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- (22) (a) The large substituent effect exerted by this CF₃ group in the β position is consistent with our contention that an alkyl arsylate ionizes via a transition state with significant carbonium ion character. (b) Rate and stereochemical experiments were carried out on each of the pure diastereomers of compound II.
- (23) (a) Cmc^{23b} of SLS at 25 °C = 8.3×10^{-3} , at 70 °C = 11.4×10^{-3} M; (b) P. Mukerjee and K. J. Mysels, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 38 (1971); (c) The temperature dependence of micellar catalyses has been repeatedly demonstrated (catalysis decreases with increased temperature); see ref 4.
- (24) Lit.^{23b} cmc of XI at 40 °C = 6.5×10^{-3} M. We measured the cmc at 25 °C = 4.5×10^{-3} M.
- (25) (a) Since the simple decomposition of monoalkyl sulfates is a well pre-empted process,^{25b} we carried out the following controls to show that we were not just observing simple surfactant decomposition. The rate of 2-tridecyl species production in our solvolysis was $\gg 10^2$ faster than that observed in water, 0.1 N HCl, and 1 N HCl. Mixing a solution of XI with a completed SLS-Ic reaction mixture resulted in no detectable decomposition of XI. Only when XI was present during an ongoing solvolysis of Ic could its decomposition be noted. Lastly, the ratio of alcohol to olefin products of XI we obtained resemble typical solvolysis products (II) and do not resemble the mixtures obtained from monoalkyl sulfate decomposition;^{25b} (b) see: J. Kurz, *J. Phys. Chem.*, 66, 2239 (1962); V. A. Motsavage and H. B. Kostenbauder, *J. Colloid Sci.*, 18, 603 (1963); R. L. Burwell, *J. Am. Chem. Soc.*, 74, 1462 (1952).
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- (27) The greater reactivity of Ia, d, and e over II indicates that the β -CF₃ substitution makes that center even less reactive than a simple primary center, so it should always cleave as shown in eq 6.
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Molecular Stereochemistry of a Nitrogen-Bridged Metalloporphyrin: μ -Nitrido-bis[$\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron]

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Abstract: The molecular stereochemistry of a nitrogen-bridged iron porphyrin, μ -nitrido-bis[$\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron] has been determined. The structures of two crystalline solvates have been studied, a xylene solvate and a chloroform solvate. Both crystallize in the orthorhombic system, space group *Fddd*, with the unit cell containing eight oligomeric molecules and sixteen solvent molecules. Unit cell constants for the xylene solvate are $a = 22.427$ (2), $b = 32.446$ (5), and $c = 21.942$ (3) Å; the calculated and experimental densities (20 \pm 1 °C) are 1.300 and 1.27 g/cm³, respectively. The unit cell constants for the chloroform solvate are $a = 22.150$ (6), $b = 30.976$ (14), and $c = 22.109$ (6) Å; calculated and experimental densities are 1.390 and 1.35 g/cm³, respectively. The complex in both solvates has required D_{2h} -222 molecular symmetry. Measurement of diffracted intensities employed θ - 2θ scans with graphite-monochromated Mo $K\alpha$ radiation on a Syntex four-circle diffractometer. All independent data for $(\sin \theta)/\lambda \leq 0.648$ Å⁻¹ were measured; 3663 (xylene) and 2908 (chloroform) reflections were retained as observed. The structures were determined using the heavy-atom method and full-matrix least-squares refinement. Final discrepancy indices are 0.076 (xylene) and 0.064 (chloroform solvate). The binuclear N₄FeNFeN₄ coordination group approximates D_{4d} - $\bar{8}2m$ symmetry with a bridging Fe-N distance of 1.6605 (7) Å, an averaged Fe-N_p distance of 1.991 (3) Å, and a linear FeNFe bridge bond. The iron atom in the square-pyramidal coordination group is displaced 0.32 Å from the mean plane of the four porphinato nitrogen atoms towards the axial nitrido ligand. The porphine skeleton departs significantly from planarity.

The thermal decomposition of azido- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III) has been investigated recently by Summerville and Cohen.² The product of the reaction was found to be a nitrogen-bridged species, μ -nitrido-bis[$\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron], hereinafter written as (FeTPP)₂N. The compound is apparently the first example of a nitrogen-bridged complex with a first row transition element, although a few examples with second and third row transition metal ions are known.³

We report herein the molecular stereochemistry of (FeTPP)₂N, determined by x-ray diffraction methods from

two different solvated derivatives. The structure of (FeTPP)₂N might be expected to be closely similar to those of the bridged μ -oxo-bis[porphinatoiron(III)] derivatives;⁴⁻⁶ however, comparison of structure reveals some substantial differences. The stereochemistry of this interesting iron porphyrin derivative is compared with other iron and manganese porphyrin derivatives as well.

Experimental Section

Attempts to obtain crystals of (FeTPP)₂N from chloroform, methylene chloride, or benzene initially yielded crystals too small for

Table I. Atomic Coordinates of the (FeTPP)₂N Molecule

Atom type	Coordinates ^a		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Fe ^b	1/8	714 (0)	1/8
N ₃	1/8	1/8	1/8
N ₁	1011 (1)	585 (1)	2099 (10)
N ₂	2107 (1)	637 (1)	1496 (1)
C _{a1}	445 (2)	484 (1)	2317 (2)
C _{a2}	1386 (2)	576 (1)	2595 (2)
C _{a3}	2335 (2)	700 (1)	2074 (2)
C _{a4}	2606 (2)	605 (1)	1123 (2)
C _{b1}	477 (2)	374 (1)	2946 (2)
C _{b2}	1050 (2)	435 (1)	3119 (2)
C _{b3}	2981 (2)	729 (1)	2047 (2)
C _{b4}	3148 (2)	663 (1)	1466 (2)
C _{m1}	2002 (2)	672 (1)	2598 (2)
C _{m2}	2588 (2)	504 (1)	513 (2)
C ₁	2300 (2)	721 (1)	3201 (2)
C ₂	2742 (2)	433 (1)	3403 (2)
C ₃	2998 (2)	485 (1)	3963 (2)
C ₄	2821 (2)	816 (2)	4337 (2)
C ₅	2384 (2)	1097 (2)	4145 (2)
C ₆	2124 (2)	1051 (1)	3581 (2)
C ₇	3166 (2)	393 (1)	199 (2)
C ₈	3431 (2)	676 (1)	-211 (2)
C ₉	3967 (3)	560 (2)	-494 (3)
C ₁₀	4237 (2)	174 (3)	-378 (3)
C ₁₁	3976 (2)	-107 (2)	17 (3)
C ₁₂	3440 (2)	5 (2)	311 (2)
Cl ₁	4757 (2)	953 (1)	758 (2)
Cl ₂	5524 (3)	853 (3)	1680 (3)
C	5136 (10)	1/8	1/8

^a Numbers in parentheses are the estimated standard deviations.

^b For Fe 10⁵y = 7139 (2).

x-ray examination. Accordingly, a crystal obtained from the original preparation of the complex (xylene solution) was employed in our initial experiments. Preliminary x-ray photographic examination established an eight-molecule orthorhombic unit cell. The systematic extinctions suggested *Fddd* (No. 70) as the probable space group.⁸ Precise lattice constants and diffracted intensities were derived from measurements carried out on a Syntex PI diffractometer using a crystal of dimensions of 0.3 × 0.3 × 0.5 mm. The setting angles of 29 reflections, each collected at ±2θ, were determined (λ 0.71069 Å) using the automatic centering program supplied with the computer-controlled diffractometer. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C. Least-squares refinement of these reflections led to the lattice constants *a* = 22.427 (4), *b* = 32.446 (10), and *c* = 21.942 (6) Å. For a cell containing eight molecules of (Fe₂N₉C₈₈H₅₆·2C₈H₁₀) the calculated density is 1.300 g/cm³; the experimental density was 1.27 g/cm³.

Intensity data were collected by θ-2θ scanning using graphite-monochromated Mo Kα radiation as described later. Two equivalent forms of data having (sin θ)/λ ≤ 0.648 Å⁻¹ were measured and averaged. The net intensities were reduced to a set of relative squared amplitudes as described previously⁹ and all data having *F*₀ > 3σ(*F*₀) were considered observed. A total of 3663 independent data were considered observed (80% of the theoretical number possible) and were used for the determination and refinement of structure. With eight oligomeric molecules per unit cell, the space group *Fddd* requires that the molecules have *D*₂₋₂₂₂ symmetry. The axial Fe-Fe bridge must be along a twofold axis; consideration of the cell metrics suggests that this twofold axis is parallel to the *b* axis. This requires the bridging nitrogen atom to have coordinates 1/8, 1/8, 1/8 and the iron atom to have atomic coordinates of 1/8, *y*, 1/8. This interpretation was confirmed by analysis of the Patterson function¹⁰ and a trial value of *y* was obtained. Completion of the structure followed the usual heavy-atom method. The xylene solvate molecule has crystallographically required twofold symmetry, along the twofold axis at *x*, 1/8, 1/8, is poorly defined and apparently disordered. The disorder can be approximately described by two orientations of the xylene molecule, one in which the plane of the molecule is parallel to the twofold axis and the second in which

the molecular plane is perpendicular to the required twofold axis. Although there is some diffuse electron density near the ring, the methyl carbon atoms could not be reliably located. Structural parameters were refined by full-matrix least-squares techniques¹¹ using standard values for scattering factors.^{12,13} Isotropic refinement was followed by a difference Fourier synthesis, which revealed electron density concentrations appropriately located for all hydrogen atom positions of the porphyrin ligand. The coordinates of the hydrogen atoms were idealized and included in the refinement as fixed contributors. The refinement was then carried to convergence using anisotropic temperature factors for all heavy atoms except that of the xylene. Owing to limitations of computer storage, these refinements were performed in two portions. The final value of *R*₁ = Σ||*F*₀ - |*F*_c||/Σ|*F*₀ was 0.076; that of *R*₂ = [Σw(|*F*₀ - |*F*_c||)²/Σw|*F*₀]^{1/2} was 0.094, the estimated standard deviation of an observation of unit weight was 1.28.

The difficulties in defining the xylene molecule led us to conclude that the structure determination for this solvate was marginally acceptable; fortunately, we were soon able to obtain crystals of satisfactory size and quality from chloroform solution. The structure determination of this solvate proceeded in a more satisfactory manner (vide infra). Consequently, the values of atomic coordinates and bond distances and angles for the xylene solvate are given only as supplementary material.

Crystals of the chloroform solvate of (FeTPP)₂N were found to crystallize in *Fddd* as well; precise lattice constants are *a* = 22.150 (6), *b* = 30.976 (14), and *c* = 22.109 (6) Å (20 ± 1 °C). For a cell containing eight molecules (Fe₂N₉C₈₈H₅₆·2CHCl₃) the calculated density is 1.390 g/cm³; the experimentally determined density was 1.35 g/cm³. Intensity data were collected using graphite-monochromated Mo Kα radiation and θ-2θ scanning methods with a scan range of 1.4° at 2θ = 0° and an increment to allow for spectral dispersion. Background counts were estimated from an analysis of the reflection profiles using a local modification of a program recently described.¹⁴ Four standard reflections, well distributed in reciprocal space, were measured after every 50 reflections during data collection and showed only random deviations from their average value. The specimen crystal measured 0.15 × 0.15 × 0.24 mm and with a linear absorption coefficient¹⁵ of 0.586 mm⁻¹, the maximum variation in intensity was seen to be less than 5%. This was confirmed by measurement of several reflections as a function of φ. Intensity data were reduced and standard deviations calculated as described previously.⁹ Data were retained as objectively observed if *F*₀ > 3σ(*F*₀), leading to 2908 observed independent data (67% of the theoretical number possible in the range examined, 2θ = 54.9°).

Given the similar cell constants and the same crystallographically required symmetry, refinement of the chloroform solvate was commenced employing the final coordinates obtained for the xylene solvate. A difference Fourier synthesis showed that the chloroform molecule was positioned on the twofold axis along *x*, 1/8, 1/8; occupancy factors of the two crystallographically unique chlorine atoms were chosen to apportion the three atoms equally amongst the four sites. The overall occupancy factor for the chloroform molecule was set at 0.8, in agreement with the observed density; occupancy factors were not varied in subsequent refinement. Further refinement of the structure was continued with anisotropic thermal parameters and with intermittent difference syntheses until all hydrogen atoms were located. The hydrogen atoms were included in subsequent refinements using fixed idealized coordinates and isotropic thermal parameters fixed one unit higher than their associated carbon atom. Refinement was by full-matrix methods; the refinement was again performed using two blocks. The final value of *R*₁ was 0.064 and *R*₂ was 0.075; the estimated standard deviation of an observation of unit weight was 2.28. The final parameter shifts were less than 10% of the estimated standard deviation during the last cycle. A final difference Fourier was free of significant features. A final listing of observed and calculated structure factors (× 10) is available.¹⁶

The atomic coordinates and the associated anisotropic thermal parameters of the atoms in the asymmetric unit of structure (chloroform solvate) are listed in Tables I and II, respectively.

Discussion

Figure 1 is a computer-drawn model in perspective of the (FeTPP)₂N molecule as it exists in the crystal.¹⁷ The molecule, with crystallographically required *D*₂₋₂₂₂ symmetry, has three

Table II. Thermal Parameters of the Atoms

Atom type	Anisotropic parameters (\AA^2) ^a					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.77 (3)	2.72 (3)	3.36 (3)	0.0	-0.05 (2)	0.0
N ₃	2.6 (2)	3.3 (2)	3.1 (2)	0.0	0.0	0.0
N ₁	3.2 (1)	3.1 (1)	3.7 (1)	-0.2 (1)	-0.1 (1)	0.2 (1)
N ₂	2.9 (1)	3.3 (1)	3.9 (1)	0.0 (1)	0.0 (1)	0.0 (1)
C _{a1}	3.6 (2)	3.9 (2)	3.7 (2)	-0.1 (1)	0.4 (1)	0.0 (1)
C _{a2}	3.5 (2)	3.2 (1)	3.7 (2)	0.3 (1)	-0.1 (1)	0.3 (1)
C _{a3}	3.6 (2)	3.1 (1)	3.9 (2)	0.3 (1)	-0.5 (1)	0.0 (1)
C _{a4}	3.1 (1)	4.0 (2)	4.3 (2)	0.3 (1)	0.3 (1)	0.2 (1)
C _{b1}	4.1 (2)	4.8 (2)	4.3 (2)	-0.3 (2)	0.5 (1)	0.6 (2)
C _{b2}	4.4 (2)	5.2 (2)	3.4 (2)	0.2 (2)	0.1 (1)	0.5 (1)
C _{b3}	3.5 (2)	5.2 (2)	4.7 (2)	-0.4 (1)	-0.4 (1)	-0.1 (2)
C _{b4}	3.0 (2)	6.1 (2)	4.6 (2)	-0.2 (1)	0.2 (1)	0.2 (2)
C _{m1}	3.6 (2)	3.1 (1)	3.7 (2)	0.2 (1)	-0.2 (1)	0.0 (1)
C _{m2}	3.2 (2)	4.1 (2)	4.4 (2)	0.1 (1)	0.2 (1)	0.3 (1)
C ₁	3.5 (2)	3.4 (2)	4.2 (2)	0.0 (1)	-0.4 (1)	0.3 (1)
C ₂	4.3 (2)	3.6 (2)	4.7 (2)	0.4 (1)	-0.2 (2)	0.2 (1)
C ₃	4.3 (2)	5.7 (2)	5.2 (2)	0.4 (2)	-0.8 (2)	1.2 (2)
C ₄	5.7 (2)	7.5 (3)	4.7 (2)	-0.6 (2)	-1.6 (2)	-0.2 (2)
C ₅	6.4 (2)	6.7 (3)	5.4 (2)	0.5 (2)	-0.7 (2)	-1.9 (2)
C ₆	4.7 (2)	5.1 (2)	4.9 (2)	1.1 (2)	-0.9 (2)	-0.7 (2)
C ₇	3.3 (2)	6.3 (2)	4.1 (2)	0.2 (2)	0.1 (1)	-0.5 (2)
C ₈	5.7 (2)	7.3 (3)	7.2 (3)	-0.3 (2)	2.0 (2)	0.1 (2)
C ₉	5.9 (3)	10.8 (4)	8.1 (3)	-1.4 (3)	3.1 (2)	-0.5 (3)
C ₁₀	4.2 (2)	13.2 (5)	8.1 (3)	1.2 (3)	2.0 (2)	-1.8 (3)
C ₁₁	5.3 (3)	11.3 (4)	8.9 (4)	4.0 (3)	0.8 (3)	0.3 (3)
C ₁₂	4.5 (2)	8.6 (3)	6.4 (3)	2.2 (2)	1.0 (2)	1.3 (2)
Cl ₁	13.7 (3)	17.0 (2)	9.7 (2)	-3.7 (2)	0.4 (2)	-0.1 (2)
Cl ₂	20.3 (6)	38.1 (7)	13.2 (4)	8.5 (6)	1.2 (4)	5.8 (5)

^a Numbers in parentheses are the estimated standard deviations. The B_{ij} are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

required twofold axes which pass through the bridging nitrogen atom; two are perpendicular to the FeNFe axis and the third is along the FeNFe axis. This third twofold axis leads to the rigorous requirement that the Fe-N-Fe angle is 180.0° , and that the two porphinato cores of the oligomer are exactly parallel. The D_2 symmetry also requires that only one quarter of the oligomer (one half of a porphyrin moiety) is structurally unique. Figure 1 shows, in addition, that the upper and lower porphinato skeletons are in a staggered configuration that corresponds, crudely, to 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 twist angle, as measured by the dihedral angle that is bisected by a required twofold axis perpendicular to the FeNFe axis, is 58.3° .

Also shown in Figure 1 is the numbering system used for the structurally unique peripheral phenyl groups of the molecule; the scheme used for the unique carbon and nitrogen atoms of the core is shown in Figure 2. Individual bond lengths and angles in the porphine skeleton are listed in Table III. The dimensional variation in bond lengths and angles of chemically analogous bond types differ immaterially from fourfold geometry. Using C_a and C_b to denote the respective α - and β -carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for a phenyl carbon atom that is bonded to the core, the averaged bond lengths (Table III) in the porphine skeleton are $N-C_a = 1.381$ (3,5), $C_a-C_m = 1.386$ (5,5), $C_a-C_b = 1.436$ (3,5), $C_b-C_b = 1.348$ (6,6), and $C_m-C_p = 1.495$ (0,5) \AA , wherein the first number in parentheses following each averaged length is the mean deviation in units of 0.001 \AA and the second is the value of the estimated standard deviation for an individually determined length. The averaged values of bond angles are $C_aNC_a = 105.6$ (1,3), $NC_aC_b = 110.0$ (3,3), $NC_aC_m = 125.5$ (3,3), $C_aC_bC_b = 107.2$ (2,3), $C_aC_mC_a = 122.6$ (5,3), and $C_aC_mC_p = 118.6$ (9,3) $^\circ$.

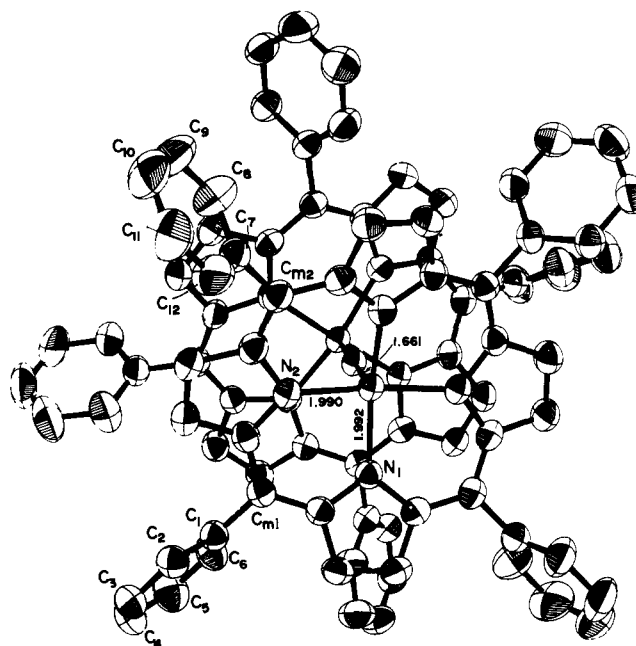


Figure 1. Computer-drawn model in perspective of the $(\text{FeTPP})_2\text{N}$ molecule. The symmetry unique atoms of the peripheral phenyl groups are identified.

The dihedral angles between the plane of the porphinato core and the plane of the two structurally unique phenyl groups are 54.0 and 65.4° . The averaged value of the internal angles in the phenyl groups is 120.0 (7,5) $^\circ$. The individual C-C bond distances in the phenyl rings of tetraphenylporphyrin derivatives are generally foreshortened from the standard 1.397- \AA distance owing to the complex thermal motion of these pe-

Table III. Bond Distances and Angles in the (FeTPP)₂N Molecule^a

A. Bond Distances					
Type	Length, Å	Type	Length, Å	Type	Length, Å
Fe-N ₃	1.6605 (7)	N ₂ -C _{a4}	1.382 (5)	C _{a3} -C _{b3}	1.436 (5)
Fe-N ₁	1.992 (3)	C _{a1} -C _{m2} ^b	1.388 (5)	C _{a4} -C _{m2}	1.385 (5)
Fe-N ₂	1.990 (3)	C _{a1} -C _{b1}	1.433 (5)	C _{a4} -C _{b4}	1.433 (5)
N ₁ -C _{a1}	1.379 (4)	C _{a2} -C _{m1}	1.396 (5)	C _{m1} -C ₁	1.495 (5)
N ₁ -C _{a2}	1.376 (5)	C _{a2} -C _{b2}	1.443 (5)	C _{m2} -C ₇	1.495 (5)
N ₂ -C _{a3}	1.386 (5)	C _{a3} -C _{m1}	1.377 (5)	C-Cl ₁	1.654 (11)
C _{b1} -C _{b2}	1.341 (5)	C _{b3} -C _{b4}	1.354 (6)	C-Cl ₂	1.775 (12)

B. Bond Angles			
Angle	Deg	Angle	Deg
N ₃ FeN ₁	101.54 (8)	N ₂ C _{a4} C _{m2}	125.1 (3)
N ₃ FeN ₂	96.86 (8)	N ₂ C _{a4} C _{b4}	110.1 (3)
N ₁ FeN ₂	88.4 (1)	C _{m2} C _{a4} C _{b4}	124.6 (3)
N ₁ FeN ₂ ' ^b	88.9 (1)	C _{a2} C _{m1} C _{a3}	122.2 (3)
N ₁ FeN ₁ ' ^b	156.9 (1)	C _{a2} C _{m1} C ₁	117.2 (3)
N ₂ FeN ₂ ' ^b	166.3 (2)	C _{a3} C _{m1} C ₁	120.5 (3)
C _{a1} N ₁ C _{a2}	105.5 (3)	C _{a4} C _{m2} C _{a1} ' ^b	123.1 (3)
C _{a3} N ₂ C _{a4}	105.7 (3)	C _{a4} C _{m2} C ₇	118.6 (3)
N ₁ C _{a1} C _{m2} ' ^b	125.4 (3)	C _{a1} 'C _{m2} C ₇	118.3 (3)
N ₁ C _{a1} C _{b1}	110.3 (3)	C _{a1} C _{b1} C _{b2}	106.8 (3)
N ₁ C _{a2} C _{m1}	125.8 (3)	C _{a3} C _{b3} C _{b4}	107.3 (3)
N ₁ C _{a2} C _{b2}	110.2 (3)	C _{a4} C _{b4} C _{b3}	107.2 (3)
C _{m1} C _{a2} C _{b2}	124.0 (3)	FeN ₁ C _{a1}	127.8 (2)
N ₂ C _{a3} C _{m1}	125.7 (3)	FeN ₁ C _{a2}	127.2 (2)
N ₂ C _{a3} C _{b3}	109.3 (3)	FeN ₂ C _{a3}	125.6 (2)
C _{m1} C _{a3} C _{b3}	124.7 (3)	FeN ₂ C _{a4}	127.4 (2)
C _{a2} C _{b2} C _{b1}	107.6 (3)	C _{m2} 'C _{a1} C _{b1}	124.2 (3)

^a Numbers in parentheses are the estimated standard deviations. ^b Primed symbol denotes an atom related to the unique atom by the twofold axis.

ripheral groups; the average C-C distance in (FeTPP)₂N is 1.379 (11,8) Å.

Figure 2, a formal diagram of the porphinato core, shows the perpendicular displacement (in units of 0.01 Å) of each unique atom from the mean plane of the core. The labeled atoms in the lower left of Figure 2 have the same displacement as the twofold related atoms in the upper right of the diagram. The skeletal configuration of the core, which will be discussed later, is seen to be best described as a quasi-*D*_{2d} or *S*₄ ruffling. As is usual, local flatness is maintained in the pyrrole rings.

The (FeTPP)₂N molecule, with its bridging nitrogen atom, is analogous to the well characterized μ -oxo-bis[porphinatoiron(III)] derivatives;⁴⁻⁶ we will compare the two classes of bridged species whenever appropriate. An obvious difference is the formal oxidation state of the iron atoms; in the neutral μ -oxo-bis[porphinatoiron] derivatives, both iron atoms are in the +3 oxidation state. In neutral (FeTPP)₂N, however, the usual assignment of the bridging nitrogen atom as N³⁻ leads to an average oxidation state of +3 1/2 for the iron atoms or (FeTPP)₂N has one fewer electron than the μ -oxo-iron derivatives. The high formal oxidation state of the iron atoms in (FeTPP)₂N is consistent with the known ability of the nitrido ligand to stabilize high oxidation states.³ It is important to note that the x-ray studies and Mössbauer studies² suggest that the two iron atoms in (FeTPP)₂N are equivalent. The Mössbauer peaks are sharp and only at liquid He temperatures is there any evidence for line broadening that could suggest inequivalence of the two iron atoms. Another important difference is the magnetic susceptibility. (FeTPP)₂N has a temperature-independent moment with $\mu = 2.04 \mu_B$ per oligomer.² (FeTPP)₂O, on the other hand, has a temperature-dependent moment¹⁸ consistent with an antiferromagnetically coupled system.

The question of the electronic ground state of the iron atoms in the bridged (FeTPP)₂N molecule is an interesting one. The

μ -oxo-bis[$\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III)] oligomer is described¹⁹ as two antiferromagnetically coupled $S = 5/2$ ions ($J = 309 \text{ cm}^{-1}$). The (FeTPP)₂N system could be described similarly (with a much larger value of J). However, the temperature independence of the magnetic moment precludes the assignment of the spin states of the individual iron atoms. The Mössbauer data also do not provide an unambiguous assignment of the spin state. It might thus be hoped that the structural data would provide some insight into this question. We will therefore compare the structural parameters of (FeTPP)₂N with those for the various classes of iron porphyrins.

The bridging Fe-N distance of 1.6605 (7) Å is considerably shorter than the 1.763 (1) Å Fe-O distance observed in (FeTPP)₂O.⁴ Similar Fe-O distances have been observed for two other μ -oxo-bis[porphinatoiron(III)] derivatives.^{5,6} The shorter Fe-N distance is consistent with the increased negative formal charge on the bridging atom. Furthermore, the N³⁻ ligand is regarded as a stronger π donor than the O²⁻ ligand, consistent with the infrared data for (FeTPP)₂N and (FeTPP)₂O.²

(FeTPP)₂N appears to be the first reported example of a first row complex with a bridging nitrido ligand; consequently, no comparison can be made with first row transition elements but only with second and third row derivatives. We compare first a ruthenium complex with a linear symmetric nitrido bridge, M₃[Ru₂NC₁₈(H₂O)₂], where Ru-N = 1.720 (4)²⁰ or 1.725 (5) Å²¹ for M = K⁺ or NH₄⁺, respectively. Note that ruthenium has a formal oxidation state of +4 or +1/2 unit higher than that of (FeTPP)₂N. Other bridged nitrido complexes are unsymmetrical. Polymeric {K₂[ReN(NC)₄·H₂O]_n has a linear Re-N...Re bridge with Re-N = 1.53 and 2.44 Å.²² Tetrameric MoNCl₃ has nonlinear bridges (Mo-N-Mo = 1.78.1 (4) and 167.3 (6)⁹) with Mo-N = 1.67 (1), 1.64 (1), 2.14 (1), and 2.20 (1) Å.²³ A series of mononuclear rhen-

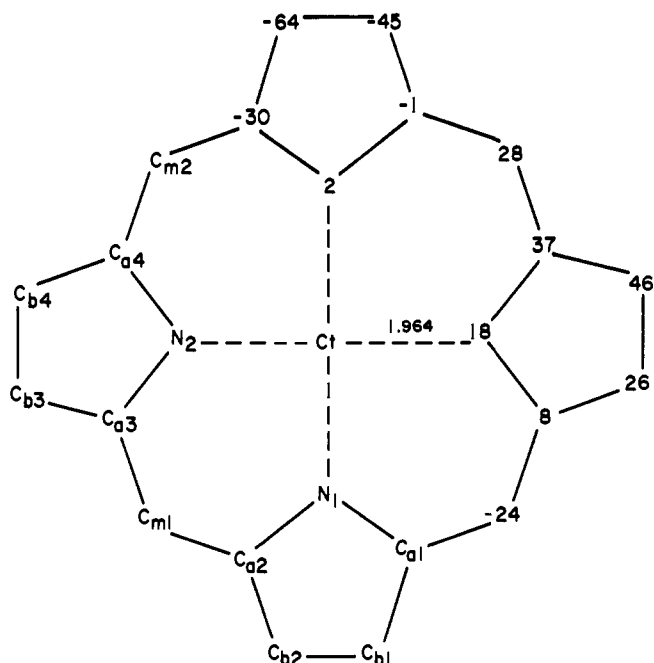


Figure 2. Formal diagram of the porphinato skeleton in $(\text{FeTPP})_2\text{N}$. On the lower left-hand side of the diagram, the numbering scheme for the atoms is displayed. On the upper right-hand half of the diagram, the special symbol identifying each atom is replaced by the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the porphinato core. One of the crystallographically required twofold axis passes through Ct and is perpendicular to the plane of the diagram. Accordingly, atoms in the lower left-hand side of the diagram have the same displacement from the mean plane as their twofold related equivalents.

ium(V) and osmium(VI) nitrido complexes have also been characterized. The Re–N bond length in a series of five- and six-coordinate complexes varies from 1.60 to 1.79 Å,²⁴ while the Os–N bond lengths are 1.600–1.614 Å.²⁵ These data further underscore the strong Fe–N bridging interaction.

The two iron–porphine nitrogen bond distances are sensibly equivalent with $\text{Fe}-\text{N}_1 = 1.992$ (3) and $\text{Fe}-\text{N}_2 = 1.990$ (3) Å. These bond distances are considerably shorter than the 2.087 Å Fe–N bond distance found for $(\text{FeTPP})_2\text{O}$,⁴ the 2.08-Å value for $[\text{Fe}(\text{Proto IX DME})_2\text{O}]$,⁶ or the 2.065-Å value for $(\text{FeODM})_2\text{O}$.⁵ Figure 3 provides diagrams in perspective of the five-coordination group around each iron atom in the oligomeric $(\text{FeTPP})_2\text{N}$ and $(\text{FeTPP})_2\text{O}$ molecules; the diagram for each has been slightly idealized by using bond parameters averaged in agreement with C_{4v} symmetry. The quasi- D_{2d} ruffling of the porphinato cores in $(\text{FeTPP})_2\text{N}$ contributes materially to the short Fe–N bond distances. It appears likely that the ruffling of the porphinato core and the concomitant short Fe–N lengths is a real property of the complex and not a consequence of crystal packing. Crystals of $(\text{FeTPP})_2\text{N}$ as the xylene solvate or the chloroform solvate display conformations of the core (and Fe–N bond distances) that differ immaterially from each other. Moreover, crystals obtained from methylene chloride or benzene, although too small for x-ray examination, display morphologies closely similar to crystals obtained from xylene or chloroform; it appears to be a reasonable presumption that these derivatives would also have the same molecular structure. It is important to note that a D_{2d} ruffling of the core provides a means²⁶ for obtaining short M–N bonds, but does not absolutely require this. Thus in $(\text{FeODM})_2\text{O}$,⁵ where a substantial D_{2d} ruffling of the cores is enforced by the steric congestion of ten peripheral alkyl groups, the coordination group distances are still those expected for the high-spin iron(III) atom.

The iron atom is displaced 0.32 Å from the plane defined

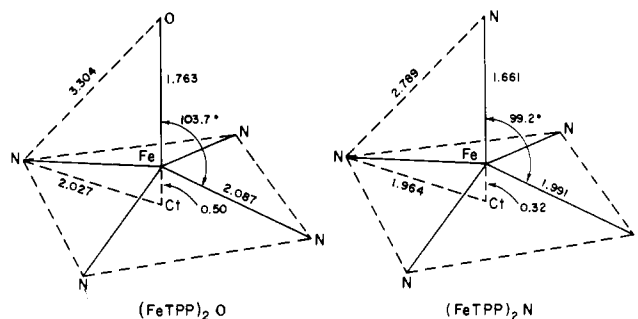


Figure 3. Slightly idealized (C_{4v}) diagram of the five-coordination group around each iron(III) atom in $(\text{FeTPP})_2\text{O}$ and $(\text{FeTPP})_2\text{N}$ molecules.

by the four porphinato nitrogen atoms and 0.41 Å from the mean plane of the core; the corresponding displacements in $(\text{FeTPP})_2\text{O}$ are 0.50 and 0.54 Å. Thus, the coordination group parameters of $(\text{FeTPP})_2\text{N}$ are seen to diverge substantially from those of the μ -oxo-bis(porphinatoiron(III)) derivatives, or indeed those of any of the five-coordinate high-spin iron(III) derivatives.²⁷ Rather, the $(\text{FeTPP})_2\text{N}$ parameters are more akin to those observed for low-spin six-coordinate iron(III) porphyrins.^{28–30} The average Fe–N bond distance of 1.990 Å for three different derivatives of this class is essentially identical with that of $(\text{FeTPP})_2\text{N}$. The iron atom in the six-coordinate derivatives is virtually centered in the porphyrin plane; some displacement of the metal atom out-of-plane towards a *single* axial ligand is to be expected from simple minimization of nonbonded contacts. It may be remarked that the porphine nitrogen–nitrido nitrogen atom contacts are a tight 2.789 Å despite the out-of-plane displacement of the iron atom. The only low-spin five-coordinate iron porphyrin is an iron(II) derivative, ONFeTPP ,³¹ in this derivative the iron atom is displaced 0.211 Å out-of-plane.

If the unpaired, delocalized electron in $(\text{FeTPP})_2\text{N}$ is in an orbital with substantial nitrido character, the electron configuration of the iron atoms approaches a d^4 configuration, isoelectronic with manganese(III). Hence, an alternative view of the structure of $(\text{FeTPP})_2\text{N}$ is that it should be comparable to those of the five-coordinate manganese(III) porphyrins rather than an iron(III) porphyrin. Five-coordinate manganese(III) porphyrins,^{32–34} which are all high-spin derivatives, have the metal atom displaced by 0.23–0.27 Å and basal Mn–N bond distances of 2.005–2.02 Å.³⁵ Clearly, these structural parameters agree best with those of $(\text{FeTPP})_2\text{N}$.

Thus, the question of whether the iron atoms in $(\text{FeTPP})_2\text{N}$ have a high-spin or a low-spin ground state is not clearly answered from structural data. If comparisons are limited solely to iron(III) porphyrins, the structural data are more consistent with structures of low-spin derivatives and suggest a low-spin ground state for $(\text{FeTPP})_2\text{N}$. When comparisons with high-spin manganese(III) porphyrins are included, a high-spin ground state does not appear at all improbable.

The addition of an electron to $(\text{FeTPP})_2\text{N}$ would yield a species isoelectronic with $(\text{FeTPP})_2\text{O}$. How closely the properties of a reduced μ -nitrido-bis[iron porphyrin] would approach those of the μ -oxo species is under active investigation.

The two porphinato cores in $(\text{FeTPP})_2\text{N}$ are separated by ~ 4.15 Å, or ~ 0.2 Å less than in the μ -oxo oligomers. The $(\text{FeTPP})_2\text{N}$ molecules are well separated in the crystal. The closest intermolecular contacts are with the chloroform solvate and range from 3.5 Å upwards.

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Supplementary Material Available. Table IV (atomic coordinates of the xylene solvate), Table V (bond distances and angles for the xylene solvate), and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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The Crystal Structure of 1-Decyl α -D-Glucopyranoside: A Polar Bilayer with a Hydrocarbon Subcell¹

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Abstract: A bilayer assembly of long polar molecules has been observed in the crystal structure of 1-decyl α -D-glucopyranoside, C₁₆H₃₂O₆. Alternating regions of polar and nonpolar groups result from the close packing of fully extended hydrocarbon chains between hydrogen-bonding layers of glucose rings. The chain packing, in which the planes of carbon-carbon bonds are parallel and equally spaced, is described by a new type of monoclinic subcell containing two CH₂ groups per asymmetric unit; its space group is $P2_1/m$ with $a_s = 4.64 \text{ \AA}$, $b_s = 7.63 \text{ \AA}$, $c_s = 2.54 \text{ \AA}$, and $\gamma_s = 90^\circ$; the volume per CH₂ group is 22.4 \AA^3 . The main cell symmetry is $P2_1$ with $a = 5.153 \text{ \AA}$, $b = 7.624 \text{ \AA}$, $c = 22.125 \text{ \AA}$, $\beta = 90.95^\circ$, and $Z = 2$; b is parallel to b_s . The structure was solved by direct phasing methods and least-squares refined to a residual of 9.3%.

Introduction

The synthesis of a series of n -alkyl derivatives of glucose, among them ethyl, n -hexyl, n -octyl, and n -decyl glucopyranoside, has been reported.² These uncharged polar molecules may serve as models for polar membrane components of similar topography. They share a number of properties with glyco- and phospholipids and, while simpler compounds, have been used for a number of physical studies. From a study of apparent molal volumes, Brown et al.² concluded that the alkyl glucopyranosides form micelles in aqueous solution; micelle formation was strongly dependent upon the structure of the sugar in that the β isomer was more soluble and formed micelles less readily than the α isomer. An investigation of the mechanism of micelle formation in the n -alkyl glucose derivatives ($n = 6$

to 10) has been carried out by Paul.³ Recently, the solid n -alkyl pyranosides have been observed to form a thermotropic liquid crystal phase above 76 °C.⁴

Five of the homologous members of the n -alkyl series have been crystallized,³ and we have now determined the crystal and molecular structure of 1-decyl α -D-glucopyranoside (**1**). The

