

cell as projected onto a plane perpendicular to the *b*-axis. This axis is the stacking direction for somewhat tilted molecules in parallel array; perpendicular separations between the porphine mean planes of contiguous molecules related by inversion centers at, respectively, the origin and 0, 0.5, 0 are 3.52 and 3.45 Å., to be compared with the analogous interplanar distance of 3.38 in both the NiPHC and PHC structures.

Many close contacts occur between successive overlying molecules (Table VI). The closest of these involving atoms of the porphine skeleton are between molecules related by the inversion center at 0, 1/2, 0 and range upward from 3.33 Å. for C··O, 3.39 Å. for C··C, and 3.53 Å. for C··N distances. Apart from the four nitrogen atoms to which it is bonded (at 1.960 Å.) within the molecule, a nickel atom has no

neighbors closer than a nitrogen at 3.41 Å., a carbon at 3.68 Å., and another nickel atom at 3.77 Å.

The shortest packing separation, 3.15 Å., is between the terminal methyl carbon of a propionic ester chain, C<sub>35</sub> in Figure 1, and a carbonyl oxygen of O<sub>3</sub> type in a second molecule related to the first by the inversion center at 1/2, 1, 1/2. Another close contact of 3.17 Å. involves C<sub>35</sub> of the first molecule and an oxygen atom of the O<sub>1</sub> type in the molecule obtained from the first by the translation,  $\vec{a} + \vec{b} + \vec{c}$ .

Benzene is present in the crystal as the uncomplexed solvent of crystallization. A benzene molecule (Figure 5) at the inversion center 1/2, 0, 1 lies between successive stacks of porphyrin molecules with its plane turned 80° from the porphine mean plane.

## The Crystal Structure and Molecular Stereochemistry of Methoxyiron(III) Mesoporphyrin-IX Dimethyl Ester<sup>1</sup>

J. L. Hoard,<sup>2,3</sup> M. J. Hamor,<sup>2</sup> T. A. Hamor,<sup>2</sup> and W. S. Caughey<sup>4</sup>

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York, and the Department of Physiological Chemistry, The Johns Hopkins School of Medicine, Baltimore, Maryland. Received January 21, 1965

*Three-dimensional X-ray diffraction data from monoclinic single crystals of methoxyiron(III) mesoporphyrin-IX dimethyl ester were used to determine structure. Disorder in the packing of molecules within the crystal is traceable to incomplete sorting of the stereochemically not very dissimilar D and L isomers onto their respective sublattices. The iron atom lies 0.49 Å. from the mean plane of the modestly domed porphine skeleton and is limited to five-coordination. Fe-N bond distances average  $2.073 \pm 0.006$  Å., and the Fe-OCH<sub>3</sub> link is  $1.842 \pm 0.004$  Å. A good deal of evidence suggests that substantial displacement of the iron atom from the plane of the nitrogen atoms is a normal structural property of high-spin iron porphyrins.*

### Introduction

The preceding report<sup>5</sup> on the structure of nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester particularly emphasizes the stereochemical adaptability of the porphine skeleton to the varying circumstances of its environment. A somewhat different aspect of this theme comes out of the structural study reported herein of another biologically significant porphyrin, methoxyiron(III) mesoporphyrin-IX dimethyl ester (henceforth abbreviated as MeOFeMeso). Background

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(2) Department of Chemistry, Cornell University, Ithaca, N. Y.

(3) Author to whom correspondence should be addressed.

(4) Department of Physiological Chemistry, The Johns Hopkins University, Baltimore, Md.

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

material beyond that presented in the introductory section of the accompanying paper<sup>5</sup> includes Kendrew's observation<sup>6</sup> that in the myoglobin structure the iron atom lies more than 0.25 Å. out of the mean plane of the heme group and his comment<sup>6</sup> that Koenig had observed a similar phenomenon by structure analysis of hemin. Following structure determination for crystalline MeOFeMeso, we obtained on loan a copy of Koenig's thesis<sup>7</sup> describing his work on chlorohemin, and found that the two studies give consistent stereochemical descriptions of the pyramidal coordination groups surrounding the Fe(III) atoms (*vide infra*). The recently published structures<sup>8</sup> for aquohydroxyiron(III) tetraphenylporphine and diaquozinc(II) tetraphenylporphine contain, by comparison, some anomalous features which will require subsequent comment.

### Experimental

Purple-black opaque crystals of methoxyiron(III) mesoporphyrin-IX dimethyl ester from a preparation by J. O. Alben and W. S. Caughey (unpublished work) were subjected to careful preliminary study by oscillation and Weissenberg X-ray techniques and were thereby shown to be monoclinic. The absence of piezoelectricity in quite sensitive tests and the subsequent analysis of the statistical distribution of diffraction intensities with  $\sin \theta$  suggested I2/m as the most probable space group; the noncentric possibilities, however, were not immediately discarded. Cell dimensions of  $a = 11.55 \pm 0.02$ ,  $b = 24.15 \pm 0.03$ ,  $c =$

(6) J. C. Kendrew, *Science*, **139**, 1259 (1963).

(7) D. F. Koenig, Thesis, The Johns Hopkins University, (1962); *Acta Cryst.*, in press.

(8) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).

$12.51 \pm 0.01 \text{ \AA}$ , and  $\beta = 98.4 \pm 0.1^\circ$  were measured on the General Electric spectrometer. With four molecules in the unit cell the calculated and measured densities both came out to be 1.31 g./cc.

It was immediately obvious during photographic examination that thermal motions and/or packing disorder in the crystal must severely limit the range of recordable diffraction intensities and that even for the largest available crystal specimen—about 0.40 mm. in average diameter—the customarily used Mo  $K\alpha$  radiation would be relatively unsatisfactory. Given also the heavy photoelectric absorption of copper  $K\alpha$  wave lengths by iron in the crystal, the practicable choice for intensity measurement became cobalt  $K\alpha$  radiation, for which the linear absorption coefficient in the porphyrin was computed to be  $16.0 \text{ cm.}^{-1}$ . Using otherwise the technique described in the accompanying paper,<sup>5</sup> we were able to measure intensities above background for 1702 of the 1941 independent  $\{hkl\}$  reflections theoretically permitted for  $(\sin \theta)/\lambda < 0.50$ ; otherwise put, the yield of observable reflections corresponded to only 42% of the total number of reciprocal lattice points lying within the "standard" copper  $K\alpha$  limiting sphere. The measured intensity data, without correction for variation of absorption with angle, were then reduced<sup>9</sup> to relative  $|F_{hkl}|^2$  values in preparation for structure determination.

**Determination of Structure.** Peaks attributable to Fe-Fe vector separations in a sharpened<sup>10</sup> Patterson synthesis<sup>9</sup> of  $|F|^2$  data were compatible with the presence of four iron atoms either in the special positions  $4i$  lying in mirror planes of  $I2/m$  or in the general positions  $4c$  of  $I2$ ; they were incompatible with the use of any other positions in either  $I2/m$  or  $I2$  or of the general positions in  $Im$ .<sup>11</sup> A structure based upon  $I2/m$ , the most probable space group according to the collateral observations cited earlier, would necessarily involve some packing disorder inasmuch as the MeOFeMeso molecule cannot have the mirror plane required by the strict application of space group theory.<sup>11</sup> With comparatively little difference in packing shapes between the enantiomorphous D and L isomers of the bulky molecule—see the molecular diagram and explanatory caption of Figure 1—packing disorder might well be thought to be more probable than not. Initial analysis based upon  $I2/m$  would not preclude, but rather would further, subsequent consideration of ordered structures based upon  $I2$  (or other space group—*vide infra*).

The phase-determining power of the iron atoms placed in  $4i$  of  $I2/m$  was utilized to initiate structure determination by Fourier synthesis<sup>9</sup> in cycles of successive approximation. The porphine skeleton, together with the directly attached carbon atom of each side chain, was fairly well delineated in the first cycle; the complete ester frameworks were next to appear, but several cycles of approximation were required to define the four terminal carbon half-atoms of the four statistically hybridized methyl-ethyl groups substituent in four positions of the statistically averaged porphyrin

(9) Cf. M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 7.

(10) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Cryst.*, **14**, 598 (1961).

(11) Cf. "International Tables for X-Ray Crystallography. Vol. I. Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, pp. 81, 87, 95.

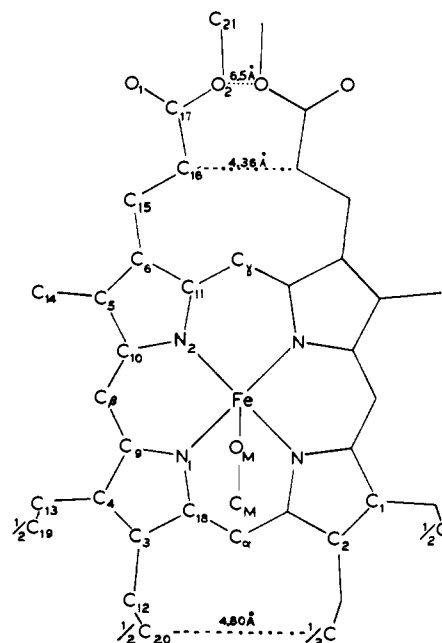


Figure 1. Formal diagram of the MeOFeMeso skeleton illustrating (1) the labeling of atoms followed in Tables I-V and (2) the pseudosymmetry resulting from packing disorder in the crystal. Iron, methoxy  $O_M$  and  $C_M$ , and methine  $C_\alpha$  and  $C_\gamma$  atoms lie in the apparent mirror plane perpendicular to the plane of the porphine ring system; the skeletons of the D and the L isomers (*i.e.*, of the 2,4-diethyl- and 1,3-diethyldeuteroporphyrins) are hybridized so that  $C_{19}$ ,  $C_{20}$ , and their mirror images all are statistically half-atoms. Although the porphine skeleton, the nine atoms (Fe and 8C) directly attached thereto, and the four half-atoms are shown in true projection, it is impracticable to do this for the methoxy and the propionate groups; see Figures 2 and 3 and Tables IV-VI. The propionate chains, as noted on the diagram, are in fact separated by  $\geq 4.36 \text{ \AA}$ .

molecule; see Figure 1. It was only in respect to these terminal half-atoms that the Fourier synthesis provided evidence of the superposition of two enantiomorphous patterns; it was clear, therefore, that, in respect to atoms other than the half-carbons, the differences between any possible ordered structure based upon  $I2$  and the averaged structure given by the Fourier synthesis could not be large.<sup>12</sup>

Refinement of structure was carried out in agreement first with  $I2/m$  and then with  $I2$ . The final stages of refinement utilized full matrix least-squares procedures with individual anisotropic thermal parameters for all atoms. The function minimized was  $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$  with  $\sqrt{w} = 1$  for  $|F_o| < 58$ ,  $58/|F_o|$  for  $|F_o| < 58$ ; 93% of the observed data were thus given full weight. Form factors from the "International Tables"<sup>13</sup> were employed. Refinement of the disordered structure based upon  $I2/m$  finally gave the parameter data listed in Table I with an  $R = \sum |F_o| - |F_c| / \sum |F_o|$  of 0.119 for the 1702 recordable  $\{hkl\}$  reflections.

Introduction of complex phases and attempted refinement of an ordered structure based upon  $I2$  gave, as compared with the disordered arrangement based upon  $I2/m$ , a further slight reduction in  $R$ , still higher

(12) Cf. J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp. 272-274.

(13) "International Tables for X-Ray Crystallography. Vol. III. Physical and Chemical Tables," The Kynoch Press, Birmingham, England, 1962, pp. 202-205.

**Table I.** Parameter Data for the MeOFeMeso Crystalline Arrangement<sup>a</sup>

Atom type	(Coordinate $\pm$ std. dev.) $\times 10^4$			$B_i$ , $\text{\AA}^2$
	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	
C <sub>3</sub>	7139 $\pm$ 4	3949 $\pm$ 3	4848 $\pm$ 4	8.6
C <sub>4</sub>	6700 $\pm$ 4	3533 $\pm$ 3	5413 $\pm$ 4	9.5
C <sub>5</sub>	4226 $\pm$ 4	3555 $\pm$ 2	8419 $\pm$ 3	7.3
C <sub>6</sub>	3772 $\pm$ 3	3964 $\pm$ 2	8991 $\pm$ 3	6.5
C <sub><math>\alpha</math></sub>	7125 $\pm$ 6	1/2 $\pm$ 0	4882 $\pm$ 5	8.0
C <sub><math>\beta</math></sub>	5506 $\pm$ 4	3565 $\pm$ 2	6940 $\pm$ 3	8.2
C <sub><math>\gamma</math></sub>	3842 $\pm$ 4	1/2 $\pm$ 0	9012 $\pm$ 4	5.8
C <sub>9</sub>	6096 $\pm$ 4	3839 $\pm$ 2	6208 $\pm$ 3	7.4
C <sub>10</sub>	4881 $\pm$ 3	3827 $\pm$ 2	7672 $\pm$ 3	6.9
C <sub>11</sub>	4142 $\pm$ 3	4498 $\pm$ 2	8610 $\pm$ 3	5.7
C <sub>12</sub>	7858 $\pm$ 4	3885 $\pm$ 4	3898 $\pm$ 4	11
C <sub>13</sub>	6744 $\pm$ 5	2910 $\pm$ 3	5283 $\pm$ 5	12
C <sub>14</sub>	4106 $\pm$ 5	2926 $\pm$ 2	8492 $\pm$ 4	9.4
C <sub>15</sub>	3012 $\pm$ 3	3890 $\pm$ 2	9870 $\pm$ 3	6.7
C <sub>16</sub>	1738 $\pm$ 4	4097 $\pm$ 2	9504 $\pm$ 3	7.2
C <sub>17</sub>	1040 $\pm$ 4	3665 $\pm$ 2	8829 $\pm$ 4	9.6
C <sub>18</sub>	6849 $\pm$ 3	4497 $\pm$ 2	5243 $\pm$ 3	7.9
1/2 C <sub>19</sub>	7628 $\pm$ 10	2684 $\pm$ 6	6009 $\pm$ 11	12
1/2 C <sub>20</sub>	9199 $\pm$ 9	4006 $\pm$ 9	4357 $\pm$ 9	13
C <sub>21</sub>	-830 $\pm$ 6	3474 $\pm$ 4	7718 $\pm$ 7	17
O <sub>1</sub>	1286 $\pm$ 4	3179 $\pm$ 2	8682 $\pm$ 4	13
O <sub>2</sub>	29 $\pm$ 3	3866 $\pm$ 2	8351 $\pm$ 3	13
Fe	5845 $\pm$ 1	1/2 $\pm$ 0	7193 $\pm$ 0	6.6
N <sub>1</sub>	6199 $\pm$ 3	4404 $\pm$ 2	6092 $\pm$ 2	7.4
N <sub>2</sub>	4825 $\pm$ 2	4405 $\pm$ 1	7803 $\pm$ 2	6.3
O <sub>M</sub>	7185 $\pm$ 3	1/2 $\pm$ 0	8193 $\pm$ 3	6.6
C <sub>M</sub>	8307 $\pm$ 7	1/2 $\pm$ 0	7965 $\pm$ 7	12

<sup>a</sup> Complete amplitude data have been submitted as Document No. 8300 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting in advance \$2.50 for photoprints or \$1.75 for 35-mm. film by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

values of the already extraordinarily large apparent thermal parameters, and an evident deterioration of internal consistency in the bond parameters of the molecule; the apparent C<sub>3</sub>-C<sub>12</sub> bond length, for example, was raised from 1.55 to 1.85  $\text{\AA}$ . Compelling evidence against an ordered structure based upon I2 came from its insistence on the reality of impossibly short intermolecular separations, about 2.3  $\text{\AA}$ ., between pairs of methyl carbon atoms of the C<sub>20</sub> type lying in contiguous molecules rendered equivalent in pairs by twofold axes.

Although the analogous impossibly short intermolecular separations between pairs of half-atoms of the C<sub>20</sub> type are formally present in the disordered structure based upon I2/m, this difficulty vanishes in the structurally and thermodynamically plausible pattern for the packing disorder to be presented in the following section. Straightforward analysis of the diffraction data leads in any event to the averaged crystalline arrangement next described.

Table I lists positional coordinates with standard deviations and an isotropic apparent thermal parameter equivalent<sup>14</sup> to the anisotropic components for each atom in the asymmetric unit (Figure 1). All apparent thermal parameters are large, extraordinarily so for atoms at or near the termini of side chains. We note also that the qualitative pattern of anisotropy suggests

(14) As defined by W. C. Hamilton, *Acta Cryst.*, 12, 609 (1959);  $B = 1/3 \sum B_i$  wherein the  $B_i$  are the values for the three principal directions of vibration.

either especially large amplitudes of vibration parallel to the  $b$ -axis for all atoms of the molecule or, much more probably (*vide infra*), a positional disorder which places the molecules in somewhat staggered arrays relative to those planes (at  $y = 0$  and  $1/2$ ) which, in the averaged structure, are mirror planes for the molecules.

## Discussion

Tables II and III list the respective bond lengths and bond angles with associated standard deviations for the MeOFeMeso molecule as computed from the data of Table I. Bond parameters within the porphine skeleton, averaged in agreement with the tetragonal symmetry of 4m (C<sub>4v</sub>) or, effectively as it turns out, 4/mmm (D<sub>4h</sub>), provide standards with which values obtained for individual parameters are to be compared. Applying the notation specified for the porphine skeleton in the accompanying paper<sup>5</sup> to the MeOFeMeso molecule, peripheral pyrrole carbons C<sub>1</sub>...C<sub>8</sub> become C<sub>p</sub>, methine carbons C <sub>$\alpha$</sub> ...C <sub>$\delta$</sub>  become C<sub>m</sub>, and pyrrole carbons bonded to nitrogen become C<sub>q</sub>. Averaged bond lengths are then N-C<sub>q</sub> = 1.395, C<sub>q</sub>-C<sub>p</sub> = 1.466, C<sub>p</sub>-C<sub>p</sub> = 1.368, and C<sub>m</sub>-C<sub>q</sub> = 1.377  $\text{\AA}$ .; the more significant averaged bond angles are C<sub>q</sub>NC<sub>q</sub> = 107.0, NC<sub>q</sub>C<sub>p</sub> = 109.1, C<sub>q</sub>C<sub>p</sub>C<sub>p</sub> = 107.4, NC<sub>q</sub>C<sub>m</sub> = 125.9, and C<sub>q</sub>C<sub>m</sub>C<sub>q</sub> = 124.1°. It is then seen (Tables II and III) that the deviations of individual bond parameters from the average for the type are not objectively significant relative to the corresponding standard deviations.

**Table II.** Bond Distances in the MeOFeMeso Molecule

Bond type	Length, $\text{\AA}$ .	$\sigma$ , $\text{\AA}$ .	Bond type	Length, $\text{\AA}$ .	$\sigma$ , $\text{\AA}$ .
Fe-O <sub>M</sub>	1.842	0.004	C <sub>6</sub> -C <sub>11</sub>	1.459	0.010
Fe-N <sub>1</sub>	2.074	0.006	C <sub>2</sub> -C <sub>4</sub>	1.367	0.014
Fe-N <sub>2</sub>	2.072	0.006	C <sub>5</sub> -C <sub>6</sub>	1.369	0.012
O <sub>M</sub> -C <sub>M</sub>	1.367	0.012	C <sub>3</sub> -C <sub>12</sub>	1.553	0.016
N <sub>1</sub> -C <sub>18</sub>	1.406	0.016	C <sub>4</sub> -C <sub>13</sub>	1.514	0.016
N <sub>1</sub> -C <sub>9</sub>	1.379	0.012	C <sub>7</sub> -C <sub>14</sub>	1.528	0.014
N <sub>2</sub> -C <sub>10</sub>	1.409	0.010	C <sub>8</sub> -C <sub>15</sub>	1.514	0.012
N <sub>2</sub> -C <sub>11</sub>	1.387	0.010	C <sub>15</sub> -C <sub>16</sub>	1.558	0.012
C <sub><math>\alpha</math></sub> -C <sub>18</sub>	1.349	0.012	C <sub>16</sub> -C <sub>17</sub>	1.501	0.014
C <sub><math>\beta</math></sub> -C <sub>9</sub>	1.387	0.012	C <sub>17</sub> -O <sub>1</sub>	1.229	0.014
C <sub><math>\beta</math></sub> -C <sub>10</sub>	1.397	0.012	C <sub>17</sub> -O <sub>2</sub>	1.324	0.012
C <sub><math>\gamma</math></sub> -C <sub>11</sub>	1.376	0.010	O <sub>2</sub> -C <sub>21</sub>	1.51	0.012
C <sub>3</sub> -C <sub>18</sub>	1.469	0.014	C <sub>12</sub> -C <sub>20</sub> <sup>a</sup>	1.60	0.028
C <sub>4</sub> -C <sub>9</sub>	1.492	0.014	C <sub>13</sub> -C <sub>19</sub> <sup>a</sup>	1.38	0.032
C <sub>5</sub> -C <sub>10</sub>	1.444	0.012			

<sup>a</sup> C<sub>19</sub> and C<sub>20</sub> are half-atoms statistically.

The averaged bond parameters for the porphine skeleton in MeOFeMeso are compared with analogous data from several other porphyrin molecules in the accompanying paper<sup>5</sup>—see Tables III and IV therein.<sup>5</sup> The very high level of apparent thermal motions in crystalline MeOFeMeso, much of which must be attributed to positional disorder, suggests that it is realistic to regard the data of Tables II and III as more than usually an indicator of precision rather than of accuracy in the structure determination.

The bond distances given in Table II for C<sub>12</sub>-C<sub>20</sub> and C<sub>13</sub>-C<sub>19</sub>, both involving half-atoms, and for O<sub>2</sub>-C<sub>21</sub> at the terminus of the methyl propionate side chain are rather crude approximations to expected values. The

**Table III.** Bond Angles in the MeOFeMeso Molecule

Angle	Deg.	$\sigma$ , deg.	Angle	Deg.	$\sigma$ , deg.
C <sub>18</sub> N <sub>1</sub> C <sub>9</sub>	107.5	0.7	C <sub>α</sub> C <sub>18</sub> C <sub>3</sub>	128.4	0.9
C <sub>10</sub> N <sub>2</sub> C <sub>11</sub>	106.5	0.6	C <sub>β</sub> C <sub>9</sub> C <sub>4</sub>	121.7	0.8
N <sub>1</sub> C <sub>18</sub> C <sub>3</sub>	106.5	0.8	C <sub>β</sub> C <sub>10</sub> C <sub>5</sub>	126.0	0.8
N <sub>1</sub> C <sub>9</sub> C <sub>4</sub>	111.4	0.8	C <sub>γ</sub> C <sub>11</sub> C <sub>6</sub>	123.9	0.7
N <sub>2</sub> C <sub>10</sub> C <sub>5</sub>	109.8	0.7	C <sub>3</sub> C <sub>β</sub> C <sub>10</sub>	124.6	0.8
N <sub>2</sub> C <sub>11</sub> C <sub>6</sub>	108.7	0.6	C <sub>18</sub> C <sub>3</sub> C <sub>12</sub>	121.4	0.9
N <sub>1</sub> C <sub>18</sub> C <sub>α</sub>	125.1	0.8	C <sub>3</sub> C <sub>4</sub> C <sub>13</sub>	126.2	0.9
N <sub>1</sub> C <sub>9</sub> C <sub>β</sub>	126.9	0.8	C <sub>4</sub> C <sub>3</sub> C <sub>12</sub>	127.0	1.0
N <sub>2</sub> C <sub>10</sub> C <sub>β</sub>	124.2	0.7	C <sub>3</sub> C <sub>4</sub> C <sub>13</sub>	130.8	1.0
N <sub>2</sub> C <sub>11</sub> C <sub>γ</sub>	127.5	0.6	C <sub>10</sub> C <sub>5</sub> C <sub>14</sub>	123.4	0.8
FeN <sub>1</sub> C <sub>18</sub>	124.8	0.5	C <sub>11</sub> C <sub>6</sub> C <sub>15</sub>	124.8	0.7
FeN <sub>1</sub> C <sub>9</sub>	126.0	0.6	C <sub>6</sub> C <sub>5</sub> C <sub>14</sub>	129.9	0.8
FeN <sub>2</sub> C <sub>10</sub>	127.3	0.5	C <sub>5</sub> C <sub>6</sub> C <sub>15</sub>	126.9	0.7
FeN <sub>2</sub> C <sub>11</sub>	124.8	0.4	C <sub>8</sub> C <sub>12</sub> C <sub>20<sup>a</sup></sub>	107.8	1.2
N <sub>1</sub> FeN <sub>2</sub>	86.7	0.2	C <sub>4</sub> C <sub>13</sub> C <sub>19<sup>a</sup></sub>	110.9	1.4
O <sub>M</sub> FeN <sub>1</sub>	102.9	0.2	C <sub>6</sub> C <sub>15</sub> C <sub>16</sub>	111.8	0.6
O <sub>M</sub> FeN <sub>2</sub>	102.5	0.2	C <sub>15</sub> C <sub>16</sub> C <sub>17</sub>	110.3	0.7
FeO <sub>M</sub> C <sub>M</sub>	125.9	0.6	C <sub>16</sub> C <sub>17</sub> O <sub>1</sub>	129.2	0.9
C <sub>18</sub> C <sub>3</sub> C <sub>4</sub>	111.6	0.9	C <sub>16</sub> C <sub>17</sub> O <sub>2</sub>	111.3	0.8
C <sub>9</sub> C <sub>4</sub> C <sub>3</sub>	103.0	0.9	O <sub>1</sub> C <sub>17</sub> O <sub>2</sub>	119.5	1.0
C <sub>10</sub> C <sub>5</sub> C <sub>6</sub>	106.7	0.7	C <sub>17</sub> O <sub>2</sub> C <sub>21</sub>	118.3	0.9
C <sub>11</sub> C <sub>6</sub> C <sub>5</sub>	108.3	0.7			

<sup>a</sup> C<sub>19</sub> and C<sub>20</sub> are half-atoms statistically.

bonds in question are, of course, those most directly affected by the packing disorder, and the atoms involved have inordinately large apparent thermal parameters. Apart, however, from the C<sub>3</sub>-C<sub>12</sub> bond, which comes out 0.04–0.05 Å. larger than anticipated for trigonal hybridization of one carbon atom (C<sub>3</sub>), other bonds to and within the substituent groups conform, in every case within twice the standard deviation, to the most frequently cited standard values.<sup>15</sup>

Table IV gives the perpendicular distance of each atom in the asymmetric unit of the molecule from the mean plane of the porphine skeleton. Computed deviations from the mean plane are small ( $\leq 0.05$  Å.) for all carbon and nitrogen atoms in the porphine skeleton and are not much larger ( $\leq 0.10$  Å.) for the eight carbon atoms which are directly substituent in the 1...8 positions on the periphery of the porphine skeleton. Over-all, however, these deviations give the porphine skeleton a modestly domed form convex toward the definitely out-of-plane (by 0.49 Å.) iron atom. A more pronounced doming and some accompanying skeletal ruffling characterize the chlorohemin molecule in the crystal.<sup>7</sup> The stereochemical role of the iron atom—surely the most interesting feature of the MeOFeMeso and chlorohemin molecules—is discussed in the final paragraphs of this paper.

It is seen that all side-chain atoms, saving those directly attached to the porphine ring system, are well out from the mean plane of the skeleton. Local flatness of the bond system emanating from each of the trigonally hybridized skeletal carbon atoms C<sub>1</sub>...C<sub>8</sub> is rather accurately maintained, but rotation about the substituent bond allows each extended side chain to turn away from the skeletal mean plane; both the propionic ester and the ethyl groups take advantage of this freedom to nearly the maximum degree consistent with maintenance of individual bond parameters.

The stereochemical feature last mentioned is evident

(15) "Tables of Interatomic Distances in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

**Table IV.** Atomic Displacements ( $D_{\perp}$ ) from the Mean Plane of the Porphine Skeleton in the MeOFeMeso Molecule

Atom	$D_{\perp}$ , Å.	Atom	$D_{\perp}$ , Å.	Atom	$D_{\perp}$ , Å.
C <sub>3</sub>	0.03	C <sub>10</sub>	0.00	1/2C <sub>20</sub>	-1.40
C <sub>4</sub>	0.01	C <sub>11</sub>	-0.01	C <sub>21</sub>	4.87
C <sub>5</sub>	0.05	C <sub>12</sub>	0.07	O <sub>1</sub>	2.38
C <sub>6</sub>	0.04	C <sub>13</sub>	0.06	O <sub>2</sub>	3.69
C <sub>α</sub>	0.02	C <sub>14</sub>	0.10	Fe	-0.490
C <sub>β</sub>	-0.02	C <sub>15</sub>	0.08	N <sub>1</sub>	-0.03
C <sub>γ</sub>	-0.04	C <sub>16</sub>	1.43	N <sub>2</sub>	-0.04
C <sub>18</sub>	0.00	C <sub>17</sub>	2.49	O <sub>M</sub>	-2.33
C <sub>9</sub>	-0.02	1/2C <sub>19</sub>	-1.20	C <sub>M</sub>	-3.14

in the edge-on view of the molecules provided by the diagram (Figure 2) of the cell contents as projected parallel to the unique monoclinic axis. Porphyrin molecules fit back to back in pairs with the propionic ester chains crossing over at the ends. Such fitting is compatible with, and conducive to, planarity in the porphine skeleton and is partially responsible for the large number of intermolecular contacts below 4.0 Å. which are listed in Table V. The somewhat domed porphine skeleton persists, most probably because the nitrogen atoms are then better oriented for bonding to the iron atom. The molecular packing is somewhat looser than in crystalline nickel(II) 2,4-diacetyldeuteroporphyrin-IX dimethyl ester but is notably tighter than in crystalline tetraphenylporphine and its metal derivatives. There is, however, the type of impossibly small intermolecular separation referred to earlier, namely, the 2.27 Å. contact (Table V) between two half-atoms of the C<sub>20</sub> class related to one another by a twofold rotation axis. This difficulty vanishes in the pattern postulated below for the packing disorder.

**Table V.** Packing Distances in the Crystalline Arrangement

Type <sup>a</sup>	Dist., Å.	Type <sup>a</sup>	Dist., Å.	Type <sup>a</sup>	Dist., Å.
C <sub>21</sub> -C <sub>4</sub> <sup>b</sup>	3.75	C <sub>9</sub> -C <sub>9</sub> <sup>c</sup>	3.65	C <sub>γ</sub> -C <sub>11</sub> <sup>d</sup>	3.70
C <sub>21</sub> -C <sub>9</sub> <sup>b</sup>	3.87	C <sub>9</sub> -N <sub>1</sub> <sup>c</sup>	3.87	C <sub>γ</sub> -O <sub>M</sub> <sup>d</sup>	3.85
C <sub>21</sub> -C <sub>19</sub> <sup>b</sup>	3.21	C <sub>10</sub> -C <sub>19</sub> <sup>c</sup>	3.47	C <sub>10</sub> -C <sub>15</sub> <sup>d</sup>	3.64
C <sub>21</sub> -C <sub>M</sub> <sup>b</sup>	3.84	C <sub>11</sub> -C <sub>12</sub> <sup>c</sup>	3.91	C <sub>11</sub> -C <sub>11</sub> <sup>d</sup>	3.74
O <sub>2</sub> -C <sub>M</sub> <sup>b</sup>	3.38	C <sub>12</sub> -C <sub>17</sub> <sup>c</sup>	3.85	C <sub>11</sub> -C <sub>15</sub> <sup>d</sup>	3.84
C <sub>4</sub> -C <sub>β</sub> <sup>c</sup>	3.63	C <sub>12</sub> -O <sub>1</sub> <sup>c</sup>	3.90	C <sub>15</sub> -N <sub>2</sub> <sup>d</sup>	3.76
C <sub>4</sub> -C <sub>9</sub> <sup>c</sup>	3.78	C <sub>12</sub> -O <sub>2</sub> <sup>c</sup>	3.99	C <sub>15</sub> -O <sub>M</sub> <sup>d</sup>	3.64
C <sub>4</sub> -C <sub>10</sub> <sup>c</sup>	3.65	C <sub>12</sub> -N <sub>2</sub> <sup>c</sup>	3.71	C <sub>16</sub> -O <sub>M</sub> <sup>d</sup>	3.68
C <sub>4</sub> -N <sub>2</sub> <sup>c</sup>	3.89	C <sub>13</sub> -C <sub>13</sub> <sup>c</sup>	3.99	C <sub>16</sub> -C <sub>M</sub> <sup>d</sup>	3.85
C <sub>4</sub> -C <sub>4</sub> <sup>c</sup>	3.91	C <sub>20</sub> -O <sub>2</sub> <sup>c</sup>	3.64	C <sub>12</sub> -C <sub>20</sub> <sup>e</sup>	3.77
C <sub>4</sub> -C <sub>β</sub> <sup>c</sup>	3.60	C <sub>20</sub> -C <sub>21</sub> <sup>c</sup>	3.66	C <sub>20</sub> -C <sub>20</sub> <sup>e</sup>	2.27
C <sub>4</sub> -C <sub>9</sub> <sup>c</sup>	3.63	N <sub>1</sub> -N <sub>1</sub> <sup>c</sup>	3.60	C <sub>14</sub> -O <sub>1</sub> <sup>f</sup>	3.79
C <sub>5</sub> -C <sub>12</sub> <sup>c</sup>	3.58	C <sub>5</sub> -C <sub>6</sub> <sup>d</sup>	3.83	C <sub>19</sub> -C <sub>21</sub> <sup>f</sup>	3.95
C <sub>6</sub> -C <sub>12</sub> <sup>c</sup>	3.83	C <sub>5</sub> -C <sub>15</sub> <sup>d</sup>	3.66	C <sub>13</sub> -O <sub>1</sub> <sup>g</sup>	3.30
C <sub>α</sub> -Fe <sup>c</sup>	3.99	C <sub>6</sub> -C <sub>6</sub> <sup>d</sup>	3.51	C <sub>19</sub> -O <sub>1</sub> <sup>g</sup>	3.73
C <sub>β</sub> -C <sub>12</sub> <sup>c</sup>	3.95	C <sub>6</sub> -C <sub>11</sub> <sup>d</sup>	3.79	C <sub>16</sub> -O <sub>2</sub> <sup>h</sup>	3.64
C <sub>β</sub> -C <sub>14</sub> <sup>c</sup>	3.86	C <sub>6</sub> -C <sub>15</sub> <sup>d</sup>	3.78	C <sub>17</sub> -O <sub>2</sub> <sup>h</sup>	3.94
C <sub>18</sub> -C <sub>9</sub> <sup>c</sup>	3.95	C <sub>γ</sub> -C <sub>γ</sub> <sup>d</sup>	3.37	C <sub>19</sub> -C <sub>19</sub> <sup>i</sup>	3.89
C <sub>18</sub> -N <sub>1</sub> <sup>c</sup>	3.68				

<sup>a</sup> The atom without superscript lies in the asymmetric unit (Table I); the atom with superscript has coordinates derived from those in Table I as follows: <sup>b</sup>  $x-1, y, z$ ; <sup>c</sup>  $1-x, y, 1-z$ ; <sup>d</sup>  $1-x, y, 2-z$ ; <sup>e</sup>  $2-x, y, 1-z$ ; <sup>f</sup>  $1/2-x, 1/2-y, 3/2-z$ ; <sup>g</sup>  $1/2+x, 1/2-y, z-1/2$ ; <sup>h</sup>  $x, y, 2-z$ ; <sup>i</sup>  $3/2-x, 1/2-y, 3/2-z$ .

It is convenient to call the C<sub>20</sub> carbon atom of an ethyl group substituent at either C<sub>2</sub> or C<sub>3</sub> the "head" of the molecule (Figure 1), and the pair of carbon atoms

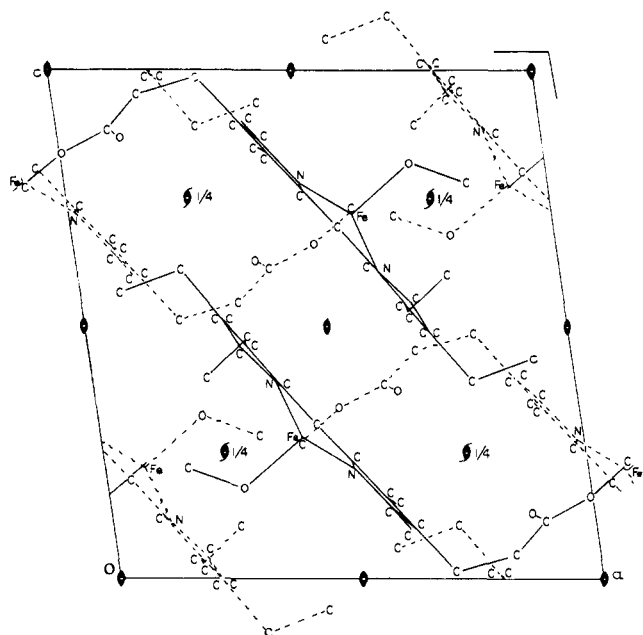


Figure 2. Packing diagram for the crystalline arrangement as viewed parallel to  $b$  and, consequently, to the mean plane of the porphine skeleton. A pair of molecules (solid lines) having Fe,  $O_M$ ,  $C_M$ ,  $C_\alpha$ , and  $C_\gamma$  atoms in the symmetry plane at  $y = 1/2$  are seen to fit back to back with propionate groups wrapping over at the ends. The twofold axes bisecting the cell edges  $a$  and  $c$  are those which, in a completely ordered arrangement, would produce intolerably short contacts between pairs of  $C_{20}$  half-atoms in "head-to-head" fitting of molecules; see text for the discussion of the disordering.

of the  $C_{21}$  type at the ester chain ends the "tail" of the molecule. Staggered quasi-infinite chains of molecules, with head-to-head fitting alternating with tail-to-tail fitting along each chain, exist in the crystal. The fitting in both cases, according to the space group  $I2/m$ , is to be taken in agreement with  $2/m$ , a requirement which can be met statistically by ignoring the difference between D and L isomers or, alternatively stated, by ignoring the difference between the substituent patterns 1,3-dimethyl-2,4-diethyl and 1,3-diethyl-2,4-dimethyl on what is otherwise the same molecular framework (Figure 1). No packing difficulty attends tail-to-tail fitting; indeed, the closest contacts, all above  $4.0 \text{ \AA}$ , involve pairs of atoms of the  $C_{17}$ ,  $C_{16}$ , and  $O_2$  types (Figure 2) rather than the  $C_{21}$  tails. The fitting can be DL, as required by a center of inversion, DD or LL, in agreement with a twofold axis, or, by neglecting perturbations from the head-to-head fitting, it can be an excellent local approximation to the combined requirements of both  $\bar{1}$  and  $2$ , *i.e.*, of  $2/m$ . Head-to-head fitting of two molecules, if taken in agreement with a twofold axis, would require the impossibly small  $2.27 \text{ \AA}$  separation between two  $C_{20}$ -type atoms (or half-atoms). This problem is eliminated if the fitting is restricted to the DL pattern required by a center of inversion.

We look now for the simplest ordered crystalline arrangement or arrangements for which no problems of packing arise while maintaining all satisfactory features of the averaged, somewhat disordered, structure already described. The restriction to be uniformly observed is that head-to-head fitting must be DL as required by a center of inversion. If tail-to-tail fitting be also

taken uniformly in agreement with an inversion center, then each formal molecular chain becomes  $\cdot\cdot\text{DLDL-DL}\cdot\cdot$  and the crystalline arrangement becomes triclinic—space group  $P\bar{1}$  (or  $I\bar{1}$  if the nonprimitive cell be retained). If, on the other hand, tail-to-tail fitting be taken uniformly as that required by a twofold axis, then each molecular chain becomes  $\cdot\cdot\text{DLLDDLLD}\cdot\cdot$ , and the crystalline arrangement retains monoclinic symmetry with the following basic changes: the space group becomes  $C2/c$  (in the most convenient description) with the molecule no longer required to simulate possession of a mirror plane which it cannot have in fact, the cell volume is doubled, and the new (primed) lattice translations become  $a' = a + c$ ,  $b' = b$ ,  $c' = c - a$ .

No experimental data in support of either ordered alternative were observed. The packing data of Table V suggest that head-to-head fitting must observe the centrosymmetric conditions but that chain or crystal growth utilizes without prejudice whichever mode of tail-to-tail fitting is suited to the immediately available molecule, be it a D or an L isomer. This provides an obvious kinetic advantage for the growth of a somewhat disordered structure in statistical conformity with the requirements of  $I2/m$ . Approximate energetic equivalence of the two ordered arrangements with one another and with the actual averaged structure is probable. Consequently, the disordered arrangement should be thermodynamically favored by a substantial entropy of mixing which, in view of the DL pairing in head-to-head fitting, is estimated to be of the order of  $0.5R \ln 2/\text{mole}$  of (monomeric) DL mixture.

In either of the unobserved ordered crystalline arrangements the equilibrium positions of the molecules would be expected to lie in somewhat staggered arrays relative to those planes which, in the averaged structure, are symmetry planes. The anticipated persistence in the disordered structure of such positional displacements correlates very well with the observed pattern of anisotropy in the apparent thermal parameters (*vide supra*).

The configuration of the five bonds formed by the Fe(III) atom with the methoxy oxygen and the four nitrogen atoms is displayed in Figure 3. The square-pyramidal coordination group illustrated therein serves equally well for the chlorohemin<sup>7</sup> molecule, provided one makes the dimensional adjustments required by the differences in effective size and bond radius of the chlorine and oxygen atoms. Table VI lists the more

Table VI. Bond Parameters for the Coordination Groups in the MeOFeMeso and Chlorohemin Molecules

	Fe-N, Å.	Fe-X, Å.	Cl-N, Å.	N-X, $\angle$ FeNCl, deg.
MeOFeMeso	2.073	1.842 <sup>a</sup>	2.022	3.06 <sup>a</sup>
Chlorohemin	2.062	2.218 <sup>b</sup>	2.008	3.36 <sup>b</sup>

<sup>a</sup> X  $\equiv$  O. <sup>b</sup> X  $\equiv$  Cl.

pertinent data needed for detailed comparisons. Inasmuch as the iron atom in MeOFeMeso lies  $0.490 \text{ \AA}$  from the mean plane of the porphine skeleton but only  $0.455 \text{ \AA}$  from the mean plane of the nitrogen atoms, *i.e.*, the base of the coordination pyramid, it appears

that doming of the skeleton arises in giving the nitrogen atoms somewhat more favorable orientations for bonding to iron. In the similarly domed and somewhat ruffled porphine skeleton of the chlorohemin molecule, the Fe(III) atom lies 0.475 Å. from the mean plane of the nitrogens.<sup>7</sup>

Displacement of the iron atom from the base toward the apex of the coordination pyramid (Figure 3) is quite evidently conducive to achievement of a (constrained) minimum in the destabilizing energy associated with the mutual repulsions of the closed-shell ligands. Simple calculations using a repulsive potential of the Born type as outlined earlier<sup>16</sup> suggest, however, that the observed displacements of the Fe(III) atom, especially in the MeOFeMeso molecule, are rather larger than needed to this end. This is indicated qualitatively by noting that the O···N and Cl···N separations (Table VI) are only 0.05 and 0.16 Å. less than the respective sum of the van der Waals radii,<sup>17</sup> whereas the N···N separations are about 0.40 Å. less than the van der Waals diameter. We shall see that there is a good deal more to be said on the matter of why, and of by how much, the iron atom is displaced from the plane of the nitrogen atoms.

The effective size of the Fe(III) atom, a function of the electronic state of the molecule, correlates fairly well with the spectroscopic state, at least for low-spin doublet Fe(III) having one unpaired 3d electron and for high-spin sextet Fe<sup>3+</sup> with five unpaired electrons in a half-filled 3d subshell. In the MeOFeMeso and chlorohemin molecules described herein, magnetic susceptibility and other data show that the iron atom certainly is not doublet Fe(III) and quite probably is sextet Fe<sup>3+</sup>; that it might be the unusual intermediate-spin quartet Fe(III) is a possibility requiring consideration for reasons to be outlined later.

Deprotonation of the nitrogen atoms in the quasi-rigid porphine skeleton leaves each such atom with a net charge of half an electronic unit and, in both classical and quantum mechanical terms, an essential deformability which give it extraordinary complexing properties. Consequently, the porphine skeleton affords a built-in trap, not merely for the usual strongly complexing transition metal cations but also for the eight-shell Mg<sup>2+</sup> and the high-spin sextet Fe<sup>3+</sup>—for ions, that is, which take a notably restrained interest in ammonia<sup>18</sup> or amino nitrogen. In two<sup>19a,b</sup> aminopolycarboxylate complexes of high-spin Fe<sup>3+</sup>, the Fe–N distance ranges from 2.29 to 2.33 Å., and, in a third such chelate,<sup>19c</sup> is still 2.22 Å. notwithstanding the evident contracting influence of ring formation. In the MeOFeMeso and chlorohemin molecules, by contrast, the Fe–N distance is down to 2.07 Å. where it is still 0.15 Å. above the 1.92 Å. expected<sup>17, 20</sup> for low-spin doublet Fe(III) forming octahedral covalent bonds or for (case I of) intermediate-spin quartet Fe(III) in

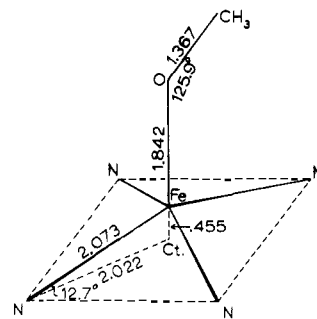


Figure 3. The square-pyramidal coordination group in the MeOFeMeso molecule.

which the initially vacant d orbital of highest energy is  $d_{x^2-y^2}$ , with lobes extending toward the nitrogen atoms.

Inasmuch as the Fe–Cl (2.218 Å.) and Fe–O (1.842 Å.) bond lengths in the chlorohemin and MeOFeMeso molecules are nearly those expected<sup>17</sup> (2.21 and 1.88 Å., respectively) for a low-spin octahedral complex, one might deduce that Fe(III) is in (case II of) the intermediate-spin state with the initially vacant highest energy d orbital now the axial  $d_{z^2}$ . It would seem, however, that a very short bond distance is consistent with high-spin Fe<sup>3+</sup> by reason of the virtually unhindered association with chloride or methoxy oxygen which is observed (Figure 3). Studies of the aminopolycarboxylate complexes of high-spin Fe<sup>3+</sup> suggest<sup>19</sup> an Fe–O bond distance in the range, 1.97–2.00 Å., for octahedral coordination, as compared with the 2.04 Å. given by the sum of the ionic radii<sup>17</sup>; a value approximately 5% lower, *i.e.*, 1.87–1.90 Å., is expected<sup>17</sup> for the still symmetrical tetrahedral coordination. The relation of ferric iron to oxygen in the configuration of Figure 3 is so nearly free of steric interference from the nitrogen atoms as to approximate fairly well to the quasi-linear two-coordinate case.

This dimensional analysis, we suggest, is consistent with high-spin or, possibly, case II of intermediate-spin Fe(III) in the MeOFeMeso and chlorohemin molecules, while excluding both low-spin and case I of intermediate-spin Fe(III) as possibilities.

For some ten porphyrin structures considered in the accompanying paper,<sup>5</sup> the radius of the central "hole" in the porphine skeleton, designated by Ct.–N and equal to the M–N bond distance in case the hole is occupied by a metal atom accurately centered among the four nitrogen atoms, varies from a minimum of 1.960 Å. in a nickel(II) derivative to a maximum of 2.06 Å. in the two crystalline forms of metal-free tetraphenylporphine. The earlier analysis<sup>5</sup> indicates, moreover, that another radius of the skeleton, the distance from the center to the methine carbon (Ct.–C<sub>m</sub>), approaches invariance for the group of porphyrins and that the bond angle at the methine carbon is seemingly quite resistant to alterations of more than a degree or two. It follows, then, that variations in the radius of the central hole require a general accommodation in the internal parameters of the skeleton. The importance of the steric repulsion between the pair of hydrogen atoms attached to diagonally opposed nitrogen atoms in a metal-free porphyrin is quite explicitly shown in the structure of the triclinic modification<sup>21</sup>

(21) S. Silvers and A. Tulinsky, *ibid.*, 86, 927 (1964).

(16) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).  
 (17) Cf. L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 256–264.  
 (18) A fact wholly apparent in elementary qualitative analysis.  
 (19) (a) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, 3, 34 (1964); (b) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, 86, 2749 (1964); (c) J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, 2, 1316 (1963).  
 (20) In the low-spin singlet ethylenediaminetetraacetatocobaltate(III) ion, Co–O bond lengths of 1.88 and 1.90 Å. and Co–N = 1.92 Å. are observed in agreement with expected values<sup>17</sup>: H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, 81, 549 (1959).

of tetraphenylporphine, wherein the diagonal separation of the nitrogen atoms carrying hydrogen is the longer by 0.14 Å. It is plausible now to conclude that the averaged radius, 2.06 Å., of the central hole in metal-free porphyrins is near the tolerable maximum and, giving first consideration to the porphine skeleton, that the energetically most suitable value for this radius in a metal derivative is likely to be near the midpoint, 2.01 Å., of the range thus far observed in porphyrins.<sup>5</sup> Experimental values of Ct.-N are 2.008 Å. in chlorohemin and 2.022 Å. in MeOMeso.

We suggest now that as long as the iron atom in a porphyrin is the stereochemically adaptable<sup>19</sup> high-spin Fe(III), either in five- or in six-coordination, the iron atom will be significantly displaced—by upwards of 0.30 Å. as a conservative guess—from the plane of the nitrogen atoms. If, on this hypothesis, the five-coordinate configuration of Figure 3 were modified by adding a sixth ligand with maintenance of the high-spin state, the iron atom should move only slightly toward the plane of the nitrogens, and steric repulsions from the nitrogen atoms would help to keep the added ligand at so large a distance from the ferric ion as necessarily to allow only weak complexing. If, on the other hand, the addition of a sixth ligand produced the rather profound change in electronic structure signaled by transition to the low-spin doublet state, the Fe(III) atom would move very nearly or exactly into the plane of the nitrogen atoms.<sup>22</sup> An interesting question is whether, in the low-spin case, the porphine skeleton is sufficiently flexible to permit the Fe(III)-N distance to go all the way down to the standard 1.92 Å.; this point bears investigation also in singlet Co(III) and Fe(II) porphyrins for which M-N distances of 1.92 and 1.93 Å. serve as comparison standards.

The crystalline arrangement recently described<sup>8</sup> for aquohydroxyiron(III) tetraphenylporphine specifies an octahedral coordination group which has Fe-N = 2.030 Å. and puts the iron atom only 0.20 Å. out of plane; relative to this partial configuration, the reported 2.18 Å. Fe-OH distance is, in our judgment, at least 0.20 Å. longer than any probable maximum for the bond length, and the 2.95 Å. Fe-OH<sub>2</sub> distance corresponds to water as dielectric filler. Apparent thermal motion of the iron atom normal to the skeletal plane so implausibly large as to preclude the anisotropic refinement of apparent thermal parameters<sup>8</sup> furnishes a part of what we regard as strong evidence for packing disorder in the crystal—a probability not considered during the original analysis based upon strictly applied requirements of the tetragonal space group I4. Assignment of equal probabilities for parallel and antiparallel orientations of the polar (C<sub>4v</sub>) coordination group with respect to the c-axis gives a dimensionally sound arrangement based upon I4/m that, relative to the ordered structure, has a greater entropy. The disordered arrangement, if correct, should then give an electron density mapping with well-resolved pairs of "half-peaks" representing Fe, OH, and OH<sub>2</sub>, along with bond distances more nearly in accord with our chemical expectations.<sup>23, 24</sup>

(22) The gist of this paragraph would remain unchanged were case II of intermediate-spin Fe(III) to replace high-spin Fe(III) throughout.

(23) Further study of this problem, using the amplitude data of Fleischer, *et al.*,<sup>8</sup> is in progress.

During theoretical discussion of electron spin resonance, Griffith<sup>25a</sup> describes an orbital pattern which, he then suggests, occurs in all metal porphyrins and phthalocyanines; his treatment assumes the point group symmetry of D<sub>4</sub> which, if scrupulously observed, requires centering of the metal atom among the nitrogens along with either no axial ligands or two equivalent axial ligands. Griffith further suggests that the iron atoms in crystalline ferric porphyrin chloride (chlorohemin), ferrous phthalocyanine, and ferrous porphyrin (presumably Fe(II) protoporphyrin-IX) are probably in intermediate-spin states. The most significant feature of the spin state, whether for Fe(II) or Fe(III), is that the  $\epsilon$ -orbital<sup>25</sup>—roughly d<sub>x<sup>2</sup>-y<sup>2</sup></sub> in our unsophisticated description of case I for intermediate spin—is vacated in consequence of its much higher energy relative to the other four members of the family.

Numerous investigators agree that the magnetic susceptibilities of crystalline chlorohemin and of other Fe(III) porphyrins which, we judge, are reasonably presumed to carry the same type of central coordination group (Figure 3) correspond very well to the high-spin  $S = 5/2$  state.<sup>26</sup> We have concluded earlier that the Fe-N bond length of 2.07 Å. in chlorohemin and MeOFeMeso is much too long to be compatible either with  $S = 1/2$  or with case I of  $S = 3/2$ . Spin resonance data<sup>27</sup> given by chloroiron(III) phthalocyanine, but erroneously attributed<sup>26b</sup> to chlorohemin by Griffiths, led him to assign<sup>25, 27c</sup> the porphyrin to case I of  $S = 3/2$ . One recognizes that the approximate theoretical treatment<sup>25</sup> of the metal-nitrogen bonding gives essentially the same answer for corresponding porphyrin and phthalocyanine derivatives. Noting, however, that the Ct.-N radius is substantially smaller for the phthalocyanine member of chemically matched derivatives,<sup>5</sup> we see that a high-spin iron(III) phthalocyanine is likely to have the iron atom so far out of plane as to give rather poor bond angles at nitrogen and, consequently, seriously weakened Fe-N bonds. Thus, it is structurally plausible that the stable form of chloroiron(III) phthalocyanine should utilize either case I of  $S = 3/2$  or  $S = 1/2$ .

Magnetic susceptibility data for methoxyiron(III) and chloroiron(III) porphyrins in chloroform, in pyridine, and in pyridine-water solutions are illuminating, but are not without some anomalous features. McLees<sup>28</sup> finds that protohemin methoxide (*i.e.*, methoxyiron(III) protoporphyrin-IX) in pyridine solu-

(24) For generally analogous (but somewhat less cogent) reasons, the completely flat porphine skeleton with the central (H<sub>2</sub>O)<sub>2</sub>ZnN<sub>4</sub> octahedral coordination group recently described<sup>8</sup> for diaquoiron(II) tetraphenylporphine in a crystalline arrangement based upon I4/m is, in our opinion, to be accepted with reserve pending investigation of possible alternatives involving disordered arrangements of polar (C<sub>4v</sub>) coordination groups. These latter include a square-pyramidal (H<sub>2</sub>O)ZnN<sub>4</sub>—the density and some other data suggest a water content below that postulated—and the quasi-octahedral modification of this obtained by adding a much less strongly attached water molecule.

(25) (a) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, London, 1961, pp. 370-373; (b) *Discussions Faraday Soc.*, 26, 81 (1959).

(26) Cf. R. Havemann, W. Haberditzl, and K.-H. Mader, *Z. physik. Chem.*, 218, 71 (1962), and other references cited therein.

(27) (a) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, 26, 72 (1959); (b) D. J. E. Ingram, *ibid.*, 26, 93 (1959); (c) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964, p. 61, carries Griffith's clarification of this matter.

(28) (a) B. D. McLees, Ph.D. Dissertation, The Johns Hopkins University, Baltimore, Md., 1964; (b) B. D. McLees and W. S. Caughey, to be published.

tion gives an effective magnetic moment ( $2.02 \mu_B$ ) corresponding rather well to low-spin ( $S = 1/2$ ) Fe(III), whereas in chloroform the effective moment ( $5.30 \mu_B$ ) is  $0.62 \mu_B$  below the (spin-only) value ( $5.92 \mu_B$ ) for sextet ( $S = 5/2$ ) Fe<sup>3+</sup>. He reports further that deuterohemin chloride (*i.e.*, chloroiron(III) deuteroporphyrin-IX) has effective moments of  $5.94$  and  $5.70 \mu_B$  in, respectively, chloroform and pyridine solutions. Only the last result appears open to question: Havemann, *et al.*,<sup>26</sup> and also Rawlinson and Scutt<sup>29</sup> report that over a period of days the effective magnetic moment of chlorohemin in pyridine drifts downward to a value between  $2$  and  $3 \mu_B$ . By employing carefully redistilled but not ultrapure pyridine, McLees found that the rate of drift of the effective magnetic moment became so small as to arouse the suspicion that the whole effect might arise from the presence of chemically reducing impurities in the pyridine.

It seems clear that the addition of a molecule of pyridine to the square-pyramidal coordination group of Figure 3 readily effects the transition from  $S = 5/2$  to  $S = 1/2$  provided that one is dealing with a methoxyiron(III) porphyrin but that either weak complexing with retention of  $S = 5/2$  or a very slow transition with high activation energy is the result for a chloroiron(III) porphyrin. One obvious structural feature contributing to a more favorable energetics of transition in the methoxy derivatives is the real difference in ligand repulsions,  $N \cdots O$  and  $N \cdots Cl$ , for the low-spin states. With the iron atom centered among the nitrogens and bond lengths appropriate to  $S = 1/2$ , the  $N \cdots O$  and  $N \cdots Cl$  separations are computed to be less by  $0.42$  and  $0.60 \text{ \AA}$ . than the respective sums of the van der Waals radii.<sup>17</sup> The associated repulsive energies are large in both cases, but that for chlorohemin would appear to be the larger by easily  $10 \text{ kcal./mole}$ .

The effective radius of high-spin quintet ferrous iron is considerably larger than that of high-spin Fe<sup>3+</sup>—by  $0.12 \text{ \AA}$ . for octahedral coordination<sup>17</sup>; consequently, it is probable that the Fe(II) atom always must lie substantially out of plane from the nitrogen atoms in any porphyrin or phthalocyanine complex of high-spin ferrous iron. Planar four-coordinate complexes of intermediate-spin ( $S = 1$ ) Fe(II) conforming to Griffith's prescription<sup>25</sup> are dimensionally plausible. Materials presumed to be four-coordinate Fe(II) porphyrins<sup>30</sup> appear, however, to be very readily autoxidized and have not been obtained as well-characterized solids; the observed behavior is that expected for high-spin Fe(II) porphyrins lacking a stabilizing environment. Reported magnetic susceptibilities<sup>25,26</sup> for the comparatively stable ferrous phthalocyanine are appreciably larger than the spin-only

(29) R. A. Rawlinson and P. B. Scutt, *Australian J. Sci. Res.*, **45**, 173 (1952).

(30) (a) H. Fischer, A. Treibs, and K. Zeile, *Z. physiol. Chem.*, **195**, 1 (1931); (b) A. H. Corwin and J. G. Erdman, *J. Am. Chem. Soc.*, **68**, 2473 (1946).

value for two unpaired electrons and would require significant orbital contributions to be consistent with intermediate-spin Fe(II) in square-planar coordination. There are precedents for magnetic behavior of this sort in other phthalocyanine and porphyrin derivatives.<sup>26,28</sup> It seems much less probable that the exaggeratedly pyramidal configuration anticipated for a four-coordinate high-spin ferrous phthalocyanine should lead to stability.

Kendrew<sup>6</sup> reports that in the metmyoglobin structure the iron atom is displaced by more than  $0.25 \text{ \AA}$ . from the mean plane of the heme. This result, according to our earlier discussion, is qualitatively the expected structural behavior for a high-spin Fe(III) porphyrin. One might argue alternatively that the observed displacement is primarily an artifact of the parent myoglobin and, consequently, that it is the structural role of high-spin Fe(II) rather than that of Fe(III) which is significant. Viewed in this light, the already stronger case for a required out-of-plane position of the iron atom in a high-spin Fe(II) porphyrin is further reinforced. One expects that the displacement of the iron atom in myoglobin will turn out to be a good deal larger than the minimum value ( $0.25 \text{ \AA}$ .) quoted for metmyoglobin.

The Fe(III) atom in metmyoglobin—or, one assumes, the Fe(II) atom in myoglobin—is displaced toward, and bonded to, a histidine ring nitrogen of the protein,<sup>6,31</sup> and the weakly coordinated sixth ligand, a water molecule, is further stabilized in this position through hydrogen bonding with a second histidine.<sup>31</sup> Replacement of this water molecule by any ligand effecting the transition from the high-spin to the low-spin state should simultaneously bring the iron and the four nitrogen atoms into virtual coplanarity with much shortened bonds.<sup>32</sup> In the reversible oxygenation of myoglobin or hemoglobin, for example, the central portion of the heme should behave as a flexible diaphragm. The amplitude of the motion, which may be  $>0.5 \text{ \AA}$ ., is easily within the capabilities of the highly flexible porphyrin framework.<sup>5</sup> If the two atoms of the oxygen molecule be symmetrically situated with respect to the iron atom<sup>33</sup> to give geometrically a seven-coordinate group, it is quite conceivable that the iron atom would need to be displaced from the plane of the nitrogens toward the oxygen molecule in order to achieve suitable overlap with the electron cloud of the latter.

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

(32) The comparison carried out by Stryer, *et al.*,<sup>31</sup> of the electron density distributions for metmyoglobin and its low-spin azide derivative was not designed to pick up detailed changes of this sort. Exactly the same set of complex phases was used in both cases, and the resolution of the analysis, which sufficed to indicate the azide group as a single peak of  $0.75 \text{ electron/\AA}^3$  on the difference map, would have been doubtfully adequate at best.

(33) Experimental evidence for symmetrical attachment of an O<sub>2</sub> molecule to Ir in a synthetic molecular oxygen carrier is provided by J. A. Ibers and S. J. LaPlaca, "Proceedings of the Eighth International Conference on Coordination Chemistry," Vienna, Austria, Sept. 1964, p. 95; *cf.* L. Vaska, *Science*, **140**, 809 (1963).