

# Stereochemistry of Low-Spin Iron Porphyrins. II.

## Bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(II)<sup>1</sup>

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**Abstract:** Bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(II) crystallizes in the triclinic system, space group  $P\bar{1}$ . The unit cell has  $a = 11.113$ ,  $b = 12.071$ , and  $c = 9.797$  Å,  $\alpha = 105.67$ ,  $\beta = 113.70$ , and  $\gamma = 101.02^\circ$  ( $\lambda = 0.71069$  Å), and contains one molecule; calculated and experimental densities are 1.278 and 1.26 (1) g/ml, respectively, at  $20 \pm 1^\circ$ . Measurement of diffracted intensities employed  $\theta$ - $2\theta$  scanning with Zr-filtered Mo  $K\alpha$  radiation on a Picker four-circle diffractometer. Of the 5297 independent reflections scanned for  $(\sin \theta)/\lambda \leq 0.648$  Å<sup>-1</sup>, the 4267 retained as observed were employed for the determination and anisotropic least-squares refinement of the 277 structural parameters. With this data/parameter ratio of 15.4, the respective conventional and weighted discrepancy factors were 0.084 and 0.090. The octahedral FeN<sub>6</sub> coordination group in the centrosymmetric ( $C_2$ ) molecule approximates dimensionally to full tetragonal symmetry. Equatorial Fe-N bond lengths average to 2.004 Å, with a mean deviation of 0.004 Å and an esd for an individual determination of 0.003 Å. Extension of the axial Fe-N bond length to 2.127 (3) Å and the accompanying opening of the FeNC bond angles at piperidine nitrogen to 116.8 (2)° are attributable to unavoidable steric interactions between nitrogen atoms of the porphinato core and the piperidine hydrogen atoms contiguous thereto. Bond distances and angles of any specified chemical class in the porphinato core display quite trivial departures from effective  $D_{4h}$  symmetry

Both the diversity and the biological importance of iron porphyrin stereochemistry are adequately stressed in the introductory paragraphs of the accompanying report<sup>2</sup> on the crystal and molecular structures of the low-spin bis(imidazole)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III) chloride (written hereinafter as [Im<sub>2</sub>-FeTPP]+Cl<sup>-</sup>).<sup>3</sup> With the sole exception of the [Im<sub>2</sub>-FeTPP]+Cl<sup>-</sup> study, all earlier X-ray analyses of crystalline structure for iron porphyrins have been limited to the high-spin iron(III) series, whereas interest in the mechanism of the reversible oxygenation of hemoglobin<sup>4,5</sup> tends to focus attention on the stereochemical behavior of the iron(II) porphyrins, equally on that of the low- and the high-spin classes.<sup>2</sup>

The limited scope of the earlier X-ray analyses is due entirely to the reluctance of the ferrous porphyrins (and of the low-spin ferric porphyrins) to yield single crystals suitable for structure determination. Thus, the bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(II) (written as Pip<sub>2</sub>FeTPP)<sup>3</sup> of this report is scarcely the ideal choice of a ferrous porphyrin for structure analysis; piperidine is much less interesting as an axial ligand of the iron(II) atom than are imidazole, carbon monoxide, and, of course, molecular oxygen. Furthermore, the preparative chemistry of the bis(piperidine)iron(II) porphyrins is not well understood,<sup>6</sup> and we remain unsure whether our success in obtaining a single crystal of (Pip)<sub>2</sub>FeTPP suitable for X-ray structural analysis is primarily attributable to judicious planning or to happenstance. Preparative and other

complications notwithstanding, this triclinic crystal provided X-ray data superior in quality and scope to that obtained in any of the earlier studies of iron porphyrins, as evidenced by the objectively estimated precision of the derived structural parameters and by generally trivial variations in bond parameters of the same chemical type.

### Experimental Section

Microcrystalline Pip<sub>2</sub>FeTPP, dark blue by reflected light, was initially prepared following Epstein, *et al.*,<sup>6</sup> with the added precaution (seemingly unnecessary) that all operations were carried out under a nitrogen atmosphere. Piperidine was added to a boiling solution of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatochloroiron(III) (ClFeTPP) in methylene chloride, with subsequent addition of methanol to further crystallization of the product. The chemical analysis of this product was in reasonable agreement with the theoretically expected composition, as also with that previously reported<sup>6</sup> for Pip<sub>2</sub>FeTPP. All attempts to induce growth of single crystals large enough for X-ray analysis by recrystallization of the microcrystalline preparation from various solvents were unsuccessful.

The preparative procedure was then modified as follows. Br-FeTPP was substituted for ClFeTPP as a reactant, the proportion of piperidine was increased, and, following reaction, a stream of nitrogen was used to evaporate some of the solvent (methylene chloride). The resulting solution, presumed to become supersaturated with respect to Pip<sub>2</sub>FeTPP upon cooling, was set aside (still under an atmosphere of nitrogen). Upon examination about a month later, it was seen that the solution had been open to the atmosphere for a considerable period. Adhering to one another and to the side of the container were unidentified colorless crystals and deeply colored porphyrin crystals mixed together in the proportions of ~1:1 by volume. Under a microscope, by transmitted light, the porphyrin crystals had a definite red coloration. A single crystal of the porphyrin, separated as cleanly as was feasible under the microscope from the adherent colorless material, was immediately subjected to X-ray examination by photographic techniques. It proved to be a quite satisfactory specimen for the diffractometric recording of quantitative data that led, as detailed below, to the precise determination of the Pip<sub>2</sub>FeTPP structure.

The internally consistent results of the determination and refinement of structure stood in contrast with the unsatisfactorily low value obtained for the carbon content from two microanalyses of mechanically separated samples of the porphyrin crystals. (Anal. Calcd for C<sub>54</sub>H<sub>50</sub>N<sub>6</sub>Fe: C, 77.32; H, 6.01; N, 10.02. Found: C, 73.12; H, 6.38; N, 9.91). For this and other reasons to be discussed later, a number of other physical measure-

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

(3) The parent tetraphenylporphine is written as H<sub>2</sub>TPP; see Figures 1 and 2 for diagrams of the carbon-nitrogen skeleton.

(4) Cf. M. F. Perutz, *Nature (London)*, **228**, 726, 734 (1970).

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

(6) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967). There seems to be general agreement on this point among porphyrin chemists.

ments were carried out on mechanically separated samples of the porphyrin crystals. These latter were generally washed prior to measurement with ethanol, a considerably better solvent for the colorless material than for the porphyrin.

The Mossbauer spectrum from a small sample of the ethanol-washed porphyrin was recorded through the kindness of E. S. Kostiner and J. J. Steger. They report that values of the isomer shift and the quadrupole splitting at liquid nitrogen temperature are in reasonable agreement with those reported by Epstein, *et al.*<sup>6</sup>

Magnetic susceptibility measurements, utilizing a Faraday balance, were kindly made by J. L. Krause on a 2.325-mg ethanol-washed sample at 78, 196, and 296°K. The reliability of the effective moment of  $\sim 1.2$  BM thus obtained is put in doubt by comparing the magnitudes of the measured paramagnetic susceptibility ( $\sim 4 \times 10^{-7}$  g<sup>-1</sup> at 296°K) with the diamagnetic correction ( $\sim 5 \times 10^{-7}$  g<sup>-1</sup>). Consequently, electron paramagnetic resonance (epr) spectra were kindly recorded by W. S. Glaunsinger for the same sample at 14.2, 14.6, 38.0, and 296°K. No epr signal was detected at any temperature,<sup>7</sup> suggesting the trivial magnitude, if not the absence, of any paramagnetism. Possible sources of a small paramagnetism are considered in the Discussion.

The crystal used for the recording of the X-ray data, dimensioned approximately as  $0.175 \times 0.25 \times 0.275$  mm, was mounted on a glass fiber with silicone adhesive. Detailed photographic study together with the experimentally measured density, 1.26 (1) g/ml by flotation at the ambient laboratory temperature of  $20 \pm 1^\circ$ , led to a triclinic unit cell containing a single molecule of Pip<sub>2</sub>FeTPP. Lattice constants,  $a = 11.113$  (3),  $b = 12.071$  (3) and  $c = 9.797$  (3) Å, and  $\alpha = 105.67$  (2),  $\beta = 113.70$  (1), and  $\gamma = 101.02$  (2)° ( $\lambda = 0.71069$  Å), came from a least-squares refinement<sup>8</sup> that utilized the setting angles of 42 reflections given by the automatic centering routine supplied with the Picker FACS-I diffractometer. These constants then led to a calculated density at  $20 \pm 1^\circ$  of 1.278 g/ml for the crystal.

Intensity data were measured on the Picker FACS-I diffractometer using the  $\theta$ - $2\theta$  scanning technique with Zr-filtered Mo K $\alpha$  radiation at a take-off angle of  $\sim 2^\circ$ . The range of each scan, taken at  $1^\circ/\text{min}$ , consisted of the estimated base width of  $1.85^\circ$  at  $2\theta = 0$  and an increment,<sup>9</sup>  $\Delta(2\theta) = (0.692 \tan \theta)^\circ$ , to allow for spectral dispersion; background counts, each of 40-sec duration, were taken at both limits of the scan. The intensities of three standard reflections, monitored periodically at the interval of 50 reflections, displayed no trend with time during collection of 80% of the data [ $(\sin \theta)/\lambda \lesssim 0.602$  Å<sup>-1</sup>], but rather fluctuations from the average amounting to a mean deviation of 2.6%. A recentering of the crystal sufficed to maintain this intensity pattern for the standard reflections during the recording of the final 20% of the data; there was no evidence of crystal deterioration.

With the cited dimensions of the crystal and a linear absorption coefficient of only  $0.40$  mm<sup>-1</sup> for Mo K $\alpha$  radiation, the maximum error in any measured intensity resulting from the neglect of absorption corrections was seen to be  $< 2\%$ , smaller, that is, than the variations in intensity attributable to imperfect stabilization of the equipment. 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 ( $Lp$ ). Standard deviations were calculated from  $\sigma_F^2 = (Ct + k^2B)/4|F_o|^2(Lp)^2$ , wherein  $Ct$  is the count of the scan,  $k$  is the ratio of scanning time to background counting time, and  $B$  is the total background count. Some 1030 scanned reflections having  $|F_o| < 2\sigma_F$  were taken to be unobserved, leaving 4267 independent  $|F_o|$  data in the range  $(\sin \theta)/\lambda \lesssim 0.648$  Å<sup>-1</sup> for the determination and refinement of structure.

Structure determination and refinement proceeded smoothly to a convincing conclusion from the initial assumption of the centrosymmetric  $P\bar{1}$  as the space group.<sup>10</sup> With the iron atom at a center

(7) The epr spectrum was run on an X-band spectrometer in the region 0–5 kG with a frequency of 9.2250 GHz. Microwave powers ranging from 130 mW to 100  $\mu$ W were used. Double modulation recording was utilized in conjunction with second-derivative recording at modulation frequencies of 100 and 1 kHz. Second derivative detection was used to avoid (frequency)<sup>-1</sup> noise and drift from the spectrometer which employed a balanced mixer bridge configuration and 1N23F crystals as detectors.

(8) Use was made of the Pick II computer program, a modification in this laboratory of W. C. Hamilton's Mode I program.

(9) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966, p 79.

(10) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-ray Crystallography, Vol. I. Symmetry Groups," 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 75.

Table I. Atomic Coordinates in the Unit Cell

Atom type	Coordinates with standard deviations <sup>a</sup>		
	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z
Fe	0	0	0
N <sub>1</sub>	204 (3)	-1591 (2)	-1004 (3)
N <sub>2</sub>	978 (3)	-51 (2)	2187 (3)
N <sub>3</sub>	-1937 (3)	-992 (3)	-272 (4)
C <sub>1</sub>	2136 (4)	493 (4)	4968 (4)
C <sub>2</sub>	2323 (4)	-550 (4)	4298 (5)
C <sub>3</sub>	274 (5)	-3237 (4)	-2822 (5)
C <sub>4</sub>	990 (4)	-3234 (4)	-1342 (5)
C <sub>5</sub>	-970 (4)	-1880 (3)	-3884 (4)
C <sub>6</sub>	1596 (4)	-1907 (3)	1462 (4)
C <sub>7</sub>	1306 (4)	813 (3)	3663 (4)
C <sub>8</sub>	1606 (4)	-889 (3)	2566 (4)
C <sub>9</sub>	-218 (4)	-2212 (3)	-2622 (4)
C <sub>10</sub>	940 (4)	-2221 (3)	-206 (4)
C <sub>11</sub>	-1494 (4)	-2750 (3)	-5582 (4)
C <sub>12</sub>	-1023 (5)	-2444 (4)	-6600 (5)
C <sub>13</sub>	-1578 (5)	-3258 (4)	-8191 (5)
C <sub>14</sub>	-2620 (5)	-4352 (4)	-8786 (5)
C <sub>15</sub>	-3079 (5)	-4676 (4)	-7789 (6)
C <sub>16</sub>	-2504 (5)	-3879 (4)	-6188 (5)
C <sub>17</sub>	2386 (4)	-2684 (3)	2109 (4)
C <sub>18</sub>	3826 (5)	-2303 (4)	2785 (7)
C <sub>19</sub>	4575 (5)	-3002 (5)	3413 (7)
C <sub>20</sub>	3902 (5)	-4103 (4)	3338 (5)
C <sub>21</sub>	2463 (6)	-4503 (4)	2672 (6)
C <sub>22</sub>	1710 (5)	-3794 (4)	2061 (6)
C <sub>23</sub>	-3079 (5)	-1724 (5)	-1948 (6)
C <sub>24</sub>	-4340 (5)	-2552 (5)	-2061 (6)
C <sub>25</sub>	-4914 (5)	-1832 (5)	-1074 (7)
C <sub>26</sub>	-3760 (5)	-1148 (5)	645 (6)
C <sub>27</sub>	-2462 (5)	-336 (4)	755 (6)

<sup>a</sup> Figures in parentheses are the estimated standard deviations.

of inversion, taken as the origin, the positions of the 30 carbon and nitrogen atoms in the asymmetric unit of structure (just half of the Pip<sub>2</sub>FeTPP molecule) were readily developed by Fourier syntheses<sup>11</sup> in successive approximation. Full-matrix least-squares refinement<sup>12</sup> of the coordinates and isotropic thermal parameters of the 31 atoms using the larger part of the  $|F_o|$  data with unit weighting was followed by fully anisotropic block-diagonal refinement<sup>13,14</sup> using all of the 4267 independent data with empirical weights,<sup>14</sup>  $w = 1/\sigma^2$ , calculated from

$$\sigma = \sum_0^3 a_n |F_o|^n$$

the  $a_n$  being coefficients from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n |F_o|^n$$

Such weighting appeared to be particularly appropriate because the precise measurement of intensities for the low-angle reflections was hampered by the rather large and variable background, the presumed consequence of superficial contamination of the Pip<sub>2</sub>FeTPP crystal by adhering residue of the colorless second phase described above. The value of the conventional  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  attained at this stage was 0.097.

A difference Fourier synthesis then revealed residual concentrations of electron density that were appropriately located and, for the most part, large enough to be convincingly interpreted as

(11) Use was made of A. Zalkin's Fourier program, FORDAP. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections for anomalous dispersion in the form factor of the iron atom from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "OR-FLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(13) The program, REFINE, written by J. J. Park in this laboratory was employed. The function minimized was  $\Sigma w(|F_o| - s|F_c|)^2$ , wherein  $w$  is the weight and  $s$  is the scaling factor.

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

**Table II.** Thermal Parameters of the Atoms in the Crystal

Atom type	Anisotropic parameters ( $\text{\AA}^2$ ) with standard deviations <sup>a</sup>					
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Fe	2.56 (3)	1.95 (2)	1.88 (2)	1.04 (2)	0.88 (2)	0.70 (2)
N <sub>1</sub>	2.4 (1)	2.0 (1)	2.0 (1)	0.95 (9)	0.8 (1)	0.67 (9)
N <sub>2</sub>	2.6 (1)	1.9 (1)	2.2 (1)	1.0 (1)	1.0 (1)	0.79 (9)
N <sub>3</sub>	3.0 (1)	2.8 (1)	2.7 (1)	1.0 (1)	1.3 (1)	0.8 (1)
C <sub>1</sub>	3.8 (2)	2.3 (2)	2.4 (1)	1.5 (1)	1.1 (1)	1.0 (1)
C <sub>2</sub>	3.3 (2)	3.1 (2)	2.5 (2)	1.2 (1)	0.8 (1)	1.3 (1)
C <sub>3</sub>	4.0 (2)	3.0 (2)	3.0 (2)	1.9 (1)	1.5 (1)	0.8 (1)
C <sub>4</sub>	3.8 (2)	2.9 (2)	3.2 (2)	2.0 (1)	1.4 (1)	1.3 (1)
C <sub>5</sub>	2.8 (2)	2.1 (1)	2.3 (1)	0.8 (1)	1.2 (1)	0.6 (1)
C <sub>6</sub>	2.4 (1)	2.2 (1)	2.5 (1)	1.1 (1)	1.0 (1)	1.0 (1)
C <sub>7</sub>	2.8 (2)	2.3 (1)	2.1 (1)	1.0 (1)	1.0 (1)	0.8 (1)
C <sub>8</sub>	2.6 (1)	2.2 (1)	2.4 (1)	1.0 (1)	0.9 (1)	1.1 (1)
C <sub>9</sub>	2.9 (2)	2.1 (1)	2.5 (1)	1.1 (1)	1.3 (1)	0.7 (1)
C <sub>10</sub>	2.7 (1)	2.0 (1)	2.6 (1)	1.1 (1)	1.1 (1)	0.9 (1)
C <sub>11</sub>	2.6 (2)	2.3 (1)	2.6 (1)	1.1 (1)	1.2 (1)	0.7 (1)
C <sub>12</sub>	3.8 (2)	3.3 (2)	3.4 (2)	1.3 (1)	2.0 (2)	1.2 (1)
C <sub>13</sub>	5.3 (2)	4.5 (2)	3.4 (2)	2.8 (2)	2.7 (2)	1.8 (2)
C <sub>14</sub>	5.4 (2)	4.0 (2)	2.6 (2)	2.6 (2)	1.4 (2)	0.4 (2)
C <sub>15</sub>	4.3 (2)	2.7 (2)	4.0 (2)	0.6 (2)	1.4 (2)	0.0 (2)
C <sub>16</sub>	4.1 (2)	2.5 (2)	3.5 (2)	0.9 (1)	2.0 (2)	0.8 (1)
C <sub>17</sub>	3.0 (2)	2.4 (1)	2.4 (1)	1.3 (1)	1.1 (1)	0.9 (1)
C <sub>18</sub>	3.1 (2)	2.9 (2)	6.5 (3)	1.1 (1)	1.5 (2)	2.1 (2)
C <sub>19</sub>	3.0 (2)	4.2 (2)	6.6 (3)	1.7 (2)	0.8 (2)	2.1 (2)
C <sub>20</sub>	4.8 (2)	4.0 (2)	3.3 (2)	2.7 (2)	1.1 (2)	1.5 (2)
C <sub>21</sub>	5.6 (2)	3.7 (2)	5.5 (2)	2.6 (2)	2.9 (2)	2.9 (2)
C <sub>22</sub>	3.8 (2)	3.4 (2)	5.1 (2)	1.7 (2)	2.0 (2)	2.4 (2)
C <sub>23</sub>	3.7 (2)	4.9 (2)	3.1 (2)	-0.3 (2)	1.4 (2)	0.1 (2)
C <sub>24</sub>	3.7 (2)	5.0 (2)	4.0 (5)	-0.6 (2)	1.6 (2)	0.0 (2)
C <sub>25</sub>	3.5 (2)	5.0 (2)	5.8 (3)	0.9 (2)	2.1 (2)	2.1 (2)
C <sub>26</sub>	4.2 (2)	5.0 (2)	4.4 (2)	1.2 (2)	2.5 (2)	1.1 (2)
C <sub>27</sub>	4.2 (2)	3.8 (2)	4.5 (2)	0.7 (2)	2.7 (2)	0.4 (2)

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

**Table III.** Bond Lengths in the Coordination Group, Porphinato Skeleton, and Piperidine Ring<sup>a</sup>

Type	Length, $\text{\AA}$	Type	Length, $\text{\AA}$	Type	Length, $\text{\AA}$
Fe-N <sub>1</sub>	2.008 (3)	C <sub>2</sub> -C <sub>8</sub>	1.448 (5)	C <sub>6</sub> -C <sub>10</sub>	1.396 (5)
Fe-N <sub>2</sub>	2.000 (3)	C <sub>3</sub> -C <sub>4</sub>	1.344 (6)	C <sub>6</sub> -C <sub>17</sub>	1.497 (5)
Fe-N <sub>3</sub>	2.127 (3)	C <sub>3</sub> -C <sub>9</sub>	1.442 (5)	N <sub>3</sub> -C <sub>23</sub>	1.483 (6)
N <sub>1</sub> -C <sub>9</sub>	1.386 (4)	C <sub>4</sub> -C <sub>10</sub>	1.440 (5)	N <sub>3</sub> -C <sub>27</sub>	1.482 (6)
N <sub>1</sub> -C <sub>10</sub>	1.380 (4)	C <sub>5</sub> -C <sub>7'</sub>	1.394 (5)	C <sub>23</sub> -C <sub>24</sub>	1.502 (7)
N <sub>2</sub> -C <sub>7</sub>	1.388 (4)	C <sub>5</sub> -C <sub>9</sub>	1.398 (5)	C <sub>24</sub> -C <sub>25</sub>	1.533 (8)
N <sub>2</sub> -C <sub>8</sub>	1.383 (4)	C <sub>5</sub> -C <sub>11</sub>	1.501 (5)	C <sub>25</sub> -C <sub>26</sub>	1.506 (8)
C <sub>1</sub> -C <sub>2</sub>	1.350 (6)	C <sub>6</sub> -C <sub>8</sub>	1.395 (5)	C <sub>26</sub> -C <sub>27</sub>	1.526 (7)
C <sub>1</sub> -C <sub>7</sub>	1.446 (5)	C <sub>5</sub> -C <sub>11</sub> <sup>b</sup>	1.501 (5)	C <sub>6</sub> -C <sub>17</sub> <sup>b</sup>	1.497 (5)

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure. <sup>b</sup> Bond connecting the methine carbon atom to the phenyl group.

C-H bond densities. Hydrogen atoms were then fixed in theoretically calculated positions (C-H = 1.05  $\text{\AA}$  in the piperidine ligand, C-H = 1.0  $\text{\AA}$  otherwise), and hydrogen contributions,<sup>15</sup> with isotropic thermal parameters fixed at somewhat larger values than those of the associated carbon atoms, were included in further least-squares refinement. Such refinement, with minor adjustment of the empirical weighting function to take account of the hydrogen contributions, led to  $R_1 = 0.084$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.090$ ; the error of fit was 1.50. The principal effect of the adjustment in the weighting scheme was to increase slightly (from 0.69 to 0.86 electron/ $\text{\AA}^3$ ) the residual peak of electron density at the origin (the iron atom) in the Fourier difference synthesis. The quasi-absolute value of the peak density observed for the iron atom was  $\sim 73$  electrons/ $\text{\AA}^3$ . No residual peak in the difference synthesis having a peak density as low as 0.3 electron/ $\text{\AA}^3$

(15) The atomic form factor used for hydrogen was from C. H. MacGillivray, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-ray Crystallography, Vol. III. Physical and Chemical Tables," 2nd ed, The Kynoch Press, Birmingham, England, 1968.

**Table IV.** Bond Angles in the Coordination Group, Porphinato Skeleton, and Piperidine Ring<sup>a</sup>

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N <sub>1</sub> FeN <sub>2</sub>	90.2 (1)	C <sub>4</sub> C <sub>3</sub> C <sub>9</sub>	106.8 (3)	C <sub>2</sub> C <sub>8</sub> C <sub>6</sub>	123.8 (3)
N <sub>1</sub> FeN <sub>3</sub>	89.3 (1)	C <sub>3</sub> C <sub>4</sub> C <sub>10</sub>	107.6 (3)	N <sub>1</sub> C <sub>9</sub> C <sub>3</sub>	110.3 (3)
N <sub>2</sub> FeN <sub>3</sub>	89.4 (1)	C <sub>7</sub> 'C <sub>5</sub> C <sub>9</sub>	124.0 (3)	N <sub>1</sub> C <sub>3</sub> C <sub>5</sub>	125.4 (3)
FeN <sub>1</sub> C <sub>9</sub>	127.4 (2)	C <sub>7</sub> 'C <sub>5</sub> C <sub>11</sub>	118.1 (3)	C <sub>3</sub> C <sub>9</sub> C <sub>5</sub>	124.3 (3)
FeN <sub>1</sub> C <sub>10</sub>	127.0 (2)	C <sub>9</sub> C <sub>5</sub> C <sub>11</sub>	117.9 (3)	N <sub>1</sub> C <sub>10</sub> C <sub>4</sub>	110.1 (3)
C <sub>9</sub> N <sub>1</sub> C <sub>10</sub>	105.2 (3)	C <sub>8</sub> C <sub>6</sub> C <sub>10</sub>	124.1 (3)	N <sub>1</sub> C <sub>10</sub> C <sub>6</sub>	125.6 (3)
FeN <sub>2</sub> C <sub>7</sub>	127.5 (2)	C <sub>8</sub> C <sub>6</sub> C <sub>17</sub>	118.0 (3)	C <sub>4</sub> C <sub>10</sub> C <sub>6</sub>	124.3 (3)
FeN <sub>2</sub> C <sub>8</sub>	126.9 (2)	C <sub>10</sub> C <sub>6</sub> C <sub>17</sub>	117.8 (3)	C <sub>23</sub> N <sub>3</sub> C <sub>27</sub>	111.3 (4)
C <sub>7</sub> N <sub>2</sub> C <sub>8</sub>	105.2 (3)	N <sub>2</sub> C <sub>7</sub> C <sub>1</sub>	110.2 (3)	N <sub>3</sub> C <sub>23</sub> C <sub>24</sub>	114.2 (4)
FeN <sub>3</sub> C <sub>23</sub>	116.8 (3)	N <sub>2</sub> C <sub>7</sub> C <sub>5</sub> '	125.6 (3)	C <sub>23</sub> C <sub>24</sub> C <sub>25</sub>	111.2 (4)
FeN <sub>3</sub> C <sub>27</sub>	116.8 (3)	C <sub>1</sub> C <sub>7</sub> C <sub>5</sub> '	124.1 (3)	C <sub>24</sub> C <sub>25</sub> C <sub>26</sub>	108.6 (4)
C <sub>2</sub> C <sub>1</sub> C <sub>7</sub>	107.3 (3)	N <sub>2</sub> C <sub>8</sub> C <sub>2</sub>	110.4 (3)	C <sub>25</sub> C <sub>26</sub> C <sub>27</sub>	112.2 (4)
C <sub>1</sub> C <sub>2</sub> C <sub>8</sub>	106.9 (3)	N <sub>2</sub> C <sub>8</sub> C <sub>6</sub>	125.8 (3)	N <sub>3</sub> C <sub>27</sub> C <sub>26</sub>	113.8 (4)

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

was positioned so as to be dimensionally interpretable as a partially occupied site for such anionic species as bromide or hydroxide ions. Thus, there could have been little or no substitution of the low-spin iron(III) [Pip<sub>2</sub>FeTPP]<sup>+</sup> cation for the neutral iron(II) species (see Discussion).

The atomic coordinates and the associated thermal parameters in the asymmetric unit of structure I<sup>6</sup> are listed in Tables I and II, respectively; bond parameters in the Pip<sub>2</sub>FeTPP molecule are given in Tables III-V. The numbering scheme employed for the

(16) A table of the 4267 observed and calculated 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 author, title of article, volume, and page number. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche.

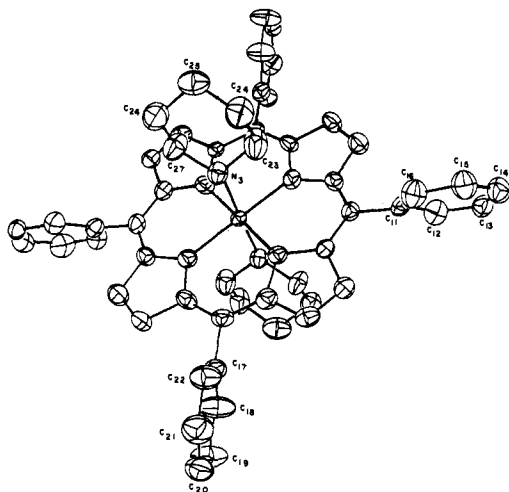


Figure 1. Computer-drawn model in perspective of the centrosymmetric  $\text{Pip}_2\text{FeTPP}$  molecule as it exists in the triclinic crystal. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table II. Also shown is the numbering scheme employed for atoms in the phenyl groups and the piperidine ligands.

several atoms is that displayed in Figures 1 and 2. Primed and unprimed symbols, *e.g.*,  $\text{C}_i$  and  $\text{C}_i'$ , denote a pair of atoms related by the center of inversion wherein the iron atom is positioned.

Table V. Bond Lengths ( $\text{\AA}$ ) in the Phenyl Groups<sup>a,b</sup>

Type I <sup>c</sup>	Length	Type II <sup>d</sup>	Length	Type III <sup>e</sup>	Length
$\text{C}_{11}-\text{C}_{12}$	1.395 (6)	$\text{C}_{12}-\text{C}_{13}$	1.394 (6)	$\text{C}_{13}-\text{C}_{14}$	1.372 (7)
$\text{C}_{11}-\text{C}_{16}$	1.383 (6)	$\text{C}_{15}-\text{C}_{15}$	1.392 (6)	$\text{C}_{15}-\text{C}_{14}$	1.377 (8)
$\text{C}_{17}-\text{C}_{18}$	1.384 (6)	$\text{C}_{18}-\text{C}_{19}$	1.386 (6)	$\text{C}_{19}-\text{C}_{20}$	1.362 (8)
$\text{C}_{17}-\text{C}_{22}$	1.384 (6)	$\text{C}_{22}-\text{C}_{21}$	1.392 (6)	$\text{C}_{21}-\text{C}_{20}$	1.382 (7)
$\text{Av}^b$	1.387 (4)	$\text{Av}^b$	1.391 (3)	$\text{Av}^b$	1.373 (6)

<sup>a</sup> The figure in parentheses following the length of a specific bond is the estimated standard deviation in units of 0.001  $\text{\AA}$ . <sup>b</sup> The figure in parentheses following the averaged length for a bond type is the mean deviation from the average. <sup>c</sup> Bond set lying nearest to the molecular center. <sup>d</sup> Bond set lying at an intermediate distance from the center, but approximately parallel to the porphinato core. <sup>e</sup> Terminal set of bonds.

## Discussion

Figure 1 is a computer-drawn model of the centrosymmetric ( $\bar{1}$ )  $\text{Pip}_2\text{FeTPP}$  molecule (without hydrogen atoms) as it exists in the triclinic crystal. Each atom is represented as an ellipsoid<sup>17</sup> of the relative size and orientation required by the thermal parameters given in Table II.

The upper half of the diagram of the porphinato core in Figure 2 carries the values (with estimated standard deviations) of all structurally independent C-C and C-N bond lengths in the core; it carries also the values of some structurally important radii of the core, of which  $\text{Ct}\cdots\text{N} \equiv \text{Fe}-\text{N}$  in this case. In the lower half of the centrosymmetric diagram, each numbered symbol for an atom is replaced by the perpendicular displacement (in units of 0.01  $\text{\AA}$ ) of this atom from the mean plane of the porphinato core; each centrosymmetrically related displacement in the upper half of the core has the same magnitude, but the opposite sign.

(17) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

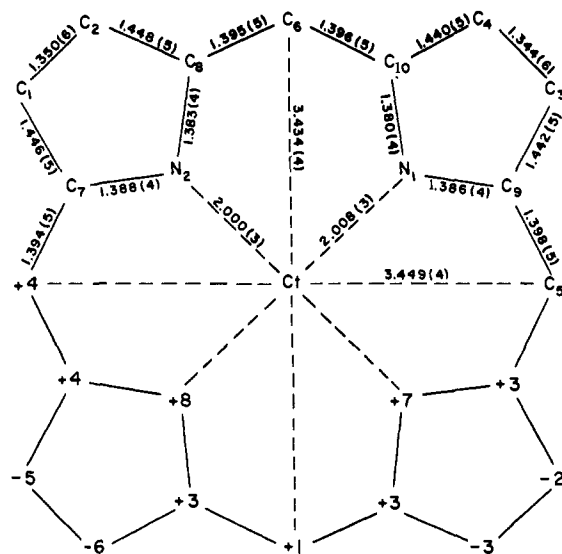


Figure 2. Diagram of the porphinato core displaying, on the upper half, the structurally independent bond lengths and the numbering scheme employed for the atoms. On the lower half of the centrosymmetric diagram, the numbered symbol for each atom is replaced by its perpendicular displacement, in units of 0.01  $\text{\AA}$ , from the mean plane of the porphinato core.

Departures from planarity of the porphinato core in this crystal are of unremarkable magnitude as compared with those observed in a number of other crystalline porphyrins.<sup>2,5</sup> Local flatness within  $\leq 0.02$   $\text{\AA}$  is preserved in the trigonal bonding patterns emanating from the carbon atoms in the inner 16-membered ring and, still more precisely, in the pyrrole rings.

Evidence that the bonding in the core is not significantly disturbed by the departures from planarity or, more generally, from  $D_{4h}$  symmetry is provided by the bond lengths listed in Table III and displayed on Figure 2. Using  $\text{C}_\alpha$  and  $\text{C}_\beta$  to denote the respective  $\alpha$ - and  $\beta$ -carbon atoms in a pyrrole ring,  $\text{C}_m$  for methine carbon, and  $\text{C}_p$  for a phenyl carbon atom that is bonded to the core, averaged bond lengths for the chemically distinctive types of bonds are:  $\text{Fe}-\text{N}$  ( $= \text{Ct}\cdots\text{N}$ ) = 2.004 (4, 3),  $\text{N}-\text{C}_\alpha$  = 1.384 (3, 4),  $\text{C}_\alpha-\text{C}_m$  = 1.396 (1, 5),  $\text{C}_\alpha-\text{C}_\beta$  = 1.444 (3, 5),  $\text{C}_\beta-\text{C}_\beta$  = 1.347 (3, 6), and  $\text{C}_m-\text{C}_p$  = 1.499 (2, 5)  $\text{\AA}$ , wherein the first figure in parentheses following each averaged value is the mean deviation, and the second is the estimated standard deviation (esd) of an individually determined length of the type.<sup>18</sup> More notable still is the lack of significant spread in the bond angles of a given chemical type within the core. Thus the individually listed bond angles in Table IV lead to the averaged angles,<sup>18</sup>  $\text{C}_\alpha\text{N}\text{C}_\alpha$  = 105.2 (0, 3),  $\text{N}\text{C}_\alpha\text{C}_\beta$  = 110.2 (1, 3),  $\text{N}\text{C}_\alpha\text{C}_m$  = 125.6 (1, 3),  $\text{C}_\alpha\text{C}_\beta\text{C}_\beta$  = 107.2 (3, 3),  $\text{C}_\alpha\text{C}_m\text{C}_\alpha$  = 124.1 (1, 3),  $\text{N}\text{F}\text{e}\text{N}$  = 90.0 (2, 1), and  $\text{C}_\alpha\text{C}_m\text{C}_p$  = 117.9 (2, 3)<sup>o</sup>.

The averaged length of the  $\text{C}_m-\text{C}_p$  bonds connecting the two structurally nonequivalent phenyl groups to methine carbon atoms, 1.499 (2, 5)  $\text{\AA}$ , compares with 1.496 (2)  $\text{\AA}$  for the analogous length in the very precisely determined structure of  $\alpha,\beta,\gamma,\delta$ -tetraphenyl-

(18) This pattern for the reporting of averaged values for both angles and bond lengths is followed throughout the discussion. Whenever the structurally nonequivalent determinations of a given chemical type of parameter carry differing values of the esd (rarely in this investigation), the root-mean-square value is reported for the esd of the individual determination.

porphinatodichlorotin(IV) ( $\text{Cl}_2\text{SnTPP}$ ).<sup>19</sup> This distance is associated with essentially pure  $\sigma$  bonding between a pair of trigonally hybridized carbon atoms. The dihedral angles between the plane of the porphinato core and the planes of the two phenyl groups in the  $\text{Pip}_2\text{FeTPP}$  molecule are 68.9 and 78.1°; the (single) analogous angle in the  $\text{Cl}_2\text{SnTPP}$  molecule of required  $C_{4h}$  symmetry is exactly  $\pi/2$ .

Experimentally determined values of the 12 C–C bonds in the two structurally nonequivalent phenyl groups, as listed in Table V, are foreshortened from the standard 1.397-Å internuclear separation in consequence of the thermal motions of the phenyl groups as quasi-rigid bodies peripherally attached to the porphinato core.<sup>20</sup> The 12 C–C bonds are classified by the quasi-fourfold symmetry into three groups within which the four bonds of a group are subject to approximately the same foreshortening (Table V). The most affected group, the terminal bonds lying farthest from the molecular center, have an averaged length, C–C = 1.373 (6, 8) Å. The set of four lying nearest to the center have  $(\text{C–C})_{\text{av}} = 1.387$  (4, 6) Å, and the least foreshortened set, in which the bonds are approximately parallel to the plane of the porphinato core, have  $(\text{C–C})_{\text{av}} = 1.391$  (3, 6) Å (*cf.* ref 19 for a more authoritative treatment of this subject).

The averaged value for the internal angles in the phenyl rings is 120.0 (8, 4)°. The sum of the bond angles subtended at each  $C_p$  atom is 360.0 (0, 6)°, corresponding to planarity of the trigonal bond systems emanating from these atoms.

The remarkable consistency in the structurally nonequivalent bond lengths within each of the several chemical classes, as set forth above, is maintained for the C–N bonds in the piperidine ring (Table III):  $(\text{C–N})_{\text{av}} = 1.483$  (1, 6) Å. It falters somewhat only for the C–C bonds in the piperidine ligand:  $(\text{C–C})_{\text{av}} = 1.517$  (12, 8) Å. The piperidine skeleton is in the “chair” form, with a CNC angle of 111.3 (4)° and the opposite CCC angle at 108.6 (4)°; the remaining pair of CCC angles average to 111.7 (5, 4)°, the NCC pair to 114.0 (2, 4)°.

The iron and the four porphinato nitrogen atoms of the octahedral ( $\bar{1}$ ) coordination group constitute a necessarily planar, almost square, equatorial entity:  $(\text{Fe–N})_{\text{av}} = 2.004$  (4, 3) Å,  $(\angle \text{NFeN})_{\text{av}} = 90.0$  (2, 1)°. The collinear Fe–N<sub>3</sub> bonds to the piperidine ligands (Figure 1; Tables III and IV) are tipped 1.0° from the normal to the equatorial girdle within a vertical plane that bisects the  $\text{N}_1\text{FeN}_2$  angle and passes within 0.01 Å of the  $C_6$  and  $C_6'$  methine carbon positions (Figure 2). This plane, indeed, serves as a quasi-mirror for all of the molecule excepting the phenyl groups. Apart from the orientations of these peripheral groups around the  $C_m$ – $C_p$  bonds joining them to the porphinato core, the molecule observes the quasi-symmetry of  $C_{2h}$ - $2/m$ ; the quasi-twofold axis lies in the equatorial girdle and bisects the opposite angles,  $\text{N}_1\text{FeN}_2'$  and  $\text{N}_1'\text{FeN}_2$ . (Note that in Figure 2 the pattern of out-of-plane dis-

placements of the atoms in the core approximates to effective  $2/m$  symmetry.)

That the  $\text{Pip}_2\text{FeTPP}$  molecule in the triclinic crystal is allowed to approximate closely to the maximum symmetry theoretically attainable in the unconstrained species implies, of course, that the crystalline arrangement involves few, if any, unduly tight contacts between molecules. Of the 26 structurally independent, intermolecular, C···C contacts below 4.0 Å, just four are below 3.70 Å, and none approach closely the 3.35–3.40 Å characteristic of the parallel stacking of planar aromatic molecules. The four contacts in the range from 3.51 to 3.68 Å are, however, between carbon atoms of partially overlapping aromatic groups.

At this juncture, we may emphasize that the structural data are in detailed agreement with the chemical formulation,  $\text{Pip}_2\text{FeTPP}$ . The presence of any appreciable concentration of an iron(III) species (in any spin state) is precluded as described in the Experimental Section. No “holes” in the crystalline arrangement suitable for the accommodation of interstitial impurities are discernible; nor is there any evidence for substitutional impurities. We conclude, consequently, that superficial contamination of the mechanically separated crystals employed for chemical analysis was responsible for the somewhat anomalous results obtained therefrom. Such contamination is also the most probable source for a small paramagnetism in the mechanically separated crystals—if this phenomenon be real; the failure to detect any epr signal from the same sample in sensitive experiments<sup>7</sup> speaks against it. A more interesting possibility that might account for a small paramagnetism in the crystal employed for the determination of structure is discussed later.

Recognizing that the  $\text{Pip}_2\text{FeTPP}$  molecules in the crystal are predominantly or wholly in the low-spin state ( $S = 0$ ), we must still take cognizance of the apparently excessive length of the axial complexing bonds, Fe–N = 2.127 (3) Å, as compared with the 1.97–1.98 Å anticipated with favorably oriented imidazole molecules axially coordinated to low-spin iron(II).<sup>2,5,21</sup> It is readily seen that steric interactions (of no less than five) of the piperidine hydrogen atoms in each axial ligand with the porphinato core are primarily responsible for the stretching of these bonds;<sup>22</sup> these interactions, indeed, retain their vigor for any orientation of the piperidine ligand around the complexing bond. In Figure 3 the derived positions of the pertinent atoms in the representative piperidine ligand are projected upward (see caption) onto the equatorial plane of the coordination group; departures from the vertical quasi-mirror are clearly small. The  $\text{H}_{28A}$  and  $\text{H}_{27A}$  hydrogen atoms, which are attached to the respective  $C_{23}$  and  $C_{27}$  atoms, are positioned almost directly beneath the respective  $\text{N}_2'$  and  $\text{N}_1'$  atoms of the porphinato core, giving calculated N···H separations of 2.66 and 2.61 Å. The normal packing separation for this geometry is  $\sim 2.90$  Å, the sum of the van der Waals radii for hydrogen (1.20 Å) and aromatic nitrogen (1.70 Å). Also rather short is the  $\text{C}_{10}'\cdots\text{H}_{27A}$  separation of 2.76 Å.  $\text{H}_{23B}$  and  $\text{H}_{27B}$  atoms are seen (Figure 3) to lie beneath

(19) D. M. Collins, W. R. Scheidt, and J. L. Hoard, submitted to *J. Amer. Chem. Soc.* The structure determination utilized  $|F_o|$  data extending to  $(\sin \theta)/\lambda = 1.03 \text{ \AA}^{-1}$ , giving a data/parameter ratio of 54.3, and a conventional  $R$  of 0.045.

(20) The effect, during least-squares refinement, of the grossly approximate model used for hydrogen contributions on the apparent C–C bond lengths in the phenyl groups and on the  $C_b$ – $C_b$  distance in the porphinato core is quantitatively appraised in the  $\text{Cl}_2\text{SnTPP}$  study.<sup>19</sup>

(21) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, **94**, 727 (1972).

(22) Some quite small fraction of the  $\sim 0.15$ -Å extension might be ascribed to the incapacity of the piperidine ligand to accept electron density by back  $\pi$  bonding from the iron(II) atom.

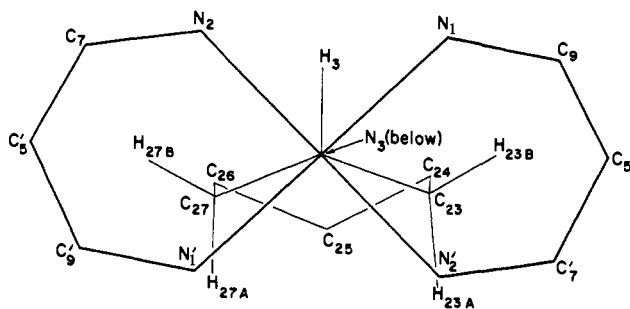


Figure 3. Diagram of the representative piperidine ligand (Table I) as projected upward onto the equatorial plane of the coordination group. The pertinent atoms of the porphinato core (Figure 2) are included in the diagram; the iron atom at the origin and the six piperidine hydrogen atoms that are not involved in steric interactions with the core are omitted.

six-membered chelate rings, so that each hydrogen atom has five, roughly equidistant, neighboring atoms in the porphinato core. Distances ( $\text{\AA}$ ) from  $\text{H}_{27\text{B}}$  to its neighbors are 2.72 to  $\text{C}_5$ , 2.76 to  $\text{C}_9$ , 2.80 to  $\text{C}_7'$  and  $\text{N}_1$ , 2.90 to  $\text{N}_2'$ , and from  $\text{H}_{27\text{B}}$  to its neighbors are 2.73 to  $\text{C}_9'$ , 2.79 to  $\text{C}_5'$ , 2.81 to  $\text{N}_1'$ , 2.83 to  $\text{C}_7$ , and 2.86 to  $\text{N}_2$ . The calculated  $\text{H}_3 \cdots \text{N}_2$  and  $\text{H}_3 \cdots \text{N}_1$  separations of 2.57 and 2.62  $\text{\AA}$  are unduly small, notwithstanding that the  $\text{N}_3\text{-H}_3$  bond is favorably polar and the porphinato nitrogen atoms carry resultant negative charge. These separations correspond to an  $\text{FeN}_3\text{H}_3$  angle of only  $92^\circ$ , a value set by requiring the  $\text{C}_{23}\text{N}_3\text{H}_3$  and  $\text{C}_{27}\text{N}_3\text{H}_3$  angles to be  $109.5^\circ$ , but observed also to be in reasonable agreement with the Fourier difference synthesis. The  $\text{FeN}_3\text{H}_3$  angle need not be as large as the  $116.8$  ( $3^\circ$ ) observed for both the  $\text{FeN}_3\text{C}_{23}$  and the  $\text{FeN}_3\text{C}_{27}$  angles to yield  $\text{H}_3 \cdots \text{N}_2$  and  $\text{H}_3 \cdots \text{N}_1$  separations of  $\sim 2.85$   $\text{\AA}$ , but it does need to be something like the regular tetrahedral value.

The cited packing separations are, for obvious reasons, only semiquantitative. Exact calculations that assume regular tetrahedral angles and standard bond lengths in the piperidine ligand illuminate the basic problem; we further assume full  $2/m$  symmetry while centering attention on the most critical  $\text{N}_2' \cdots \text{H}_{27\text{A}}$  and  $\text{N}_1' \cdots \text{H}_{27\text{A}}$  separations (which become structurally equivalent). With  $\text{Fe-N}_3 = 1.98$   $\text{\AA}$ , these  $\text{N} \cdots \text{H}$  separations would be only 2.14  $\text{\AA}$ , and with  $\text{Fe-N}_3 = 2.13$   $\text{\AA}$ , they would be increased only to 2.29  $\text{\AA}$ . Indeed, the stretching of the  $\text{Fe-N}_3$  bond is somewhat less important than the gross modification required of the bond angles at the nitrogen atom to yield tolerable packing relations—though both are necessary. Increase of the  $\text{FeN}_3\text{C}$  bond angles to  $116.8^\circ$  pushes the contiguous  $\text{CH}_2$  groups farther above the equatorial plane and, in conjunction with the  $\text{CN}_3\text{C}$  angle of  $111.3^\circ$ , tips the  $\text{C}_{23}\text{-C}_{24}$  and  $\text{C}_{27}\text{-C}_{28}$  bonds parallel to the quasi-mirror in the direction (Figure 3) to give a further significant increase in the  $\text{N}_2' \cdots \text{H}_{27\text{A}}$  and  $\text{N}_1' \cdots \text{H}_{27\text{A}}$  separations. Such large deviations from the regular tetrahedral value of the bond angles at nitrogen are quite unusual, as is demonstrated in the extensive structural data that are available for the ethylenedi-

aminetetraacetato chelates of a variety of cations; the observed deviations therein rarely exceed  $|4|^\circ$ .

Our recognition, during structure refinement, that the  $\text{Fe-N}_3$  bond length must be significantly greater than 2.10  $\text{\AA}$  raised the possibility of iron(II) in the unusual intermediate-spin state ( $S = 1$ ), and thus prompted the search for paramagnetism in the crystals. The results of this search (see Experimental Section) show that only a small fraction, if any, of the molecules can be paramagnetic. If, moreover, the chemical formulation,  $\text{Pip}_2\text{FeTPP}$ , were uniformly applicable to all of the molecules, a temperature-dependent distribution between species having  $S = 0$  and  $S = 1$  would give rise to a temperature-dependent effective moment; the measured susceptibility seems, however, to follow the Curie law between 78 and 296  $^\circ\text{K}$ .

A rather intriguing possibility that calls for an effective moment sensibly independent of temperature remains for consideration. The calculated and experimental densities are compatible with somewhat less than the stoichiometric proportion of piperidine. Although it is stereochemically improbable, if not altogether impossible, that five-coordinate high-spin ( $S = 2$ )  $\text{PipFeTPP}$  molecules can be accommodated in the crystalline arrangement,<sup>5</sup> it is conceivable that the five-coordinate species could be coerced by the packing relations into the intermediate spin state in which the  $d_{z^2}$  (but not the  $d_{x^2-y^2}$ ) orbital of the iron(II) atom is assigned one of the two unpaired electrons. The expectations in this event are a displacement of the iron atom by  $\sim 0.10$   $\text{\AA}$  from the center of inversion toward the piperidine ligand with little or no shift in position of the latter, and occupancy of the other axial position by the unpaired electron as a "phantom" ligand.<sup>23</sup> With equal probabilities for the alternative orientations of the polar axis, there is no prospect that statistically superimposed small displacements ( $\pm$ ) from the center of inversion of a small fraction of the iron atoms can be directly confirmed by X-ray diffraction analysis.<sup>5,14</sup> The model does call for some enhancement of the apparent thermal parameter corresponding to vibration of the iron atom normal to the porphinato core and for a general enhancement of the apparent thermal parameters for atoms in the piperidine ligands. The thermal parameter for out-of-plane vibration of the iron atom is slightly larger than those of the porphinato nitrogen atoms, whereas the thermal parameters vibration in the plane of the core are, as is usual, somewhat smaller for the iron atom. Thermal parameters in the piperidine ligands are more nearly comparable with those in the phenyl groups than with the generally smaller values in the porphinato core. Thus the model is compatible with such wholly indirect evidence as is available.

**Acknowledgment.** We thank Professor E. S. Kostiner, Dr. J. L. Krause, and Messrs. W. S. Glaunsinger and J. J. Steger for their contributions to this study as detailed under the Experimental Section.

(23) See 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 for discussion of the intermediate spin state in an iron porphyrin.