# The Crystal and Molecular Structure of the Ferrihemochrome Bis(1-methylimidazole)-(protoporphyrin IX)iron–Methanol–Water

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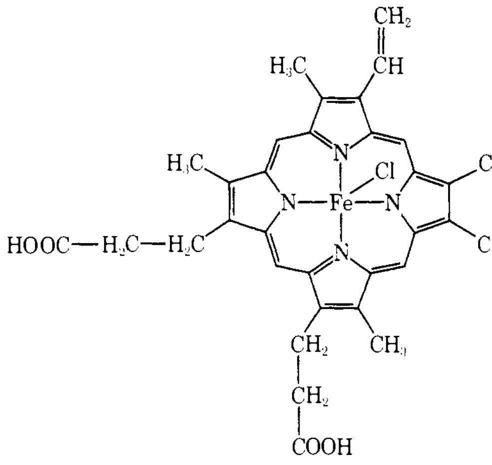
**Abstract:** The six-coordinate Fe(III) porphyrin complex Fe(1-Me-Im)$_2$(PP-IX)·CH$_3$OH·H$_2$O (1-Me-Im = 1-methylimidazole, PP-IX = protoporphyrin IX) has been prepared and has been characterized by a complete X-ray structural determination. The complex crystallizes with four formula units in space group $C_{2h}{}^5$-$P2_1/c$ in a cell of dimensions $a$ = 9.975 (6) Å, $b$ = 21.215 (12) Å, $c$ = 19.241 (13) Å, and $\beta$ = 92.32 (2)°. The calculated and observed densities are 1.35 and 1.36 (1) g/cm$^3$. The structure has been refined anisotropically to a final weighted $R$ index (on $F^2$) of 0.14 for the 5757 measured intensities. The $R$ index (on $F$) for the 3256 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ is 0.08. The complex may be described as a ferric porphyrin, for which the counterion is an ionized carboxyl group of the porphyrin. The average Fe–N(porphyrin) bond length is 1.990 Å. The two axial Fe–N(1-Me-Im) bond lengths are perhaps unequal (1.966 (5) and 1.988 (5) Å) and show a variation similar to those observed in the Fe(imidazole)$_2$(TPP)$^+$ ion. The porphyrin displays a significantly ruffled inner core (±0.14 Å) and has apparently unequal C$_a$–C$_b$ and C$_a$–C$_m$ bond lengths. The vinyl groups at the periphery of the porphyrin have rotated out of the planes of the pyrroles by 24 and 41°. The crystal consists of ribbons of the complex stretched out along the $x$ direction because of a strong (2.41 Å) hydrogen bond between the propionate groups of adjacent molecules. The two propionate groups of a porphyrin are connected together by a bridging water molecule. The methanol molecule also hydrogen bonds to a propionate group.

In 1930 Fischer, Treibs, and Zeile[1] reported that strongly basic solutions of ferric protoporphyrin IX chloride (hemin chloride, Fe(Cl)(PP-IX)[2]) (I) reacted with pyridine to give a crystalline addition product, which they termed a *para*-haemitin. Subsequently, Langenbeck[3] reinvestigated this material, and prepared several new compounds containing either imidazole, 5-methylimidazole, or pilocarpine. Langenbeck demonstrated that these compounds contain two molecules of the nitrogenous bases per heme and that their visible spectra closely resemble that of methemoglobin. He concluded that the compounds have the stoichiometry Fe(L)$_2$(PP-IX)(OH).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In more recent years it has been shown[4,5] that ferric porphyrins readily dimerize in the presence of aqueous base to give $\mu$-oxo dimers. The molecular structure of one such dimer has recently been determined.[5] Since these $\mu$-oxo bridges are not easily cleaved, it was somewhat surprising that the compounds prepared by Fischer et al. and Langenbeck contained two molecules of base per heme. We decided to determine the structure of one on these *para*-haemitins, since they were reported[1,3] to be readily crystalline. To date only one ferric PP-IX complex (Fe(Cl)(PP-IX)) has yielded to crystallographic examination.[6] Because of crystallographic disorder one of the more interesting features of that structure, the orientation and chemical consequences of the two vinyl substituents, was obscured.

Working under the assumption that these *para*-haemitins had to be hemichromes (six-coordinate Fe(L)$_2$(PP-IX)$^+$ complexes) we felt that crystallographic disorder would be unlikely. We reasoned that in Fe(Cl)(PP-IX) two enantiomers were present in the crystal (vide infra) because a single axial ligand destroys the mirror symmetry of the inherently prochiral Fe$^{III}$(PP-IX) molecule. Two axial ligands, on the other hand, would preserve this symmetry. If this were true, then the major force guiding the crystalline arrangement of the molecules would reside with the steric requirements of the dissymmetrically disposed vinyl groups. Such reasoning had proven valid in the case of another important porphyrin, H$_2$MP-IX DME.[7] Thus, there appeared to be an opportunity for a relatively accurate determination of the structure of this biologically important Fe porphyrin.

## Experimental Section

The 1-methylimidazole complex of Fe(Cl)(PP-IX) was prepared by a procedure that is essentially that of Langenbeck.[3] Fe(Cl)(PP-IX) (obtained from Sigma Chemical Co.), 0.4 g, was dissolved in 40 ml of 5% (by weight) aqueous KOH, and then precipitated by the addition of concentrated acetic acid. The precipitated solid was filtered off and washed with dilute acetic acid. The dissolution and precipitation procedure was repeated until the filtrate was free from chloride ion, as indicated by the absence of a precipitate upon the addition of silver nitrate to the filtrate.

The washed, but still moist, solid was dissolved in 100 ml of a 1:1 mixture of chloroform and methanol containing 1.2 g of 1-methylimidazole. The solution was filtered to remove any undissolved material and then the volume reduced and more methanol added. Slow evaporation of such solutions produced large rectangular crystals which were invariably twinned. The crystals were insoluble in either chloroform or methanol but were soluble in a mixture of the two. Anal. Calcd for Fe(1-Me-Im)$_2$(PP-IX)·CH$_3$OH·H$_2$O; C$_{43}$H$_{49}$FeN$_8$O$_6$: C, 62.24; H, 5.95; N, 13.50. Found: C, 62.51; H, 6.10; N, 13.13. As a result of the full crystallographic examination, the compound may also be formulated as a ferric (protoporphyrin IX)-bis(1-methylimidazole) complex, in which the counterion is an ionized carboxylate group of the PP-IX ligand.

The crystal employed for the structure determination was obtained by slow diffusion of hexane, over a 6-month period, into a

Table I. Positional and Thermal Parameters for the Atoms of $Fe(1\text{-}Me\text{-}IM)_2(PP\text{-}IX)\cdot CH_3OH\cdot H_2O$

| ATOM | X[a] | Y | Z | B11[b] OR B,A$^2$ | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|---|---|---|
| FE | 0.479271(97) | 0.252747(49) | 0.488635(44) | 116.3(12) | 23.40(25) | 14.31(25) | -7.02(53) | 9.15(39) | 0.42(23) |
| C(1 ) | 0.20352(74) | 0.21246(39) | 0.43505(32) | 119.(10) | 37.7(26) | 14.8(20) | -6.5(45) | 11.7(36) | -2.8(19) |
| C(2 ) | 0.08351(76) | 0.23586(43) | 0.40052(36) | 121.(11) | 49.1(33) | 21.7(23) | -0.8(48) | 3.7(38) | -1.9(21) |
| C(3 ) | 0.10553(77) | 0.29755(43) | 0.38690(35) | 125.(11) | 43.5(30) | 19.6(22) | 8.4(48) | -1.5(38) | -5.0(22) |
| C(4 ) | 0.23842(76) | 0.31165(38) | 0.41341(33) | 123.(11) | 32.0(25) | 17.5(21) | 6.9(44) | 7.2(37) | 0.4(19) |
| C(5 ) | 0.30338(79) | 0.36865(36) | 0.40656(34) | 149.(11) | 32.0(23) | 22.8(23) | 21.1(44) | 1.2(40) | 1.3(18) |
| C(6 ) | 0.43174(75) | 0.38307(32) | 0.42728(31) | 152.(10) | 23.3(18) | 15.6(20) | 5.6(39) | 9.5(37) | -2.1(16) |
| C(7 ) | 0.50039(86) | 0.44283(32) | 0.41479(34) | 197.(12) | 18.5(19) | 19.8(23) | -1.1(42) | 16.3(43) | -0.4(16) |
| C(8 ) | 0.62572(87) | 0.43637(32) | 0.44004(37) | 163.(12) | 21.2(19) | 28.8(26) | -21.4(44) | 19.8(47) | -0.4(17) |
| C(9 ) | 0.63950(75) | 0.37283(31) | 0.47074(32) | 140.(10) | 13.2(18) | 22.8(21) | -11.8(39) | 17.7(38) | -1.8(16) |
| C(10) | 0.75174(70) | 0.34879(32) | 0.50169(34) | 121.3(96) | 23.0(19) | 25.4(23) | -13.2(37) | 5.9(38) | 1.9(17) |
| C(11) | 0.76388(69) | 0.28968(31) | 0.53099(32) | 95.5(89) | 23.8(19) | 20.1(21) | -8.9(36) | 5.1(35) | 0.0(16) |
| C(12) | 0.88186(72) | 0.26646(33) | 0.56503(35) | 124.(10) | 27.3(22) | 25.8(22) | -14.9(39) | 4.9(39) | -6.0(17) |
| C(13) | 0.85091(85) | 0.20863(38) | 0.58813(40) | 151.(13) | 33.2(25) | 35.3(29) | 4.8(48) | -14.0(47) | 10.5(22) |
| C(14) | 0.71571(68) | 0.19469(33) | 0.56783(32) | 104.5(93) | 25.6(21) | 24.0(22) | -3.8(37) | 1.5(35) | -0.5(17) |
| C(15) | 0.64849(76) | 0.13936(31) | 0.58011(35) | 143.(11) | 21.8(19) | 29.3(24) | -10.4(39) | 2.8(41) | 4.6(17) |
| C(16) | 0.52438(69) | 0.12543(29) | 0.55678(31) | 126.5(94) | 18.1(16) | 21.1(20) | -9.3(35) | 12.7(35) | 1.5(15) |
| C(17) | 0.45616(80) | 0.06576(31) | 0.56669(34) | 181.(12) | 19.2(19) | 22.4(23) | -9.8(41) | 20.8(43) | -0.7(16) |
| C(18) | 0.33860(76) | 0.06726(34) | 0.52956(35) | 162.(11) | 25.1(21) | 24.3(23) | -15.6(42) | 20,4(41) | -5.3(18) |
| C(19) | 0.33081(73) | 0.12952(33) | 0.49830(33) | 140.(18) | 26.5(20) | 18.4(22) | -10.4(41) | 17.4(38) | -2.5(17) |
| C(20) | 0.22023(73) | 0.15199(38) | 0.46015(35) | 141.(11) | 32.9(24) | 22.8(23) | -30.7(43) | 10.1(39) | -1.4(19) |
| C(21) | -0.03723(84) | 0.19574(50) | 0.38313(46) | 140.(12) | 66.5(44) | 48.5(37) | -18.5(61) | -33.7(52) | 2.3(32) |
| C(22) | 0.01415(93) | 0.34340(52) | 0.35139(43) | 170.(12) | 64.7(42) | 31.4(29) | 12.5(67) | -18.1(49) | -11.3(28) |
| C(23) | -0.1102(10) | 0.34591(66) | 0.34316(51) | 201.(15) | 110.9(68) | 47.5(39) | 16.5(87) | -33.4(64) | -19.8(40) |
| C(24) | 0.43622(86) | 0.49821(34) | 0.37941(38) | 266.(16) | 22.6(20) | 30.9(27) | 17.9(49) | 6.8(50) | 1.4(19) |
| C(25) | 0.72750(84) | 0.48356(45) | 0.43581(50) | 218.(12) | 37.9(33) | 53.9(42) | -8.0(53) | -10.3(58) | 6.5(30) |
| C(26) | 0.8132(12) | 0.50075(65) | 0.47707(67) | 15.08(41) | | | | | |
| C(27) | 1.01288(73) | 0.30037(35) | 0.57319(38) | 125.(10) | 34.8(24) | 42.5(29) | -12.2(41) | 1.0(42) | -2.3(21) |
| C(28) | 0.9384(10) | 0.16494(60) | 0.65139(65) | 203.(16) | 81.5(50) | 97.5(63) | -58.2(75) | 88.3(85) | -58.5(48) |
| C(29) | 0.9961(11) | 0.12564(65) | 0.60824(53) | 251.(18) | 99.1(59) | 44.3(41) | -53.8(89) | 47.6(73) | -26.6(42) |
| C(30) | 1.1033(12) | 0.09169(58) | 0.67400(69) | 214.(19) | 47.5(42) | 95.7(63) | 31.5(75) | 6.1(93) | 34.8(43) |
| C(31) | 0.51200(78) | 0.01270(34) | 0.61073(36) | 207.(12) | 22.4(21) | 27.2(25) | -3.7(43) | 20.6(44) | 3.8(19) |
| C(32) | 0.46248(72) | 0.01610(34) | 0.68606(35) | 178.(11) | 25.5(21) | 29.5(24) | -4.7(41) | 18.3(41) | 10.7(19) |
| C(33) | 0.51823(83) | 0.07245(39) | 0.72440(35) | 158.(12) | 32.1(23) | 21.8(23) | -10.9(49) | 9.2(42) | 4.0(19) |
| C(34) | 0.23146(81) | 0.01704(34) | 0.52201(40) | 242.(13) | 26.8(21) | 38.3(30) | -36.5(46) | 24.2(50) | -2.3(20) |
| C(35) | 0.57273(64) | 0.25857(32) | 0.34391(32) | 136.9(90) | 25.1(19) | 20.0(21) | -2.5(37) | 8.4(35) | 0.1(17) |
| C(36) | 0.58828(79) | 0.16433(34) | 0.38335(35) | 219.(13) | 24.7(20) | 22.7(23) | -8.8(44) | 30.8(43) | -2.4(17) |
| C(37) | 0.63343(76) | 0.16427(35) | 0.31828(34) | 196.(12) | 25.6(21) | 27.5(22) | -14.5(43) | 23.9(41) | -6.9(17) |
| C(38) | 0.66833(76) | 0.24657(39) | 0.22673(32) | 200.(12) | 40.6(26) | 19.6(20) | -2.7(51) | 24.0(40) | 2.2(21) |
| C(39) | 0.35587(62) | 0.24966(33) | 0.62827(32) | 123.1(83) | 26.0(19) | 21.8(20) | -1.7(40) | 6.9(34) | 41.4(19) |
| C(40) | 0.40576(96) | 0.34390(40) | 0.60087(39) | 314.(17) | 32.9(26) | 29.2(28) | -22.9(57) | 46.4(57) | -9.5(22) |
| C(41) | 0.3505(10) | 0.34722(46) | 0.66351(40) | 339.(20) | 40.4(31) | 25.8(27) | -31.5(66) | 55.7(59) | -11.3(24) |
| C(42) | 0.25836(65) | 0.25764(31) | 0.74559(35) | 172.4(88) | 47.2(21) | 21.5(24) | -5.1(35) | 29.2(37) | 5.9(17) |
| C(43) | 1.0937(11) | -0.07801(52) | 0.81120(60) | 16.20(31) | | | | | |
| N(1 ) | 0.29881(52) | 0.25034(27) | 0.44365(24) | 116.7(70) | 25.2(17) | 17.3(15) | -6.2(32) | 8.5(26) | -1.5(16) |
| N(2 ) | 0.51939(54) | 0.34205(24) | 0.46098(24) | 126.5(71) | 19.5(14) | 17.2(16) | -0.9(30) | 9.5(27) | 1.0(13) |
| N(3 ) | 0.66249(47) | 0.24542(24) | 0.53198(22) | 95.9(62) | 13.3(13) | 16.8(15) | -1.4(29) | 1.1(24) | -0.3(13) |
| N(4 ) | 0.44294(52) | 0.16413(24) | 0.51648(25) | 115.4(73) | 19.6(14) | 20.6(16) | -14.5(30) | 10.6(28) | 0.5(13) |
| N(5 ) | 0.62297(52) | 0.22393(26) | 0.29355(24) | 125.6(72) | 28.1(17) | 16.0(15) | 2.8(29) | 12.5(27) | -2.3(13) |
| N(6 ) | 0.54975(49) | 0.22419(23) | 0.39998(23) | 117.2(69) | 18.7(13) | 15.4(15) | -4.3(25) | 3.7(25) | 1.2(12) |
| N(7 ) | 0.31997(58) | 0.28727(30) | 0.68084(26) | 146.2(85) | 34.8(20) | 16.0(17) | -6.5(35) | 15.3(30) | -1.7(15) |
| N(8 ) | 0.41048(52) | 0.28271(26) | 0.57843(24) | 116.9(73) | 25.5(15) | 15.3(16) | -11.2(29) | 8.6(27) | -0.9(13) |
| O(1 ) | 1.08011(68) | 0.03958(38) | 0.69324(43) | 254.(12) | 55.6(28) | 110.2(46) | 19.7(49) | 5.2(55) | 42.4(30) |
| O(2 ) | 1.21046(66) | 0.12406(35) | 0.68400(37) | 192.4(97) | 50.1(27) | 67.2(32) | 15.2(42) | 10.7(48) | 19.2(23) |
| O(3 ) | 0.43275(53) | 0.11731(26) | 0.73705(25) | 214.0(86) | 30.3(15) | 35.1(19) | 10.8(32) | 15.8(34) | 0.7(14) |
| O(4 ) | 0.63599(56) | 0.07544(28) | 0.74234(27) | 159.0(79) | 46.3(21) | 40.7(22) | -6.5(36) | -0.3(34) | 2.4(16) |
| O(5 ) | 0.81841(89) | -0.02438(48) | 0.71710(50) | 20.92(30) | | | | | |
| O(6 ) | 1.19002(64) | -0.05638(31) | 0.76534(35) | 14.29(18) | | | | | |

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

concentrated solution of the 1-methylimidazole adduct in methanol-chloroform. A small amount of free 1-methylimidazole had been added to the solution. Only one crystal of satisfactory size and quality was obtained.

Preliminary precession photographs taken with Cu K$\alpha$ radiation showed monoclinic symmetry and systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with the space group $C_{2h}{}^5$-$P2_1/c$. The crystal was a flat plate with major bounding faces of the forms {010}, {100}, {001}. The distances between the faces of these forms are 0.067, 0.571, and 0.755 mm. The crystal was mounted with the $c$ axis approximately along the spindle axis. It was then coated lightly with hair spray.

The lattice parameters, obtained as previously described[8] by hand centering of 15 reflections with Cu K$\alpha_1$ radiation ($\lambda$ 1.540562 Å) in the range $30 \leq 2\theta \leq 60°$ are $a$ = 9.975 (6) Å, $b$ = 21.215 (12) Å, $c$ = 19.241 (13) Å, and $\beta$ = 92.32 (2)°. The calculated density, based on four molecules of porphyrin complex, four molecules of methanol, and four of water per unit cell, is 1.35 g/cm$^3$ and agrees well with an observed value of 1.36 (1) g/cm$^3$, as measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of $2\theta$ by the $\theta$-$2\theta$ scan method using Cu K$\alpha$ radiation prefiltered with Ni foil. The scan range in $2\theta$ was from 1.5° below the Cu K$\alpha_1$ peak to 1.5° above the Cu K$\alpha_2$ peak. The takeoff angle was 3.9° and the receiving counter was positioned 33 cm from the crystal with an aperture 3.4 mm high and 3.7 mm wide. The pulse height analyzer was set to admit about 90% of the Cu K$\alpha$ peak. Initially background counts of 10 sec were taken at the end of each scan range. Past a $2\theta$ of 60° this was increased to 20 sec. A scan range of 2° in $2\theta$ per minute was used. Data were collected in the range $1 < 2\theta \leq 118°$. Data collection was terminated when less than 10% of the measured reflections were statistically observable. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. The deviations of these standards were all within counting statistics.

The data were processed as previously described using a value of

Table III. Root-Mean-Square Amplitudes of Vibration (Å)[a]

| Atom | Min | Inter | Max |
|---|---|---|---|
| Fe | 0.157 (2) | 0.209 (2) | 0.251 (1) |
| C(1) | 0.157 (11) | 0.244 (11) | 0.298 (10) |
| C(2) | 0.201 (10) | 0.247 (11) | 0.335 (11) |
| C(3) | 0.187 (11) | 0.247 (11) | 0.321 (11) |
| C(4) | 0.178 (10) | 0.243 (11) | 0.277 (11) |
| C(5) | 0.205 (10) | 0.228 (10) | 0.311 (10) |
| C(6) | 0.164 (11) | 0.230 (9) | 0.280 (10) |
| C(7) | 0.184 (11) | 0.205 (10) | 0.318 (10) |
| C(8) | 0.182 (12) | 0.227 (10) | 0.314 (11) |
| C(9) | 0.187 (10) | 0.200 (10) | 0.285 (10) |
| C(10) | 0.196 (10) | 0.225 (10) | 0.267 (10) |
| C(11) | 0.189 (10) | 0.206 (11) | 0.248 (10) |
| C(12) | 0.198 (10) | 0.228 (10) | 0.285 (9) |
| C(13) | 0.204 (12) | 0.284 (12) | 0.310 (10) |
| C(14) | 0.212 (10) | 0.225 (11) | 0.246 (10) |
| C(15) | 0.199 (11) | 0.244 (10) | 0.278 (10) |
| C(16) | 0.175 (10) | 0.209 (9) | 0.264 (9) |
| C(17) | 0.187 (10) | 0.206 (10) | 0.313 (10) |
| C(18) | 0.192 (10) | 0.221 (11) | 0.312 (10) |
| C(19) | 0.169 (11) | 0.231 (11) | 0.286 (10) |
| C(20) | 0.191 (11) | 0.212 (10) | 0.326 (10) |
| C(21) | 0.208 (13) | 0.336 (12) | 0.399 (13) |
| C(22) | 0.215 (12) | 0.298 (11) | 0.398 (13) |
| C(23) | 0.240 (12) | 0.348 (12) | 0.517 (16) |
| C(24) | 0.217 (10) | 0.241 (10) | 0.372 (11) |
| C(25) | 0.280 (12) | 0.305 (13) | 0.356 (9) |
| C(27) | 0.235 (11) | 0.281 (10) | 0.296 (10) |
| C(28) | 0.215 (14) | 0.275 (14) | 0.586 (16) |
| C(29) | 0.231 (13) | 0.323 (13) | 0.524 (16) |
| C(30) | 0.225 (13) | 0.344 (15) | 0.475 (16) |
| C(31) | 0.197 (11) | 0.240 (10) | 0.330 (10) |
| C(32) | 0.174 (11) | 0.277 (10) | 0.308 (9) |
| C(33) | 0.190 (11) | 0.261 (11) | 0.297 (11) |
| C(34) | 0.202 (11) | 0.259 (11) | 0.381 (10) |
| C(35) | 0.190 (10) | 0.238 (9) | 0.265 (9) |
| C(36) | 0.179 (11) | 0.234 (10) | 0.347 (10) |
| C(37) | 0.197 (10) | 0.236 (10) | 0.335 (10) |
| C(38) | 0.172 (10) | 0.305 (10) | 0.326 (10) |
| C(39) | 0.190 (10) | 0.250 (10) | 0.251 (10) |
| C(40) | 0.189 (11) | 0.264 (11) | 0.423 (11) |
| C(41) | 0.164 (13) | 0.283 (13) | 0.448 (12) |
| C(42) | 0.159 (14) | 0.312 (7) | 0.331 (7) |
| N(1) | 0.175 (8) | 0.227 (9) | 0.257 (8) |
| N(2) | 0.173 (8) | 0.212 (8) | 0.255 (7) |
| N(3) | 0.177 (8) | 0.209 (8) | 0.221 (7) |
| N(4) | 0.173 (9) | 0.204 (8) | 0.264 (8) |
| N(5) | 0.161 (8) | 0.252 (8) | 0.259 (7) |
| N(6) | 0.168 (8) | 0.205 (8) | 0.245 (7) |
| N(7) | 0.161 (9) | 0.265 (8) | 0.293 (8) |
| N(8) | 0.164 (9) | 0.217 (8) | 0.267 (8) |
| O(1) | 0.257 (9) | 0.363 (8) | 0.513 (10) |
| O(2) | 0.277 (8) | 0.311 (8) | 0.404 (9) |
| O(3) | 0.248 (7) | 0.258 (7) | 0.337 (7) |
| O(4) | 0.273 (7) | 0.282 (7) | 0.329 (7) |

[a] Atoms C(26), C(43), O(5), and O(6) were refined isotropically.

0.04 for $p$.[8] Of the 6367 reflections measured, 5757 are unique and of these 3256 have $F_o^2 > 3\sigma(F_o^2)$. Sample calculations[9] for an absorption correction were made using a linear absorption coefficient of 34.7 cm$^{-1}$. The transmission factors calculated ranged from 0.24 to 0.78, and an absorption correction was therefore applied.

**Solution and Refinement of the Structure.** Normalized structure factors ($E$'s), scaled such that $\langle E^2 \rangle = 1.0$, were calculated from the measured structure amplitudes.

Using the quantities $E^2 - 1$ a sharpened, origin-removed Patterson map was calculated which indicated that the Fe atom was located at $y \sim 1/4$. A direct methods approach placed the Fe atom slightly away from $y = 1/4$, and gave the positions of the four N atoms of the porphyrin core. A subsequent series of difference Fourier maps and structure factor calculations revealed the positions of all the nonhydrogen atoms in the porphyrin, as well as those of the two 1-methylimidazole groups, the methanol, and the water molecule.

Three cycles of least-squares refinement, based on $F$, of the 58 independent nonhydrogen atoms, using isotropic thermal parameters reduced $R$ and $R_w$ to 0.13 and 0.15, respectively.[10] The structure was refined by full-matrix least-squares techniques. Values of the atomic scattering factors and the anomalous terms[11] were taken from the usual sources.

The H atoms at the methine (C–H = 0.95 Å), methylene (C–H = 1.0 Å), and imidazole ring (C–H = 0.95 Å) positions were idealized, ($B$(H) = $B$(C) + 1.0 Å$^2$) and added as fixed contributions to ensuing cycles of refinement. Next, five cycles of anisotropic full-matrix least-squares refinement on $F^2$, rather than $F$, were carried out. In the refinement anisotropic thermal parameters were assigned to all atoms except C(26) (a terminal vinyl carbon atom) and the three nonhydrogen atoms of the methanol and water molecules. These atoms had unusually high isotropic thermal parameters in the early stages of the calculations. The full-matrix refinement of 503 variables used all 5757 measured intensities (including those with $F_o^2 < 0$), and converged to values of $R$ and $R_w$ (on $F^2$) of 0.14 and 0.20, respectively.

A structure factor calculation on $F$ for the 3256 reflections having $F_o^2 > 3\sigma$ ($F_o^2$) gave conventional agreement indices of 0.08 and 0.12 for $R$ and $R_w$, respectively. The values of $F_o^2$ and $F_c^2$ are available.[12] The final atomic parameters and their errors are listed in Table I. The calculated atomic parameters for the hydrogen atoms are given in Table II.[12] Table III presents the root-mean-square amplitudes of thermal vibration.

## Description and Discussion of the Structure

On the basis of the structural results (vide infra) and the analytical data the crystal consists of discrete molecules of Fe(1-Me-Im)$_2$(PP-IX)·CH$_3$OH·H$_2$O. The Fe porphyrin itself may best be formulated as a ferric protoporphyrin IX complex for which the counterion is an ionized carboxylate group of the porphyrin. The presence of hydrogen bonds has been inferred from the observed stereochemistry. The quality of the data set has not enabled us to locate hydrogen atoms directly.

The contents of one unit cell are shown in Figure 1 and the hydrogen bonding scheme is illustrated in Figure 2. The numbering scheme[13] for the complex is shown in Figure 3. Because of the strong intermolecular hydrogen bonds (2.41 Å) between the C(30) and C(33) carboxylate groups of *adjacent* porphyrin molecules, the structure may best described as consisting of ribbons of Fe(1-Me-Im)$_2$(PP-IX) molecules stretched out along the $x$ direction. The planes of the porphyrin rings are canted slightly to the $x$-$y$ plane in the crystal.

A weak *intra*molecular hydrogen bond between adjacent propionate groups on a PP-IX ring results from the presence of a water molecule (O(5)) in the lattice (Figure 2). The compound could be alternatively formulated as [Fe(1-Me-Im)$_2$(PP-IX)]$^+$[OH$^-$] although this is not consistent with the p$K_a$'s of the propionate groups (p$K_a \approx 5$). Such a formulation would require only a shift in the position of one of the hydrogen atoms of the water molecule (O(5)) toward the oxygen atom of a carboxylate group. The observed C–O bond lengths in the carboxylate groups do not allow us to make such a distinction. A methanol molecule, C(43)–O(6), in the lattice forms a third hydrogen bond to carboxyl oxygen atom O(1). There is no hydrogen bonding in the $y$ or $z$ directions in the crystal.

The bond distances and bond angles observed in this structure are given in Table IV. The equations of, and dihedral angles between, the best least-squares planes through the molecule are presented in Table V. The table also gives the deviations of individual atoms from these planes. In addition to the individual bond lengths, Table IV also presents the averaged values of the bond distances and bond angles in the porphyrin core. In some instances (C$_a$–C$_b$ and C$_m$–C$_a$) the standard deviation of a single observation, as estimated on the assumption that all members averaged are from the same population, somewhat exceeds the estimate obtained from the inverse matrix. In view of the good agreement between the chemically equivalent bond distances and

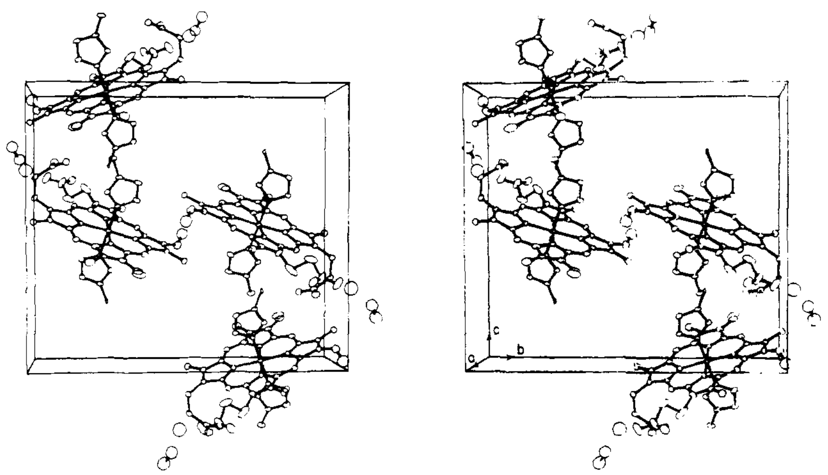

Figure 1. Stereoscopic view of the contents of one unit cell. The hydrogen atoms have been omitted for clarity.

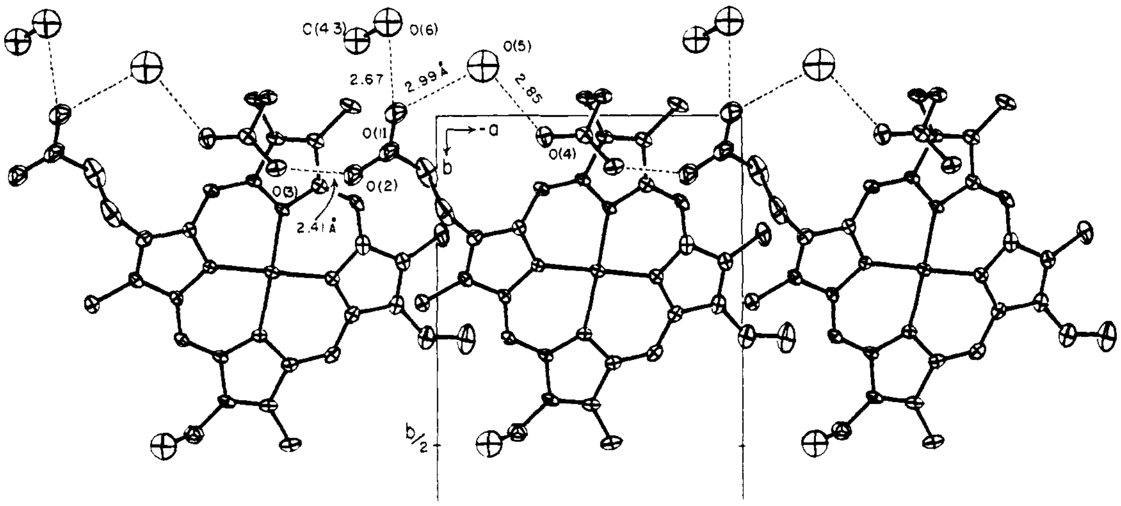

Figure 2. Drawing to indicate the hydrogen bonding network in the crystal. The hydrogen-bonded atoms are connected by dashed lines. The axial methylimidazoles and the hydrogen atoms have been omitted from the drawing for clarity. The oxygen atom of the water molecule is labeled O(5) and that of the methanol molecule O(6).

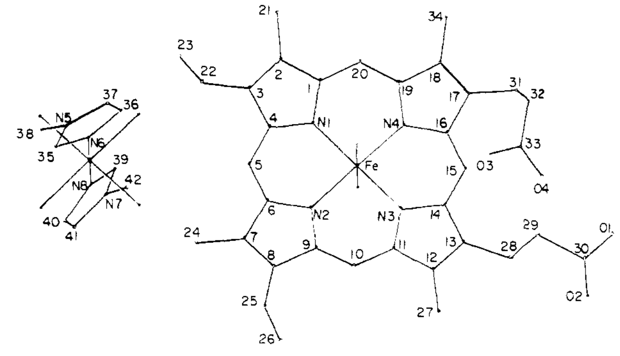

Figure 3. Diagram to indicate the numbering scheme used in this paper for the 55 nonhydrogen atoms in the Fe(1-Me-Im)$_2$(PP-IX) molecule. The oxygen atoms of the water and methanol molecules, which are not shown, are numbered O(5) and O(6) respectively, and the carbon atom of the methanol molecule is C(43). The orientation of the complex in the drawing is identical with that in Figure 4.

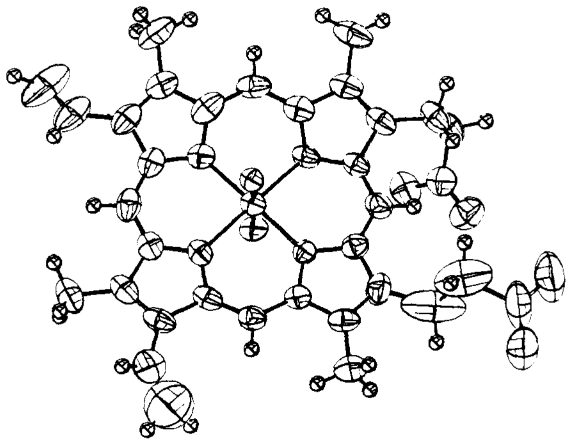

Figure 4. A drawing of the porphyrin molecule and coordination sphere about the central Fe atom. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been drawn artificially small for clarity.

bond angles in the two 1-methylimidazole groups this suggests that the bonds in the porphyrin core are in fact nonequivalent.

An equally large dissymmetric pattern can be discerned in the structure of Fe(Cl)(PP-IX),[6] but the differences observed are at the limit of the accuracy of that structure. The nonequivalence of these bond lengths appears to reflect the asymmetric ruffling of the macrocycle rather than the pattern of substitution around the periphery of the porphyrin. In the structure of H$_2$MP-IXDME[7] there is no detectable effect of the substituents on the bond lengths within the porphyrin core.

Because of the chemically unreasonable bond distances and thermal parameters associated with the C(28) and C(29) carbon atoms of the propionate chain substituent at C(13), we conclude that there is some disorder associated with this propionate group. It is unlikely that the disorder

Table IV. Distances (Å) and Angles (deg) in Fe$^{III}$(1-Me-Im)$_2$(PP-IX)·CH$_3$OH·H$_2$O[a]

| Bond | | Average | Type |
|---|---|---|---|
| Fe–N(1) | 1.973 (6) | 1.990 (16) | Fe–N$_{porph}$ |
| Fe–N(2) | 2.012 (5) | | |
| Fe–N(3) | 1.985 (5) | | |
| Fe–N(4) | 1.992 (5) | | |
| Fe–N(6) | 1.966 (5) | | |
| Fe–N(8) | 1.988 (5) | | |
| N(1)–C(1) | 1.392 (8) | 1.376 (8) | N–C$_a$[b] |
| N(1)–C(4) | 1.368 (8) | | |
| N(2)–C(6) | 1.378 (8) | | |
| N(2)–C(9) | 1.371 (8) | | |
| N(3)–C(11) | 1.381 (7) | | |
| N(3)–C(14) | 1.374 (7) | | |
| N(4)–C(16) | 1.373 (7) | | |
| N(4)–C(19) | 1.372 (8) | | |
| C(1)–C(2) | 1.435 (9) | 1.443 (22) | C$_a$–C$_b$ |
| C(3)–C(4) | 1.433 (9) | | |
| C(6)–C(7) | 1.465 (9) | | |
| C(8)–C(9) | 1.476 (9) | | |
| C(11)–C(12) | 1.413 (9) | | |
| C(13)–C(14) | 1.420 (9) | | |
| C(16)–C(17) | 1.453 (8) | | |
| C(18)–C(19) | 1.452 (9) | | |
| C(2)–C(3) | 1.354 (10) | 1.345 (10) | C$_b$–C$_b$ |
| C(7)–C(8) | 1.330 (9) | | |
| C(12)–C(13) | 1.345 (9) | | |
| C(17)–C(18) | 1.350 (9) | | |
| C(5)–C(4) | 1.380 (10) | 1.368 (19) | C$_m$–C$_a$ |
| C(5)–C(6) | 1.361 (9) | | |
| C(10)–C(9) | 1.348 (9) | | |
| C(10)–C(11) | 1.378 (8) | | |
| C(15)–C(14) | 1.377 (9) | | |
| C(15)–C(16) | 1.333 (8) | | |
| C(20)–C(19) | 1.385 (9) | | |
| C(20)–C(1) | 1.379 (10) | | |
| C(2)–C(21) | 1.502 (10) | 1.500 (10) | C$_b$–C$_{methyl}$ |
| C(7)–C(24) | 1.490 (9) | | |
| C(12)–C(27) | 1.495 (9) | | |
| C(18)–C(34) | 1.512 (9) | | |
| C(3)–C(22) | 1.482 (11) | 1.456 (37) | C$_b$–C$_{vinyl}$ |
| C(8)–C(25) | 1.430 (10) | | |
| C(22)–C(23) | 1.246 (10) | 1.224 (32) | Vinyl |
| C(25)–C(26) | 1.201 (12) | | |
| C(13)–C(28) | 1.74 (2) | | Propionate |
| C(17)–C(31) | 1.503 (9) | | |
| C(28)–C(29) | 1.324 (12) | | |
| C(31)–C(32) | 1.551 (9) | | |
| C(29)–C(30) | 1.78 (2) | | |
| C(32)–C(33) | 1.500 (10) | | |
| C(30)–O(1) | 1.191 (12) | | |
| C(30)–O(2) | 1.278 (12) | | |
| C(33)–O(3) | 1.307 (9) | | |
| C(33)–O(4) | 1.213 (8) | | |
| N(5)–C(35) | 1.329 (7) | 1.338 (10) | Methyl-imidazoles |
| N(7)–C(39) | 1.348 (8) | | |
| N(5)–C(37) | 1.355 (8) | 1.354 (8) | |
| N(7)–C(14) | 1.352 (10) | | |
| N(6)–C(35) | 1.330 (8) | 1.326 (8) | |
| N(8)–C(39) | 1.322 (7) | | |
| N(6)–C(36) | 1.368 (8) | 1.368 (8) | |
| N(8)–C(40) | 1.369 (9) | | |
| C(36)–C(37) | 1.347 (8) | 1.347 (8) | |
| C(40)–C(41) | 1.347 (9) | | |
| N(5)–C(38) | 1.461 (7) | 1.466 (8) | |
| N(7)–C(42) | 1.471 (8) | | |
| C(43)–O(6) | 1.406 (11) | | Methanol |
| Fe–N(6)–C(35) | 127.9 (4) | | Methyl-imidazole |
| Fe–N(8)–C(39) | 128.8 (4) | | |
| Fe–N(6)–C(36) | 127.0 (4) | | |
| Fe–N(8)–C(40) | 126.5 (4) | | |
| C(39)–N(8)–C(40) | 104.7 (5) | | |

| Bond | | Average | Type |
|---|---|---|---|
| C(35)–N(6)–C(36) | 105.1 (5) | | |
| N(6)–C(35)–N(5) | 111.7 (5) | | |
| N(8)–C(39)–N(7) | 111.1 (6) | | |
| C(35)–N(5)–C(37) | 106.6 (5) | | |
| C(39)–N(7)–C(41) | 107.6 (5) | | |
| N(5)–C(37)–C(36) | 107.5 (6) | | |
| N(7)–C(41)–C(40) | 106.0 (7) | | |
| C(38)–N(5)–C(35) | 126.7 (6) | | |
| C(42)–N(7)–C(41) | 125.5 (6) | | |
| N(1)–Fe–N(2) | 88.8 (2) | | FeN$_6$ polyhedron |
| N(1)–Fe–N(3) | 178.8 (2) | | |
| N(1)–Fe–N(4) | 91.1 (2) | | |
| N(1)–Fe–N(6) | 89.7 (2) | | |
| N(1)–Fe–N(8) | 90.9 (2) | | |
| N(2)–Fe–N(3) | 89.7 (2) | | |
| N(2)–Fe–N(4) | 179.0 (2) | | |
| N(2)–Fe–N(6) | 88.8 (2) | | |
| N(2)–Fe–N(8) | 90.4 (2) | | |
| N(3)–Fe–N(4) | 89.3 (2) | | |
| N(3)–Fe–N(6) | 89.2 (2) | | |
| N(3)–Fe–N(8) | 90.2 (2) | | |
| N(4)–Fe–N(6) | 91.0 (2) | | |
| N(4)–Fe–N(8) | 89.7 (2) | | |
| N(6)–Fe–N(8) | 179.0 (2) | | |
| C(1)–N(1)–C(4) | 104.0 (6) | 105.9 (14) | C$_a$–N–C$_a$ |
| C(6)–N(2)–C(9) | 107.4 (5) | | |
| C(11)–N(3)–C(14) | 105.7 (5) | | |
| C(16)–N(4)–C(19) | 106.4 (5) | | |
| N(1)–C(1)–C(2) | 110.9 (7) | 109.9 (12) | N–C$_a$–C$_b$ |
| N(1)–C(4)–C(3) | 111.7 (7) | | |
| N(2)–C(6)–C(7) | 109.4 (6) | | |
| N(2)–C(9)–C(8) | 108.2 (6) | | |
| N(3)–C(11)–C(12) | 110.7 (6) | | |
| N(3)–C(14)–C(13) | 108.6 (6) | | |
| N(4)–C(16)–C(17) | 109.0 (6) | | |
| N(4)–C(19)–C(18) | 110.6 (6) | | |
| C(1)–C(2)–C(3) | 106.6 (7) | 107.2 (12) | C$_a$–C$_b$–C$_b$ |
| C(2)–C(3)–C(4) | 106.7 (7) | | |
| C(6)–C(7)–C(8) | 106.8 (6) | | |
| C(7)–C(8)–C(9) | 108.2 (6) | | |
| C(11)–C(12)–C(13) | 105.9 (6) | | |
| C(12)–C(13)–C(14) | 109.1 (7) | | |
| C(16)–C(17)–C(18) | 108.2 (6) | | |
| C(17)–C(18)–C(19) | 105.8 (6) | | |
| N(1)–C(1)–C(20) | 124.1 (7) | 124.7 (10) | N–C$_a$–C$_m$ |
| N(1)–C(4)–C(5) | 122.7 (7) | | |
| N(2)–C(6)–C(5) | 124.6 (7) | | |
| N(2)–C(9)–C(10) | 125.9 (6) | | |
| N(3)–C(11)–C(10) | 124.9 (6) | | |
| N(3)–C(14)–C(15) | 125.0 (6) | | |
| N(4)–C(16)–C(15) | 125.4 (6) | | |
| N(4)–C(19)–C(20) | 125.1 (6) | | |
| C(5)–C(4)–C(3) | 125.4 (7) | 125.3 (8) | C$_m$–C$_a$–C$_b$ |
| C(5)–C(6)–C(7) | 125.9 (7) | | |
| C(10)–C(11)–C(12) | 124.4 (6) | | |
| C(10–C(9)–C(8) | 125.8 (7) | | |
| C(15)–C(14)–C(13) | 126.4 (7) | | |
| C(15)–C(16)–C(17) | 125.6 (7) | | |
| C(20)–C(1)–C(2) | 124.9 (8) | | |
| C(20)–C(19)–C(18) | 124.1 (7) | | |
| C(1)–C(20)–C(19) | 126.1 (7) | 126.3 (8) | C$_a$–C$_m$–C$_a$ |
| C(4)–C(5)–C(6) | 127.5 (7) | | |
| C(9)–C(10)–C(11) | 125.7 (6) | | |
| C(14)–C(15)–C(16) | 125.7 (7) | | |
| C(1)–C(2)–C(21) | 123.6 (8) | 124.6 (17) | C$_a$–C$_b$–C$_{alkyl}$ |
| C(4)–C(3)–C(22) | 124.8 (8) | | |
| C(6)–C(7)–C(24) | 124.2 (7) | | |
| C(9)–C(8)–C(25) | 127.4 (8) | | |
| C(11)–C(12)–C(27) | 126.1 (6) | | |
| C(14)–C(13)–C(28) | 121.8 | | |
| C(16)–C(17)–C(31) | 124.1 (7) | | |
| C(19)–C(18)–C(34) | 125.1 (7) | | |
| C(2)–C(3)–C(22) | 128.4 (8) | 127.9 (16) | C$_b$–C$_b$–C$_{alkyl}$ |

Table IV (*Continued*)

| Bond | | Average | Type |
|---|---|---|---|
| C(3)–C(2)–C(21) | 129.7 (8) | | |
| C(7)–C(8)–C(25) | 124.5 (7) | | |
| C(8)–C(7)–C(24) | 129.0 (7) | | |
| C(13)–C(12)–C(27) | 128.0 (7) | | |
| C(12)–C(13)–C(28) | 127.0 (16) | | |
| C(18)–C(17)–C(31) | 127.7 (7) | | |
| C(17)–C(18)–C(34) | 129.1 (7) | | |
| C(13)–C(28)–C(29) | 97 (1) | | Propionate |
| C(17)–C(31)–C(32) | 111.6 (6) | | |
| C(28)–C(29)–C(30) | 94 (1) | | |
| C(31)–C(32)–C(33) | 111.8 (6) | | |
| C(29)–C(30)–O(1) | 119 (1) | | |
| C(29)–C(30)–O(2) | 111 (1) | | |
| C(32)–C(33)–O(3) | 116.1 (7) | | |
| C(32)–C(33)–O(4) | 121.2 (8) | | |

| Nonbonded Contacts and Angles | | | |
|---|---|---|---|
| HC(20)–H2C(29) | 2.52 | O(4)–O(5) | 2.85 (1) |
| H2C(23)–H2C(28) | 2.34 | N(2)–HC(35) | 2.51 |
| H2C(24)–H2C(32) | 2.61 | N(2)–HC(40) | 2.51 |
| H1C(27)–H2C(42) | 2.65 | N(4)–HC(36) | 2.60 |
| H2C(28)–H1C(38) | 2.40 | N(4)–HC(39) | 2.54 |
| HC(39)–O(2) | 2.46 | O(1)–O(5)–O(4) | 104.8 (4) |
| H3C(42)–O(2) | 2.43 | O(3)–O(2)–C(30) | 141.4 (7) |
| O(1)–O(5) | 2.99 (1) | O(5)–O(1)–O(6) | 85.3 (3) |
| O(1)–O(6) | 2.67 (1) | O(5)–O(1)–C(30) | 130.5 (7) |
| O(2)–O(3) | 2.41 (1) | O(6)–O(1)–C(30) | 141.9 (8) |

[a] The figure in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. [b] The notation $C_a$, $C_b$, and $C_m$ is that of J. L. Hoard, *Science*, 174, 1295 (1971).

would affect the bond distances and bond angles within the porphyrin core nor is there evidence that it affects the O(2)-O(3) distance.

The vinyl groups at C(3) and C(8) are not coplanar with the pyrrole rings upon which they are substituent. The dihedral angles between the planes of the vinyl groups and the planes of the pyrrole groups are 24 and 41°, respectively. Similar angles have been observed in Fe(Cl)(PP-IX).[6] In $Fe(SC_6H_4NO_2)$(PP-IXDME)[14] the corresponding angles are 52 and 16°. The orientation of the vinyl groups with respect to the other substituents about the periphery of the porphyrin appears to be unstructured, and we conclude that the vinyl groups possess at least a limited degree of rotational freedom. This is best illustrated by the structure of Fe(Cl)(PP-IX)[6] where the crystal contains equal amounts of the two enantiomeric forms of the complex. The disordering of the vinyl groups reflects the racemic nature of the crystal but also illustrates that the *conformation* of the vinyl groups in the two enantiomers is different. Figure 3 of ref 6 clearly illustrates that the vinyl groups have rotated about the C(3)-C(22) and C(8)-C(25) bonds to accommodate the packing forces in the crystal. A lack of coplanarity of conjugated groups in aromatic systems is often observed. The structures of biphenyl,[15] stilbene, and azobenzene[16] are good examples of this phenomenon.

As the data in Table VI indicate the averaged Fe-N(porphyrin) bond length in $Fe(1\text{-}Me\text{-}Im)_2(PP\text{-}IX)\cdot CH_3OH\cdot H_2O$ (1.990 (16) Å) is equal, within experimental error, to that observed in the model complex $[Fe(Im)_2(TPP)^+][Cl^-]$.[17] The individual Fe-N(porphyrin) bonds are not required to be equal, and the observed variation among them may in fact reflect a nonequivalence which would be in accord with the pronounced ruffling of the porphyrin core.

The axial Fe-N(1-Me-Im) bond lengths are possibly nonequivalent, (1.966 (5) and 1.988 (5) Å) with the Fe atom displaced out of the porphyrin plane toward the farther ligand. A similar nonequivalence was found in $[Fe(Im)_2(TPP)^+][Cl^-]$, where the two axial bond lengths are 1.957 (5) and 1.991 (5) Å. Collins et al.[17] suggested that the nonequivalence of these bond lengths in the latter complex was the result of steric interactions associated with the differing orientations of the two axial ligands. In their analysis of this feature of the structure, Collins et al. used an idealized model in which the axial Fe-N bond length is taken to be a twofold axis of rotation. A dihedral angle, $\varphi$, is then defined between the plane of the axial imidazole ligand and a second plane passing through the twofold axis and one of the nitrogen atoms of the porphyrin ring. If $\varphi$ is 0 or 90° it was suggested that there will be a maximum in the steric interaction between the nitrogen atoms of the porphyrin ring and the hydrogen atoms of the axial imidazole ligand. At a $\varphi$ value of 45° these interactions would be at a minimum. In the $Fe(Im)_2(TPP)^+$ ion the two independent imidazole groups had $\varphi$ values of 18 and 39°. The longer Fe-N(imidazole) bond was associated with the smaller $\varphi$ value. In the $Fe(Im)_2$(PP-IX) molecule the two 1-methylimidazole groups have $\varphi$ values of 16 and 3°, respectively. The longer axial bond, Fe-N(8) (1.988 (5) Å), is again associated with the smaller $\varphi$ value. The calculated H···N separations are short, as expected, at 2.5-2.6 Å (HC(40)-N(2), HC(36)-N(4), HC(39)-N(4), HC(35)-N(2)). We note, however, that both of the $\varphi$ values in the PP-IX structure (16 and 3°) are less than the minimal, sterically hindered value (18°) found in the TPP structure.[17]

Collins et al.[17] have presented a convincing argument that the poorly oriented imidazole group in the TPP complex is involved in substantial hydrogen bonding to a chloride ion in the lattice and have suggested that the constraints imposed by that interaction were responsible for the unfavorable orientation. At present it is difficult to assess the forces acting to orient the 1-methylimidazole groups in the PP-IX complex, but hydrogen bonding involving the imidazole groups is definitely not a factor. It should be remarked that in two apparently equivalent five-coordinate Co porphyrin complexes,[18,19] in which steric hindrance is at least minimized because of the out-of-plane displacement of the metal toward the axial ligand, the observed $\varphi$ values are 0 and 10°, respectively. This suggests that bonding considerations may be an important factor in aligning the planes of the axial ligands along a M-N(porphyrin) bond.

Despite the possible nonequivalence of the individual bond lengths and bond angles in $Fe(1\text{-}Me\text{-}Im)_2$(PP-IX), the averaged values in the molecule compare well with those observed in $[Fe(Im)_2(TPP)^+][Cl^-]$[17] (Table VI). As expected the differences in the pattern of substitution of the two porphyrins (PP-IX and TPP) are reflected in the bond angles about the methine carbon atoms ($C_m$). The average $C_a$-$C_m$-$C_a$ bond angle is 126.3 (8)° in the PP-IX complex compared with 123.7 (12)° in the TPP complex. The larger $C_a$-$C_m$-$C_a$ angle observed in this octaalkyl porphyrin complex parallels the difference observed in the free base porphyrins, MP-IXDME,[7] octaethylporphyrin,[20] and *meso*-tetrapropylporphyrin.[21] The ruffling of the porphyrin core (Table V) in $Fe(1\text{-}Me\text{-}Im)_2$(PP-IX) displays the same quasi-$S_4$ symmetry as observed in the $Fe(Im)_2(TPP)^+$ ion. The magnitude of the ruffling is, however, smaller; the methine carbon atoms are alternately ±0.14 Å above and

Table V. Deviations in Units of 0.001 Å and Equations of Weighted Least-Squares Planes[a]

| | Plane | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Fe | −28 | −11 | −13 | 56 | 57 | −53 | 32 | −29 |
| N(1) | −6 (4) | 8 (4) | −4 (4) | | | | | |
| N(2) | −34 (5) | −8 (5) | | 3 (5) | | | | |
| N(3) | −12 (4) | 8 (4) | | | 3 (4) | | | |
| N(4) | −16 (5) | −8 (5) | | | | −11 (5) | | |
| C(1) | 110 (6) | 118 | 6 (6) | | | | | |
| C(2) | 73 (7) | 81 | −4 (7) | | | | | |
| C(3) | −46 (7) | −32 | −1 (7) | | | | | |
| C(4) | −86 (6) | −69 | 6 (6) | | | | | |
| C(5) | −123 (6) | −99 | 90 | 5 | | | | |
| C(6) | −86 (6) | −58 | | 0 (6) | | | | |
| C(7) | −33 (7) | 23 | | −6 (6) | | | | |
| C(8) | 63 (7) | 100 | | 9 (7) | | | | |
| C(9) | 42 (6) | 73 | | −7 (6) | | | | |
| C(10) | 115 (6) | 146 | | −3 | −45 | | | |
| C(11) | 80 (6) | 106 | | | −7 (6) | | | |
| C(12) | 117 (6) | 143 | | | 8 (6) | | | |
| C(13) | 15 (8) | 34 | | | −6 (8) | | | |
| C(14) | −59 (6) | −44 | | | −2 (6) | | | |
| C(15) | −134 (7) | −126 | | | 25 | 131 | | |
| C(16) | −115 (6) | −110 | | | | 20 (6) | | |
| C(17) | −124 (6) | −125 | | | | −17 (6) | | |
| C(18) | 46 (6) | 42 | | | | 7 (6) | | |
| C(19) | 108 (6) | 110 | | | | 6 (6) | | |
| C(20) | 174 (7) | 176 | −45 | | | −76 | | |
| C(21) | 189 | | | | | | | |
| C(22) | −115 | | | | | | | |
| C(23) | −466 | | | | | | | |
| C(24) | −68 | | | | | | | |
| C(25) | 191 | | | | | | | |
| C(26) | −300 | | | | | | | |
| C(27) | 240 | | | | | | | |
| C(28) | −415 | | | | | | | |
| C(31) | −283 | | | | | | | |
| C(34) | 118 | | | | | | | |
| N(6) | 1937 | | | | | | | |
| N(8) | −2016 | | | | | | | |
| C(35) | | | | | | | 0 (6) | |
| C(36) | | | | | | | −1 (8) | |
| C(37) | | | | | | | 2 (8) | |
| C(38) | | | | | | | 87 | |
| N(5) | | | | | | | −1 (5) | |
| N(6) | | | | | | | 0 (5) | |
| N(7) | | | | | | | | 5 (6) |
| N(8) | | | | | | | | 4 (5) |
| C(39) | | | | | | | | −6 (6) |
| C(40) | | | | | | | | −5 (10) |
| C(41) | | | | | | | | −5 (10) |
| C(42) | | | | | | | | 20 |

Angles between the Normals to the Planes[b]

| Plane A | Plane B | Angle (deg) | Plane A | Plane B | Angle (deg) |
|---|---|---|---|---|---|
| 1 | 2 | 0.3 | 3 | 5 | 9.3 |
| 1 | 3 | 5.2 | 3 | 6 | 8.3 |
| 1 | 4 | 3.7 | 4 | 5 | 2.9 |
| 1 | 5 | 4.3 | 4 | 6 | 9.7 |
| 1 | 6 | 6.2 | 5 | 6 | 8.7 |
| 1 | 7 | 91.6 | 7 | 8 | 18.4 |
| 1 | 8 | 90.6 | 3 | 9 | 24.3 |
| 3 | 4 | 7.6 | 4 | 10 | 41.1 |

| Plane | *A* | *B* | *C* | *D* | Group |
|---|---|---|---|---|---|
| 1 | 3.803 | −7.007 | −16.886 | −8.171 | Porphyrin |
| 2 | 3.825 | −6.918 | −16.900 | −8.162 | Pyrrole N atom |
| 3 | 4.038 | −5.192 | −17.242 | −7.789 | Pyrrole 1 |
| 4 | 3.201 | −7.359 | −17.185 | −8.780 | Pyrrole 2 |
| 5 | 3.337 | −8.250 | −16.754 | −8.729 | Pyrrole 3 |
| 6 | 4.720 | −7.415 | −15.902 | −7.329 | Pyrrole 4 |
| 7 | 9.096 | 4.142 | 6.257 | 8.432 | 1-Me-Im |
| 8 | 8.851 | −2.370 | 7.937 | 7.550 | 1-Me-Im |
| 9 | 0.864 | −11.000 | −16.420 | −9.535 | Vinyl; C(22), C(23), C(3) |
| 10 | −6.397 | 14.451 | 7.270 | 5.502 | Vinyl; C(25), C(26), C(8) |

[a] The entrees for which an error is not indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in monoclinic coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Table VI. Average Bond Lengths (Å) and Bond Angles (deg) in Two Ferric Porphyrin Complexes

| Bond | $[\mathrm{Fe^{III}(Im)_2(TPP)^+}]$[a] | $\mathrm{Fe^{III}(1\text{-}Me\text{-}Im)_2(PP\text{-}IX)}$[b] |
|---|---|---|
| $\mathrm{Fe{-}N_{porph}}$ | 1.989 (5) | 1.990 (16) |
| $\mathrm{Fe{-}N_{Im}}$ | 1.957–1.991 (5) | 1.966–1.988 (5) |
| $\mathrm{N{-}C_a}$ | 1.378 (8) | 1.376 (8) |
| $\mathrm{C_a{-}C_b}$ | 1.437 (8) | 1.443 (22) |
| $\mathrm{C_a{-}C_m}$ | 1.392 (9) | 1.368 (19) |
| $\mathrm{C_b{-}C_b}$ | 1.350 (9) | 1.345 (10) |
| $\mathrm{C_a{-}N{-}C_a}$ | 106.1 (5)[c] | 105.9 (14) |
| $\mathrm{N{-}C_a{-}C_b}$ | 109.7 (5)[c] | 109.9 (12) |
| $\mathrm{C_a{-}C_b{-}C_b}$ | 107.2 (7)[c] | 107.2 (12) |
| $\mathrm{N{-}C_a{-}C_m}$ | 126.0 (6)[c] | 124.7 (10) |
| $\mathrm{C_m{-}C_a{-}C_b}$ | 124.2 (7)[c] | 125.3 (8) |
| $\mathrm{C_a{-}C_m{-}C_a}$ | 123.7 (12)[c] | 126.3 (8) |

[a] Reference 17. [b] This work. [c] Calculated from the data given in ref 17, on the assumption that the bond angles are equivalent.

below the plane of the porphyrin in the PP-IX complex, compared with ±0.31 Å in the TPP complex. The results of these two structural investigations suggest that the porphyrin group may be significantly puckered in oxyhemoglobin. As a result it must be recognized[18,22] that the porphyrin in the six-coordinate Fe-oxygen complex has a very definite conformation and a width that is greater than that expected for the planar molecule.

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**Supplementary Material Available.** A table of structure amplitudes and Table II, the parameters for the hydrogen atoms, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journal Department, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4532.

## References and Notes

(1) H. Fischer, A. Treibs, and K. Zeile, *Z. Physiol. Chem.*, **193**, 138 (1930).

(2) The following abbreviations are used throughout: PP-IX, 2,7,12,18-tetramethyl-3,8-divinylporphine-13,17-dipropionic acid dianion; PP-IX DME, dimethyl ester of the dianion of PP-IX; MP-IX, 2,7,12,18-tetramethyl-3,8-diethylporphine-13,17-dipropionic acid dianion; $\mathrm{H_2}$MP-IXDME, dimethyl ester of the free base form of MP-IX; Im, imidazole; 1-Me-Im, 1-methylimidazole. In this paper we have used the abbreviation PP-IX in two ways in order to avoid an otherwise cumbersome and probably confusing system of symbols. PP-IX denotes *both* the dianionic porphyrin (in which both amino pyrroles are ionized) and the trianionic porphyrin (as perhaps in $\mathrm{Fe(1\text{-}Me\text{-}Im)_2(PP\text{-}IX){\cdot}CH_3OH{\cdot}H_2O}$ in which one of the propionate carboxyl groups may be ionized).

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(10) In the refinement of $F$ the quantity minimized is $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, $w$, are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$. The error in an observation of unit weight is defined as $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ where $n$ is the number of observations and $m$ is the number of variables. In the refinement on $F^2$ the quantity minimized is $\sum w(F_o^2 - F_c^2)^2$, where the weights, $w$, are taken as $1/\sigma^2(F_0^2)$. The agreement indices are defined as $R = \sum |F_0^2 - F_c^2| / \sum F_0^2$ and $R_w = (\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4)^{1/2}$. The error in an observation of unit weight is defined as $[\sum w(F_o^2 - F_c^2)^2/(n - m)]^{1/2}$.

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