond to the axial ligand. Inasmuch as the ferric porphyrins of formula type XFeTPP (X = Cl, Br, I, SCN) display a common thermomagnetic behavior characteristic for the high-spin sextet state,[9] they are strongly presumed to constitute an isostructural family involving the minimum of variation in the geometrical parameters of the five-coordination group.[9]

An obvious candidate for inclusion in the foregoing isostructural family is the analogous hydroxoiron(III) porphyrin, HOFeTPP. A material approximating rather closely to this composition is easily prepared and crystallized in a variety of circumstances,[9–11] but it displays thermomagnetic, chemical, and spectral behavior that are incompatible with the high-spin monomeric formulation. Thus, the magnetic susceptibility decreases with decreasing temperature from a value that, even at 310°K, is still below expectation for *low-spin* iron(III).[9,10] The molecular weight[11] in methylene chloride is compatible either with the (slightly dissociated) dimer, (HOFeTPP)$_2$, or with the anhydride, O(FeTPP)$_2$, *i.e.*, the simplest oligomer of HOFeTPP; the latter formulation is supported by infrared absorption bands[10,11] at ~875 and 890 cm^{-1} that are assigned to antisymmetric stretching in a bridging Fe–O–Fe bond system. X-Ray structure analysis provides the definite identification of this material as the oligomer, μ-oxo-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III)].[10] Full documentation of the X-ray analysis, requiring the more numerous X-ray data of greater range in $(\sin \theta)/\lambda$ recordable with Mo Kα radiation to give a quantitatively detailed description of the structure, is presented herein.

The stereochemistry of the coordination group in the O(FeTPP)$_2$ molecule differs in essential details from that of the μ-oxo-bis[phthalocyaninatopyridinemanganese(III)] oligomer[12] and that of the μ-oxo-bis[N-hydroxyethylethylenediaminetriacetatoiron(III)] anion;[13] see the Discussion.

Experimental Section

Single crystals of O(FeTPP)$_2$ from three laboratories (Pittsburgh,[9] Chicago,[10] and Cornell) gave similar X-ray diffraction patterns of orthorhombic D_{2h}-mmm symmetry. Systematic extinctions diagnostic of the probable space group(s) were characteristic for D_{2h}^{18}-$Cmca$ and C_{2v}^{17}-$C2ca$, of which the latter proved subsequently to be the correct choice.[14] Precise lattice constants and diffracted intensities were derived from measurements carried out on a Picker FACS-1 fully automated diffractometer using the largest available crystal (0.28 × 0.37 × 0.37 mm) to give, with Mo Kα radiation, data of barely adequate range in $(\sin \theta)/\lambda$ for a definitive structure determination.[15]

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(8) The parent $\alpha,\beta,\gamma,\delta$-tetraphenylporphine is written as H$_2$TPP. A formal diagram of the carbon–nitrogen skeleton is displayed in Figure 1.

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(14) "International Tables for X-Ray Crystallography. Vol. I. Symmetry Groups," Kynoch Press, Birmingham, England, 1952, p 127.

(15) This crystal specimen was from a preparation supplied by Dr. D. K. Straub.[9]

The angular settings of 24 reflections, paired at 12 values of $\pm 2\theta$, were determined (λ = 0.71069 Å) using the automatic centering program supplied with the computer-controlled diffractometer, each setting being repeated until a stable average was obtained. All measurements were made at the ambient laboratory temperature of 20 ± 1°. Least-squares refinement[16] of the diffraction geometry of these 24 reflections led to the lattice constants, a = 15.197 (5), b = 25.077 (12), and c = 18.074 (6) Å. For a cell containing four oligomeric molecules the density was calculated to be 1.30 g/cm^3, as compared with measured values of 1.31 g/cm^3 (Chicago[10]) and 1.28 g/cm^3 (Cornell).

Intensity measurement utilized Mo Kα radiation and the θ–2θ scanning technique on the computer-controlled diffractometer. Each scan, taken at the rate of 1°/min in 2θ, included a variable increment in angle above the minimum (2.0° at 2θ = 0) to allow for spectral dispersion; background counts, each of 40-sec duration, were taken at the extremes of the scan. The data were collected in concentric shells of increasing $(\sin \theta)/\lambda$, each such shell comprising one-tenth of the volume of the theoretical Cu Kα limiting sphere. Data in the first four shells were collected using a quartz monochromator, the remainder with Zr-filtered radiation, and separate scale factors were employed during the subsequent refinement of structure. The intensities of three standard reflections, measured periodically after each addition of 100 new data, showed no significant variations during the course of the measurements. Furthermore, the measured intensities of several hundred pairings of general hkl and $\bar{h}\bar{k}\bar{l}$ reflections were apparently consistent with a centrosymmetric arrangement of the atoms in the crystal.

With the cited dimensions of the crystal and a linear absorption coefficient for Mo Kα radiation of 0.49/mm, the maximum error in any measured intensity from the neglect of absorption corrections was estimated to be ~2%. Consequently, the net intensities were reduced directly to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (Lp). Retention as objectively observed of those data for which $|F_o| > 0.50\sigma_F$, σ_F being computed from $\sigma_F^2 = (Ct + k^2B)/4|F_o|^2(\mathrm{Lp})^2$, with Ct the total count from the scan, k the ratio of scanning time to total background counting time, and B the background count, left 3501 independent data for the determination of structure.

At this point the lack of objectively significant differences in the measured intensities of paired hkl and $\bar{h}\bar{k}\bar{l}$ reflections and the negative results of sensitive tests for piezoelectricity (using a Geibe-Schiebe detector) both supported the choice of the centrosymmetric space group, *Cmca*; the averaged value of 1.6 for $(|E|^2 - 1)^2$, by contrast, provided a small bias toward *C*2*ca*. The straightforward interpretation of a Patterson synthesis of the $|F_o|^2$ data led to pairings of iron atoms separated by ~3.50 Å, consistent in either space group with oligomeric oxo bridging (or with dimeric hydroxo bridging). The symmetry, C_{2h}-$2/m$, required of the oligomeric (or dimeric) molecule in *Cmca* was seen to require that four of the phenyl groups be positioned either within or astraddle of the mirror plane; the first possibility led to highly implausible steric interference between pairs of phenyl groups, the second required the still less plausible coplanarity of each such phenyl group with the mean plane of a porphine skeleton. Furthermore, a centrosymmetric Fourier synthesis of the observed amplitudes, phased in agreement with the iron contributions, displayed the (necessarily linear) Fe–O–Fe linkage, but was otherwise incompatible with the eclipsed quasi-D_{4h} orientation of the two porphine skeletons in the oligomer that, in *Cmca*, would allow the molecular configuration to observe the required minimum symmetry of C_{2h}-$2/m$. Thus, it became necessary to sort a sufficient fraction of the peaks in this rather diffuse synthesis into two enantiomorphous groups, to employ one of these for the introduction of complex phases, and to develop by successive approximation the complete structure based upon the noncentrosymmetric *C*2*ca*. With the symmetry required of the molecule thereby reduced to C_2, a single twofold axis passing through the bridging oxygen atom and serving as the perpendicular bisector of the Fe···Fe separation, the oligomer was allowed to take the staggered quasi-D_{4d} configuration (Figure 2) that, despite its high effective symmetry, lacks a center of inversion.[17]

Initial refinement of the coordinates and isotropic thermal parameters of the 50 atoms (excluding hydrogen) in the asymmetric unit (half of the oligomeric molecule) utilized full-matrix least-squares minimization of the function,[18] $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1$ and initial neglect of the imaginary correction to the anomalous scattering of the iron atom. The location of the origin of coordinates on a polar twofold axis of the structure was arbitrarily specified by fixing the x coordinate of the iron atom of the asymmetric unit. Following refinement, the description of the structure was recast by translation along a so as to put the unique oxygen atom of a molecule at the origin. Anisotropic refinement of the 447 parameters utilized the block-diagonal least-squares program described and tested in earlier studies.[19,20] Empirical weights ($w = 1/\sigma^2$) were calculated from $\sigma = \Sigma_0{}^3 a_n|F_o|^n$, the a_n being the coefficients from the least-squares fitting of the curve, $||F_o| - |F_c|| = \Sigma_0{}^3 a_n|F_o|^n$. In the final cycles of block-diagonal refinement, all parameter shifts were held to less than half of their estimated standard deviations and refinement was continued until a stable average for every parameter was obtained. A Fourier difference synthesis then gave evidence of reasonably placed bond densities in the eight C–H bonds formed by the pyrrole β-carbon atoms and in four of the 20 C–H bonds in the peripheral phenyl groups.[21] Hydrogen atoms were then introduced in calculated positions, fixed each 0.98 Å from the appropriate carbon atom, and were assigned isotropic thermal parameters that were allowed to vary during otherwise anisotropic least-squares cycles of refinement. Introduction of the imaginary component ($\Delta f''$) of the scattering by the iron atom, with and without reversal of the roles previously assigned to the general (hkl) and ($\bar{h}\bar{k}\bar{l}$), led to significantly different positions along a for the iron atom and, consequently, to significantly different values for the Fe–N complexing distances, but otherwise to quite inconsequential variations in the description of the structure; differences of ~0.001 in both the conventional R_1 and the weighted R_2 afforded a consistent, but not in itself convincing, basis for selecting the correct alternative. A more detailed comparison of these alternatives was then provided by additional cycles of anisotropic full-matrix refinement in which the parameters of the iron, oxygen, four nitrogen, and eight innermost carbon atoms were allowed to vary, the origin being determined by the remainder of the structure; this latter carried the fixed values of the parameters given by the block-diagonal refinements. Results were obtained as follows.

Alternative I. R_1 = 0.0709; R_2 = 0.0801; averaged Fe–N = 2.087 (6, 5) Å, wherein the figures in parentheses are, respectively, the mean deviation from the average and the estimated standard deviation of an individual bond length.

Alternative II. R_1 = 0.0721; R_2 = 0.0814; averaged Fe–N = 2.087 (22, 5) Å. The mean deviation from the average for the Fe–N distance (0.022 Å) is much larger than that for any chemical type of C–C or N–C bond length in the porphine skeleton.

Alternative I yields the lower values for both R_1 and R_2 and it better preserves in the coordination group the quasi-fourfold symmetry that otherwise characterizes the bond parameters in the porphine skeleton. Consequently, the atomic coordinates for the asymmetric unit of structure listed in Table I, the associated thermal parameters listed in Table II, and the bond parameters given in Tables III–V are all derived from the final least-squares refinement of structure, as specified above, for this interpretation of the effects of anomalous dispersion.[22]

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(16) Use was made of the Pick II program, a minor revision of W. C. Hamilton's Mode I program.

(17) The subsequent refinement of structure made it clear that both the absence of significant piezoelectricity and the apparently centrosymmetric nature of the intensity data were associated with the close approach to D_{4d} symmetry by the molecule in the crystal. The departure of the Fe–O–Fe bridge from centrosymmetric geometry was limited to a 5.5° bending from linearity, corresponding to a polar component along the required twofold axis (the direction of maximum polarity) of only 0.085 Å in the O–Fe displacement vectors. Furthermore, the imaginary component of the atomic form factor of iron was only ~0.9 electron.

(18) Following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); corrections for anomalous scattering were from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(19) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970).

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(21) The "washing out" of direct evidence for most of the C–H bonds in the phenyl groups was the obvious consequence of the excessively large (but individually distinctive) thermal motions of these groups; *cf.* the thermal ellipsoids illustrated in Figure 2 for the several atoms in the molecular skeleton.

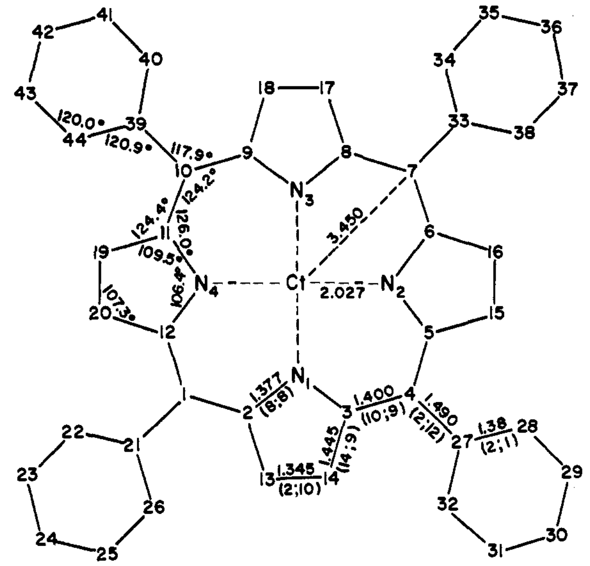

Figure 1. Formal diagram of the $\alpha,\beta,\gamma,\delta$-tetraphenylporphinato skeleton in the asymmetric unit of $O(FeTPP)_2$. Symbols for carbon atoms are replaced by the numbers identifying these atoms in the tables. Bond lengths and angles in the porphinato skeleton, averaged in agreement with C_{4v} symmetry, are entered on the diagram; bond lengths and angles shown for the phenyl groups are general averages. The first figure in parentheses following an averaged bond length is the mean deviation, the second is the (root-mean-square) value of the estimated standard deviation for an individual determination, both expressed in units of 0.001 Å (except for the C–C bond length in the phenyl groups wherein it is 0.01 Å).

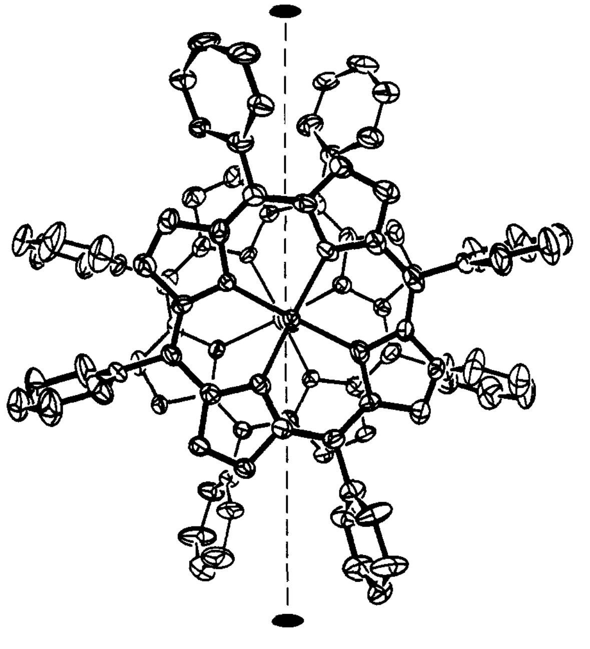

Figure 2. Computer-drawn model in perspective of the $O(FeTPP)_2$ molecule. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table II. The required twofold axis, which passes through the bridging oxo oxygen atom, requires structural equivalence of the upper and lower halves of the oligomer.

Table I. Atomic Coordinates in the Unit Cell

Atom type	Coordinates with standard deviations[a] 10^4x	10^4y	10^4z
Fe[b]	−55 (1)	4944 (0)	4029 (0)
O	0 (6)	1/2	1/2
N_1	548 (4)	4207 (2)	3861 (3)
N_2	1129 (3)	5286 (2)	3673 (3)
N_3	−679 (3)	5628 (2)	3625 (3)
N_4	−1249 (3)	4558 (2)	3868 (3)
C_1	−739 (5)	3628 (2)	4077 (4)
C_2	151 (4)	3723 (2)	3981 (4)
C_3	1440 (5)	4114 (3)	3820 (4)
C_4	2102 (4)	4498 (2)	3733 (4)
C_5	1933 (4)	5044 (3)	3662 (4)
C_6	1264 (4)	5819 (2)	3566 (4)
C_7	624 (4)	6208 (3)	3471 (4)
C_8	−277 (4)	6105 (2)	3468 (4)
C_9	−1575 (5)	5719 (3)	3543 (4)
C_{10}	−2233 (5)	5333 (3)	3677 (4)
C_{11}	−2075 (4)	4798 (3)	3842 (3)
C_{12}	−1405 (5)	4026 (3)	4015 (4)
C_{13}	819 (5)	3311 (2)	4039 (5)
C_{14}	1598 (5)	3555 (3)	3928 (5)
C_{15}	2610 (4)	5442 (3)	3553 (5)
C_{16}	2217 (4)	5922 (3)	3499 (4)
C_{17}	−941 (5)	6496 (3)	3256 (4)
C_{18}	−1727 (5)	6251 (3)	3291 (4)
C_{19}	−2738 (5)	4401 (3)	4016 (5)
C_{20}	−2320 (5)	3935 (3)	4111 (5)
C_{21}	−1033 (5)	3070 (3)	4223 (4)
C_{22}	−1216 (9)	2911 (4)	4916 (6)
C_{23}	−1446 (11)	2382 (4)	5062 (8)
C_{24}	−1508 (8)	2021 (3)	4507 (7)
C_{25}	−1333 (9)	2178 (4)	3808 (6)
C_{26}	−1074 (8)	2702 (3)	3662 (5)
C_{27}	3034 (5)	4312 (3)	3689 (4)
C_{28}	3589 (6)	4359 (4)	4293 (5)
C_{29}	4467 (6)	4216 (4)	4238 (6)
C_{30}	4782 (6)	4008 (4)	3592 (6)
C_{31}	4254 (6)	3959 (5)	3003 (6)
C_{32}	3374 (6)	4110 (4)	3045 (5)
C_{33}	918 (5)	6767 (3)	3329 (4)
C_{34}	926 (9)	7145 (3)	3882 (6)
C_{35}	1168 (10)	7673 (4)	3720 (7)
C_{36}	1453 (8)	7809 (3)	3048 (7)
C_{37}	1461 (8)	7444 (4)	2492 (7)
C_{38}	1196 (6)	6926 (3)	2629 (5)
C_{39}	−3162 (4)	5519 (3)	3666 (4)
C_{40}	−3442 (5)	5945 (3)	4100 (5)
C_{41}	−4320 (6)	6124 (3)	4092 (6)
C_{42}	−4902 (5)	5880 (4)	3619 (5)
C_{43}	−4651 (5)	5465 (4)	3180 (5)
C_{44}	−3779 (5)	5284 (3)	3202 (4)

[a] Numbers in parentheses are the estimated standard deviations.
[b] For Fe $10^5x = -554\,(12)$, $10^5y = 49443\,(3)$, and $10^5z = 40287\,(4)$.

Discussion

The numbering system employed in Tables I–V for the carbon and nitrogen atoms in the asymmetric unit of crystalline $O(FeTPP)_2$ is displayed on the formal diagram of Figure 1. Individual bond lengths and bond angles in the porphine skeleton are listed in Tables III and IV, respectively; bond parameters in the peripheral phenyl groups are given in Table V.

A computer-drawn model of the $O(FeTPP)_2$ molecule, as it exists in the crystal, is shown in Figure 2. The required twofold axis passes through the oxygen atom, is perpendicular to a line joining the two iron atoms, and requires structural equivalence of the upper and lower halves of the oligomer. The precisely determined Fe–O bond length of 1.763 (1) Å is accompanied by a precisely determined Fe–O–Fe angle of 174.5 (1)° that departs appreciably from linearity; consequently,

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(22) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code-number JACS-72-3620. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

Table II. Thermal Parameters of the Atoms in the Crystal

Atom	Anisotropic parameters (Å²) with standard deviations[a]						
type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å²
Fe	2.02 (2)	1.88 (2)	2.03 (2)	−0.27 (4)	0.12 (4)	−0.06 (2)	1.96
O	2.7 (2)	2.9 (2)	2.1 (2)	0	0	−0.4 (2)	2.6
N_1	2.7 (2)	2.1 (2)	2.9 (2)	−0.5 (2)	0.3 (2)	−0.5 (2)	2.5
N_2	2.4 (2)	2.2 (2)	2.0 (2)	−0.2 (2)	0.0 (2)	−0.1 (2)	2.2
N_3	1.9 (2)	2.2 (2)	2.8 (2)	0.0 (2)	0.1 (2)	0.5 (2)	2.2
N_4	2.2 (2)	2.3 (2)	2.4 (2)	−0.7 (2)	−0.1 (2)	−0.2 (2)	2.2
C_1	3.5 (3)	2.4 (2)	2.4 (3)	−0.7 (2)	0.2 (2)	−0.2 (2)	2.7
C_2	3.6 (4)	2.1 (2)	3.2 (3)	0.1 (2)	0.3 (3)	−0.1 (2)	2.9
C_3	2.7 (3)	2.6 (3)	2.7 (3)	0.1 (2)	0.2 (2)	−0.3 (2)	2.7
C_4	1.6 (2)	2.5 (2)	2.7 (2)	0.2 (2)	0.3 (2)	−0.1 (2)	2.2
C_5	2.5 (2)	2.3 (2)	3.2 (3)	−0.1 (2)	0.0 (2)	0.4 (2)	2.6
C_6	2.2 (3)	2.5 (2)	2.9 (3)	−0.4 (2)	0.0 (2)	0.2 (2)	2.5
C_7	2.1 (2)	2.5 (3)	3.4 (3)	−0.8 (2)	0.2 (2)	0.2 (2)	2.5
C_8	2.1 (3)	2.5 (2)	2.7 (2)	0.0 (2)	0.0 (2)	0.3 (2)	2.4
C_9	3.0 (3)	2.8 (3)	2.5 (3)	−0.2 (2)	−0.1 (2)	0.2 (2)	2.7
C_{10}	2.7 (3)	3.2 (3)	2.7 (3)	0.4 (2)	−0.2 (2)	0.1 (2)	2.8
C_{11}	1.5 (2)	3.1 (3)	2.5 (3)	−0.3 (2)	−0.1 (2)	0.1 (2)	2.3
C_{12}	3.0 (3)	2.5 (3)	2.7 (3)	−0.8 (2)	0.2 (3)	−0.1 (2)	2.7
C_{13}	4.2 (3)	1.7 (2)	4.6 (4)	0.1 (2)	0.4 (3)	0.5 (3)	3.2
C_{14}	2.8 (3)	2.6 (3)	4.9 (4)	0.4 (2)	−0.3 (3)	−0.2 (3)	3.2
C_{15}	2.1 (3)	3.0 (3)	4.9 (4)	−0.3 (2)	−0.5 (3)	0.7 (3)	3.1
C_{16}	1.8 (3)	3.2 (3)	4.5 (4)	−0.9 (2)	0.0 (3)	0.7 (3)	2.8
C_{17}	3.1 (3)	2.1 (2)	3.8 (3)	0.3 (2)	0.2 (3)	0.3 (2)	2.9
C_{18}	3.7 (4)	2.9 (3)	4.0 (4)	0.6 (3)	0.0 (3)	0.9 (3)	3.4
C_{19}	2.5 (3)	3.6 (3)	4.4 (4)	−0.9 (2)	0.2 (3)	1.0 (3)	3.2
C_{20}	3.5 (3)	3.7 (3)	4.0 (4)	−1.2 (3)	−0.1 (3)	−0.3 (3)	3.6
C_{21}	3.2 (3)	2.3 (2)	3.7 (3)	−0.9 (2)	0.6 (3)	0.0 (2)	2.8
C_{22}	10.4 (8)	3.8 (4)	4.7 (5)	−2.4 (5)	−0.3 (6)	−0.3 (4)	5.4
C_{23}	13.9 (11)	5.4 (6)	7.5 (7)	−5.2 (7)	−2.1 (8)	3.5 (5)	6.2
C_{24}	6.6 (6)	3.0 (4)	10.7 (8)	−1.6 (4)	0.2 (6)	2.2 (4)	5.3
C_{25}	11.1 (9)	3.1 (4)	6.7 (6)	−3.4 (5)	1.8 (6)	−1.3 (4)	5.2
C_{26}	7.7 (6)	3.8 (4)	5.1 (4)	−1.8 (4)	0.3 (5)	−1.0 (3)	5.0
C_{27}	2.6 (3)	2.9 (3)	3.7 (3)	0.5 (2)	−0.2 (2)	0.0 (2)	3.0
C_{28}	3.3 (4)	6.1 (5)	4.5 (4)	0.5 (3)	−1.1 (3)	−0.6 (4)	4.3
C_{29}	3.2 (4)	7.6 (6)	6.5 (6)	0.8 (4)	−2.3 (4)	0.2 (5)	4.9
C_{30}	3.9 (4)	5.0 (4)	7.7 (6)	1.4 (3)	−0.1 (4)	−0.1 (4)	5.1
C_{31}	2.8 (4)	11.4 (8)	6.5 (6)	1.5 (5)	1.2 (4)	−2.7 (6)	5.3
C_{32}	2.9 (3)	7.6 (6)	4.0 (4)	1.3 (4)	0.2 (3)	−1.1 (4)	4.3
C_{33}	3.0 (3)	2.1 (2)	4.4 (4)	−0.4 (2)	−0.3 (3)	0.4 (2)	3.0
C_{34}	11.6 (9)	3.3 (4)	5.8 (5)	−3.0 (5)	2.1 (6)	−0.3 (4)	5.4
C_{35}	12.3 (10)	3.4 (4)	9.5 (8)	−2.5 (6)	1.3 (8)	−2.2 (4)	6.6
C_{36}	8.3 (7)	2.5 (3)	9.6 (7)	−0.8 (4)	−0.1 (6)	1.8 (4)	5.4
C_{37}	8.0 (6)	4.4 (4)	6.9 (5)	−1.1 (5)	1.3 (6)	2.4 (4)	5.6
C_{38}	5.4 (4)	3.9 (4)	4.0 (4)	−1.3 (4)	0.1 (4)	1.0 (3)	4.2
C_{39}	1.9 (2)	4.1 (3)	2.3 (3)	−0.4 (2)	−0.1 (2)	0.6 (2)	2.6
C_{40}	2.6 (3)	4.3 (4)	4.7 (4)	0.2 (3)	0.4 (3)	0.0 (3)	3.7
C_{41}	3.5 (4)	5.3 (4)	5.5 (5)	0.3 (3)	1.1 (4)	−0.2 (4)	4.5
C_{42}	1.7 (3)	6.6 (5)	6.2 (5)	0.3 (3)	0.8 (3)	1.8 (4)	3.9
C_{43}	2.8 (3)	6.2 (4)	4.6 (4)	−0.7 (3)	−1.4 (3)	1.3 (4)	4.0
C_{44}	3.4 (3)	4.1 (3)	2.8 (3)	−0.7 (3)	−0.1 (3)	0.7 (3)	3.3

[a] Numbers in parentheses are the estimated standard deviations. The B_{ij} are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameters as calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Lengths within the Porphine Skeleton[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
Fe–O	1.763 (1)	N_4–C_{11}	1.392 (9)	C_7–C_8	1.393 (9)
Fe–N_1	2.087 (4)	N_4–C_{12}	1.381 (7)	C_8–C_{17}	1.458 (10)
Fe–N_2	2.094 (6)	C_1–C_2	1.384 (9)	C_9–C_{10}	1.413 (9)
Fe–N_3	2.090 (5)	C_1–C_{12}	1.428 (8)	C_9–C_{18}	1.429 (9)
Fe–N_4	2.076 (5)	C_2–C_{13}	1.450 (9)	C_{10}–C_{11}	1.396 (10)
N_1–C_2	1.373 (8)	C_3–C_4	1.401 (9)	C_{11}–C_{19}	1.451 (10)
N_1–C_3	1.377 (11)	C_3–C_{14}	1.434 (8)	C_{12}–C_{20}	1.419 (9)
N_2–C_5	1.364 (8)	C_4–C_5	1.400 (9)	C_{13}–C_{14}	1.347 (10)
N_2–C_6	1.367 (8)	C_5–C_{15}	1.447 (9)	C_{15}–C_{16}	1.348 (10)
N_3–C_8	1.374 (8)	C_6–C_7	1.389 (9)	C_{17}–C_{18}	1.344 (10)
N_3–C_9	1.389 (8)	C_6–C_{16}	1.475 (9)	C_{19}–C_{20}	1.341 (10)

[a] Numbers in parentheses are the estimated standard deviations.

the mean planes of the upper and lower porphine skeletons are not quite parallel to one another, though the dihedral angle between them is only 3.7°. Figure 2 shows, moreover, that the upper and lower porphine skeletons are in a staggered configuration that corresponds to quasi-D_{4d} symmetry for the molecule as a whole. For exact D_{4d} symmetry, the angle of twisting the upper skeleton about the true $\bar{8}$ axis from exact superposition with the lower skeleton would be 45°; the observed angle of twist, as measured by the dihedral angle that is bisected by the required twofold axis, is 54.6°.

Bond lengths in the porphine skeleton (Table III) approach the effective fourfold symmetry that corresponds to the simplest chemical classification of bond types. Using C_a and C_b to denote the respective α- and β-carbon atoms in a pyrrole ring, and C_m to denote methine carbon, we obtain averaged values for bond lengths in the porphine skeleton as folows: N–C_a,

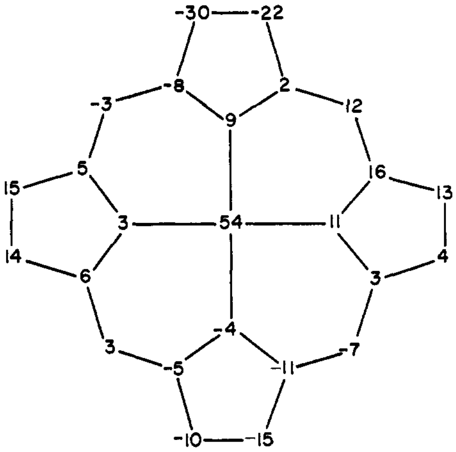

Figure 3. Diagram to illustrate the ruffling of the porphinato core in the asymmetric unit of the $O(FeTPP)_2$ molecule. The perpendicular displacements of the atoms from the mean plane, in units of 0.01 Å, replace the symbols of these atoms that are carried on the identically oriented diagram of Figure 1.

1.377 (8, 8); C_a–C_m, 1.400 (10, 9); C_a–C_b, 1.445 (14, 9); C_b–C_b, 1.345 (2, 10) Å, wherein the first figure in parentheses is the mean deviation in units of 0.001 Å and the second is the (root-mean-square) value for the estimated standard deviation (esd) of an individually determined length. Comparison of the mean deviation with the esd for each of the several distances shows that the averaged values are quite appropriate for description of the unconstrained molecule. These data and similarly averaged values for the chemical classes of bond angles are entered on Figure 1. Also cited for comparison are the significantly more precise values for the averaged bond lengths in the core of the low-spin bis(piperidine)-α,β,γ,δ-tetraphenylporphinatoiron(II) molecule:[23] Fe–N ≡ Ct···N, 2.004 (4, 3); N–C_a, 1.384 (3, 4); C_a–C_m, 1.396 (1, 5); C_a–C_b, 1.444 (3, 5); C_b–C_b, 1.347 (3, 6) Å.

Table IV. Bond Angles Associated with the Porphine Skeleton[a]

Angle	Deg	Angle	Deg	Angle	Deg
$OFeN_1$	101.2 (1)	$C_2C_1C_{12}$	124.3 (5)	$C_7C_8C_{17}$	123.8 (6)
$OFeN_2$	103.4 (2)	$C_2C_1C_{21}$	118.4 (5)	$N_3C_9C_{10}$	124.3 (6)
$OFeN_3$	107.7 (1)	$C_{12}C_1C_{21}$	117.2 (5)	$N_3C_9C_{18}$	110.3 (5)
$OFeN_4$	102.6 (2)	$N_1C_2C_1$	127.0 (6)	$C_{10}C_9C_{18}$	125.4 (6)
N_1FeN_2	86.5 (3)	$N_1C_2C_{13}$	109.4 (6)	$C_9C_{10}C_{11}$	124.9 (7)
N_2FeN_3	87.0 (2)	$C_1C_2C_{13}$	123.5 (6)	$C_9C_{10}C_{39}$	117.1 (6)
N_3FeN_4	86.4 (2)	$N_1C_3C_4$	126.6 (5)	$C_{11}C_{10}C_{39}$	118.0 (6)
N_4FeN_1	87.2 (2)	$N_1C_3C_{14}$	108.8 (5)	$N_4C_{11}C_{10}$	125.3 (6)
N_1FeN_3	151.1 (1)	$C_4C_3C_{14}$	124.5 (6)	$N_4C_{11}C_{19}$	108.8 (6)
N_2FeN_4	153.9 (2)	$C_3C_4C_5$	123.4 (6)	$C_{10}C_{11}C_{19}$	125.9 (7)
FeOFe	174.5 (1)	$C_3C_4C_{27}$	118.2 (6)	$N_4C_{12}C_1$	124.7 (5)
FeN_1C_2	124.6 (6)	$C_5C_4C_{27}$	118.3 (6)	$N_4C_{12}C_{20}$	110.4 (6)
FeN_1C_3	126.2 (4)	$N_2C_5C_4$	126.8 (8)	$C_1C_{12}C_{20}$	124.9 (6)
$C_2N_1C_3$	106.9 (5)	$N_2C_5C_{15}$	109.5 (5)	$C_2C_{13}C_{14}$	106.4 (6)
FeN_2C_5	126.3 (4)	$C_4C_5C_{15}$	123.8 (6)	$C_3C_{14}C_{13}$	108.5 (6)
FeN_2C_6	125.0 (4)	$N_2C_6C_7$	126.8 (6)	$C_5C_{15}C_{16}$	108.0 (6)
$C_5N_2C_6$	107.3 (5)	$N_2C_6C_{16}$	109.3 (5)	$C_6C_{16}C_{15}$	105.9 (6)
FeN_3C_8	125.8 (4)	$C_7C_6C_{16}$	123.7 (6)	$C_8C_{17}C_{18}$	107.2 (6)
FeN_3C_9	128.1 (4)	$C_6C_7C_8$	124.0 (6)	$C_9C_{18}C_{17}$	107.3 (6)
$C_8N_3C_9$	105.7 (5)	$C_6C_7C_{33}$	118.1 (6)	$C_{11}C_{19}C_{20}$	107.2 (7)
FeN_4C_{11}	126.2 (3)	$C_8C_7C_{33}$	117.9 (6)	$C_{12}C_{20}C_{19}$	107.9 (6)
FeN_4C_{12}	125.0 (4)	$N_3C_8C_7$	126.7 (6)		
$C_{11}N_4C_{12}$	105.6 (5)	$N_3C_8C_{17}$	109.4 (6)		

[a] Numbers in parentheses are the estimated standard deviations.

Table V. Bond Parameters Associated with the Phenyl Groups[a,b]

Type	Length, Å	Type	Length, Å	Type	Length, A
C_1–C_{21}	1.49 (1)	C_{27}–C_{28}	1.38 (1)	C_{36}–C_{37}	1.36 (2)
C_4–C_{27}	1.49 (1)	C_{27}–C_{32}	1.37 (2)	C_{37}–C_{38}	1.38 (1)
C_7–C_{33}	1.49 (1)	C_{28}–C_{29}	1.39 (1)	C_{39}–C_{40}	1.39 (1)
C_{10}–C_{39}	1.49 (1)	C_{29}–C_{30}	1.37 (1)	C_{39}–C_{44}	1.39 (1)
C_{21}–C_{22}	1.34 (1)	C_{30}–C_{31}	1.34 (1)	C_{40}–C_{41}	1.41 (1)
C_{21}–C_{26}	1.37 (1)	C_{31}–C_{32}	1.39 (1)	C_{41}–C_{42}	1.37 (1)
C_{22}–C_{23}	1.40 (1)	C_{33}–C_{34}	1.38 (1)	C_{42}–C_{43}	1.36 (1)
C_{23}–C_{24}	1.36 (2)	C_{33}–C_{38}	1.39 (2)	C_{43}–C_{44}	1.40 (1)
C_{24}–C_{25}	1.35 (2)	C_{34}–C_{35}	1.40 (1)		
C_{25}–C_{26}	1.40 (1)	C_{35}–C_{36}	1.33 (2)		

[a] Numbers in parentheses are the estimated standard deviations. [b] For each phenyl group the interior angles average 120.0°; the bond angles around C_{21}, C_{27}, C_{33}, and C_{39} in each case total 360.0°.

The four nitrogen atoms of the porphine skeleton (Figure 1) are not quite coplanar; one pair of diagonally opposite atoms (N_2 and N_4) lies ~0.02 Å above the mean plane, the other pair (N_1 and N_3) the same distance below. The iron atom is displaced 0.50 (1) Å from this mean plane toward the oxygen atom of the tight Fe–O–Fe bridge.

Departures of the carbon and nitrogen atoms in the porphine skeleton from the mean plane of this structural entity are displayed graphically in Figure 3, which is drawn in the same orientation as Figure 1. Each numbered atomic symbol in the porphine skeleton of Figure 1 is replaced in Figure 3 by the out-of-plane displacement of the corresponding atom in units of 0.01 Å. An S_4 type of ruffling is seen to contribute materially to the skeletal configuration. Neither the qualitative pattern nor the magnitude of the departure from planarity is particularly unusual for a crystalline porphyrin.[24] What is usual is that local flatness (within 0.02 Å) is preserved in the trigonal-bond patterns emanating from the carbon atoms in the inner 16-membered rings and, of course, in the pyrrole rings as well;[20,25] indeed, there is little reason to suppose that the delocalized π bonding is seriously affected by the undulations in the skeletal configuration. The mean planes defined, respectively, by the four nitrogen atoms and the entire porphine skeleton are separated by ~0.05 Å; consequently, the iron is displaced ~0.54 Å from the mean skeletal plane.

The averaged length of the four structurally nonequivalent bonds connecting phenyl groups to methine carbon atoms, 1.490 (2, 12) Å, corresponds to nearly pure σ bonding between trigonally hybridized carbon atoms.[20,23,24] Dihedral angles between the mean plane of the porphine skeleton and the planes of three of the phenyl groups are large: 82.8, 82.7, and 77.0°; the fourth such angle, involving the phenyl group $C_{33}\cdots C_{38}$ (Figure 1), is unusually small at 53.3°.

Figure 4 is a diagram in perspective of the five-coordination group around each iron(III) atom in the

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(23) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972).

(24) Structure determination for α,β,γ,δ-tetraphenylporphinatodichlorotin(IV) (Cl_2SnTPP) provides the sole established example of a crystalline porphyrin in which the equilibrium configuration of the porphine skeleton seems unambiguously to be planar; D. M. Collins, W. R. Scheidt, and J. L. Hoard, *ibid.*, submitted for publication.

(25) *Cf.* J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 573–594, and references cited therein.

oligomeric $O(FeTPP)_2$ molecule; the diagram is slightly idealized by employing bond parameters averaged in agreement with C_{4v} symmetry. Lacking structural data for the parent HOFeTPP species,[26] the stereochemical parameters observed for the square-pyramidal $OFeN_4$ coordination group in the high-spin methoxyiron(III) porphyrin,[6] MeOFeMeso (*vide supra*), then come to mind for comparison with those displayed on Figure 4. In MeOFeMeso, Ct···N = 2.022 (1, 6), Ct···Fe = 0.46 (1), Fe–N = 2.073 (1, 6), and Fe–O = 1.842 (4) Å. Further comparisons with the stereochemical parameters reported for the high-spin chlorohemin[5] and ClFeTPP[7] fully support the conclusion that the coordination group around each iron(III) atom in the $O(FeTPP)_2$ molecule follows the pattern (in a slightly exaggerated form) that is typical for high-spin ferric porphyrins.

The coordination group in the oligomeric μ-oxo-bis[*N*-hydroxyethylethylenediaminetriacetatoiron(III)] anion[13] (written $O(FeHEDTA)_2{}^{2-}$) displays quasi-D_{4d} geometry, with each iron(III) atom in octahedral coordination, and bridging Fe–O bond lengths of 1.79 (1) and 1.80 (1) Å; all other complexing bonds are long (Fe–O, 2.00–2.05; Fe–N, 2.20–2.27 Å), being comparable with those in the monomeric high-spin ethylenediaminetetraacetato complexes of ferric iron.[27] The much shorter Fe–N bonds observed in the monomeric, high-spin, ferric porphyrins (2.07 Å) and in the $O(FeTPP)_2$ oligomer (2.09 Å) exemplify the fact that the strongly complexing porphinato core is also very resistant to undue radial expansion (or contraction) in its mean plane. Miminum radial strain in the porphine skeleton corresponds to a Ct···N radius (Figures 1, 3, and 4) of ~2.01 Å;[20,25] the values of this radius observed in the iron porphyrins remain near 2.01 Å, ranging from 1.989 (5, 4) Å in the low-spin six-coordinate bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) cation[28] to 2.027 (5, 5) Å in the $O(FeTPP)_2$ molecule.

Thermomagnetic data[29] for the $O(FeHEDTA)_2{}^{2-}$ oligomer, which are generally similar to those of $O(FeTPP)_2$,[9,10] are well fitted by assuming that the two high-spin ($S = {}^5/_2$) ferric ions are spin coupled with $J = -95\ \text{cm}^{-1}$. The supporting analysis of the electronic absorption spectrum utilizes (ligand field) energy levels calculated for a high-spin octahedral FeO_6 coordination group,[29] a model that is not applicable to the $OFeN_4$ five-coordination group in $O(FeTPP)_2$. Further evidence that particularly strong antiferromagnetic interaction is a characteristic property of a μ-oxo-bis(iron(III) porphyrin] is provided by the thermomagnetic study of carefully purified μ-oxo-bis[protoporphyrin-IX dimethyl ester iron(III)],[30] $O(FeProto)_2$; Caughey, *et al.*,[30] find that the value of the coupling constant required to fit the data is fully twice that reported for the $O(FeHEDTA)_2{}^{2-}$ oligomer.

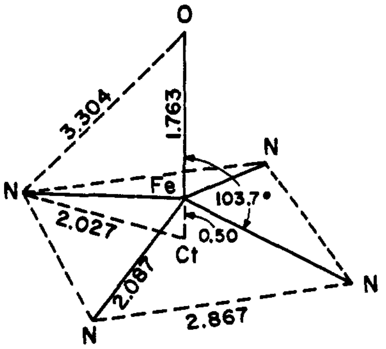

Figure 4. Slightly idealized (C_{4v}) diagram of the five-coordination group around each iron(III) atom in the $O(FeTPP)_2$ molecule.

The binuclear coordination group in the μ-oxo-bis[phthalocyaninatopyridinemanganese(III)] oligomer[12] (written $O(PyMnPc)_2$ with Py ≡ pyridine, Pc ≡ phthalocyaninato) approximates closely to D_{4d} geometry, with the pyridine ligands completing the octahedral coordination around each Mn(III) atom. Averaged bond lengths involving the d^4 Mn(III) atom are 1.71 (0, 1) Å to the oxo oxygen atom, 2.15 (0, 1) Å to the pyridine ligands, and 1.96 (1.5, 1) Å to the phthalocyaninato nitrogen atoms. The shortness of the 1.96-Å distance relative to the analogous Fe–N bond length of 2.09 Å in the $O(FeTPP)_2$ oligomer strongly suggests that it is the $d_{x^2-y^2}$ orbital of the high-spin Mn(II) atom from which the electron is lost during the oxidation, by molecular oxygen in pyridine solution, of the monomeric phthalocyaninatomanganese(II) complex to give the oligomeric $O(PyMnPc)_2$ species.[31] For inasmuch as the value of the Ct···N radius that minimizes radial strain in the quasirigid phthalocyanine skeleton appears to be substantially smaller than the analogous radius in the porphinato core,[6,25] certainly <1.95 Å, the complexing bond length of 1.96 Å presumably requires the $d_{x^2-y^2}$ orbital of the Mn(III) atom to be fully available as a σ acceptor of electron density from the phthalocyaninato nitrogen atoms.[32] The paramagnetic susceptibility at room temperature for crystalline $O(PyMnPc)_2$ corresponds to an effective moment of only ~0.71 BM per Mn(III) atom,[31b] a value so small that one might be tempted to ascribe it to the presence of paramagnetic impurity in a diamagnetic material. But even with the strongest σ donors as ligands, a monomeric octahedral complex of manganese(III) should still be strongly paramagnetic ($S = 1$).[34] Consequently, the very small moment in $O(PyMnPc)_2$ at room temperature suggests extraordinarily strong spin coupling of the manganese(III) ions to give antiferromagnetism that is less markedly temperature dependent than in the oligomeric iron(III) species. There appears, indeed, to be an inverse

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(26) The structure reported as that of $(HOFeOH_2)TPP$ [E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **86**, 2342 (1964)] was derived from X-ray data given by a crystal that subsequently was shown to be ClFeTPP. Orientational disorder of the ClFeTPP molecules in the crystal was shown to be primarily responsible for X-ray data that were inconsistent only in a few essential details with the erroneous chemical formulation.[7]

(27) (a) J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, **2**, 1316 (1963); (b) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **3**, 34 (1964).

(28) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972).

(29) H. B. Gray, *Advan. Chem. Ser.*, No. 100, 365 (1971), and references cited therein.

(30) W. S. Caughey, private communication.

(31) (a) J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959); (b) G. Englesma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962). The product was originally formulated as the monomeric Mn(IV) species, MnPcPyO.

(32) This conclusion derives from principles that have been shown[20,25,33] to be fully applicable to the metalloporphyrins.

(33) J. L. Hoard, *Science*, **174**, 1295 (1971).

(34) The phthalocyaninatoacetatopyridinemanganese(III) molecule, presumably a monomeric octahedral species, has $S = 2$ at room temperature.[31b]

correlation between the length of the bridging linkage and the strength of the spin coupling in these binuclear oligomeric species, an interesting phenomenon for detailed theoretical study.

Being trans to the exceedingly short bridging Mn–O bonds, the rather long bonds (2.15 Å) to the pyridine ligands in $\mathrm{O(PyMnPc)_2}$ may be subject to a structural trans effect. Indeed, the lengthening and weakening of these bonds by some sort of generalized synergistic mechanism[35] is rendered the more probable by the antiferromagnetic behavior of the molecule. Quite apart from such speculation, it is noteworthy that steric interactions of each phthalocyaninato core with the contiguous pair of pyridine–hydrogen atoms are not trivial, even though the observed orientations of both pyridine ligands[12] are nearly ideal for minimizing the steric repulsions.[36] Each of the specified hydrogen atoms lies above a six-membered chelate ring with three nitrogen and two carbon atoms of the aromatic core as near neighbors at calculated distances ranging from 2.68 to 2.80 Å. The van der Waals packing distance corresponding to direct superposition of a hydrogen above a core atom is 2.90 Å; a smaller value, perhaps as low as 2.80 Å, is more appropriate to the observed geometry of the five H···N and H···C contacts, and the energetic implications of the calculated separations are modest. A gross reduction of the axial Mn–N distance from the observed 2.15 Å to, let us say, the 1.96 Å that characterizes the equatorial Mn–N bonds is quite another matter, because it calls for a reduction in the critical H···N and H···C contacts (of which there are 20 in the molecule) to the range 2.51–2.64 Å.

The steric constraints imposed upon piperidine[23] and imidazole[28] molecules as axial ligands in low-spin iron porphyrins are detailed elsewhere.[23,28] Pyridine, in a similar role, is somewhat less constrained than is piperidine, but definitely more so than imidazole. (Differences in the geometries of five- and six-membered aromatic ring systems are surprisingly significant in this connection.)

The mean planes of the two porphinato cores in the $\mathrm{O(FeTPP)_2}$ molecule are separated by ~5.20 Å, whereas the phthalocyaninato cores in the $\mathrm{O(PyMnPc)_2}$ molecule approach ~3.40 Å, the characteristic spacing of fully aromatic molecules stacked in parallel array. Close approach of the porphinato cores in $\mathrm{O(FeTPP)_2}$ to one another is debarred by the packing of the bulky phenyl substituents, a circumstance that may seriously affect the pattern of complexing bonds. Interactions between the porphinato cores in the $\mathrm{O(FeProto)_2}$ molecule (*vide supra*) are sterically less constrained, and the role played by the vinyl substituents commands special interest. Structure and bonding in this oligomer may display features that are intermediate between those observed for the $\mathrm{O(FeTPP)_2}$ and the $\mathrm{O(PyMnPc)_2}$ molecules. Structure determination for a triclinic crystal of $\mathrm{O(FeProto)_2}$ is currently in progress.[37]

(35) *Cf.* (a) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); (b) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968), for a discussion of synergistic mechanisms.

(36) See ref 28, especially Figure 4 therein, for a detailed treatment of a closely related problem.

(37) L. J. Radonovich, W. S. Caughey, and J. L. Hoard.

Communications to the Editor

An Inversion Component in the Solvolytic Displacement Reactions of Alkyl-Substituted Vinyl Trifluoromethanesulfonates

Sir:

Solvolytic displacement at unsaturated (vinyl, sp^2) centers seems in nearly every case reported so far to have proceeded with complete randomization of stereochemistry, and this has formed one of the principal pieces of evidence for the existence of "free" vinyl cations.[1,2] Theoretical calculations support the inference that direct backside displacement should be more difficult at a vinyl than at a tetrahedral center.[3] As has been pointed out, however,[2] many of the substrates so far examined from which stereochemical information has been obtained are "activated"; *i.e.*, they generate rather highly stabilized vinyl cations. We now wish to report a study of simple, alkyl-substituted vinyl substrates which demonstrates that (in contrast to the behavior reported for activated systems[1]) their SN1 ionization reactions proceed with a significant amount of *inversion* of configuration at the vinyl center.

Solvolysis of 3-methyl-2-heptenyl trifluoromethanesulfonates (triflates) (*Z*)-**1** and (*E*)-**1**[4] took place readily at 60° in dry trifluoroethanol buffered with 2,6-lutidine and gave vinyl trifluoroethyl ethers (*Z*)-**2** and (*E*)-**2** as well as 1-methyl-1-*n*-butylallene (**3**) in the proportions

(1) (a) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970); (b) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971); (c) Z. Rappoport and Y. Apeloig, *Proc. Israel J. Chem.*, **7**, 34 (1969); (d) Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, **91**, 6734 (1969).

(2) One apparent exception is noted: some excess *retention* of configuration has been observed in silver-catalyzed reactions in nonsolvolytic media; *cf.* G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970).

(3) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1953 (1971).

(4) (a) Trifluoromethanesulfonates were prepared in all cases by reaction of the appropriate ketones with trifluoromethanesulfonic anhydride.[4b] Synthesis of the ketones will be described in a full paper; all new compounds exhibited analytical properties consistent with their assigned structures. Stereochemistries of vinyl triflates and trifluoroethyl ethers were assigned on the basis of chemical shifts[5a] and homoallylic coupling constants for the methyl groups ($J_{\text{trans}} = 1.4 \pm 0.1$ Hz, $J_{\text{cis}} = 0.9 \pm 0.1$ Hz).[4c] (b) T. E. Deuber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. von R. Schleyer, K. Hummel, S. Blocker, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970); (c) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(5) Vinyl triflates have been unequivocally shown to undergo SN1 solvolysis in protic media, even in alkyl-substituted cases. See, for example: (a) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969); (b) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969). In addition, trifluoroethanol has been shown to efficiently promote SN1 ionization: *cf.* (c) W. S. Trahanovsky and M. P. Doyle, *ibid.*, **89**, 4867 (1967); (d) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (e) V. J. Shiner, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969).