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 (21) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 4F_o^2 / \sigma^2(F_o^2)$. In least-squares refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized.
 (22) Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
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Structure of a Dioxygen Adduct of (1-Methylimidazole)-*meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphinatoiron(II). An Iron Dioxygen Model for the Heme Component of Oxymyoglobin^{1a}

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The structure of a solvate of mono(1-methylimidazole)(dioxygen)-*meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphinatoiron(II), $[\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)] \cdot \frac{1}{2}(\text{C}_6\text{H}_6) \cdot \frac{1}{2}(\text{N}_2\text{C}_4\text{H}_6)$, has been determined using three-dimensional x-ray diffraction data collected by counter methods. Crystal symmetry is consistent with the monoclinic space groups $C2/c$ or Cc . The unit cell parameters are $a = 18.690$ (3) Å, $b = 19.154$ (3) Å, $c = 18.638$ (3) Å, $\beta = 91.00$ (1)°, and $Z = 4$. Least-squares refinement of the structure in space group $C2/c$ has led to a conventional R factor (on F) of 0.109 using 1784 reflections with $I > \sigma_f$. The crystal structure consists of monomeric units of $\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)$ with benzene or 1-methylimidazole molecules occupying one solvate site in the asymmetric unit. Dioxygen is coordinated to the iron atom in the end-on bent bond mode. The Fe-O separation is 1.75 (2) Å. As a consequence of the twofold symmetry imposed on the molecule, the 1-methylimidazole group and the terminal oxygen atom are disordered. Additional disorder is found for the *tert*-butyl groups and for the terminal oxygen atom which can also occupy either of two crystallographically independent sites and which thus exhibits overall fourfold disorder. The two crystallographically independent O-O separations are 1.15 (4) and 1.17 (4) Å and the respective Fe-O-O bond angles are 133 (2) and 129 (2)°. The O-O separations may be underestimated by as much as 0.15 Å. The Fe-N_{porph} separations are 1.99 (1) and 1.97 (1) Å and the iron atom is displaced 0.03 Å from the mean plane of the porphinato nitrogen atoms toward the dioxygen ligand. The Fe-N_{imid} separation is 2.07 (2) Å. Precise structure analysis is prevented by limited data of poor quality and by the disorder and high thermal motion of many parts of the structure.

Introduction

For many years there has been considerable interest in the geometry of the iron-dioxygen bond in oxyhemoglobin and oxymyoglobin.²⁻⁴ Pauling² originally proposed an angular, end-on



geometry and Griffith³ a side-on, π -bonded



structure. Both models could account for the apparent diamagnetism of oxygenated hemes.⁵ Both structural types have been characterized by single-crystal x-ray diffraction techniques.⁶ The side-on mode has been observed for complexes of many transition metals but it has yet to be observed for an iron-dioxygen complex;^{6d} the O-O separations are almost invariably in the range 1.4-1.5 Å. The end-on mode has been associated with dioxygen adducts of d⁷ cobalt(II) complexes,⁷⁻¹³ and O-O separations in the range 1.27 (1)¹⁰ to 1.302 (3) Å¹¹ and Co-O-O bond angles of approximately 120° have been determined, except for the anionic complex $[\text{Co}$ -

$(\text{CN})_5(\text{O}_2)]^{3-}$, where the respective parameters were found to be 1.24 (2) Å and 153 (2)°.¹³ These separations are slightly less than that observed for the superoxide ion (1.32-1.35 Å^{14,15}).

The results from a large number of other studies including ESR,¹⁶ infrared,¹⁷ and x-ray photoelectron (ESCA) spectroscopy,¹⁸ and linear-free-energy relationships^{17,19} may be used to support the formulation of these complexes as $\text{Co}^{\text{III}}-\text{O}_2^-$ species. Recent ESR studies²⁰ indicated that this formulation may be inappropriate for some Co-O₂ complexes of quadridentate, dianionic, conjugated ligand systems. That the unpaired electron resides in a molecular orbital which is predominantly $\pi^*(\text{O}_2)$ in character is well established.^{16,20}

In view of the additional valence electron which these Co-O₂ complexes possess compared to a dioxygen adduct of an iron(II) complex, the applicability of these cobalt models to oxyhemoglobin and oxymyoglobin may be questioned. However, both hemoglobin and cobalt-substituted hemoglobin possess similar cooperativity in their binding of dioxygen.^{21,22} A bent bond configuration is also exhibited by cobalt-nitrosyl complexes,²³ which are formally isoelectronic with Fe-O₂ systems. The relationship between Co-NO and Fe-O₂ systems has been discussed.²⁴ The recent report that the triplet state of oxyhemoglobin is only 146 cm⁻¹ above the ground state²⁵ is of interest since the triplet state is consistent with an Fe^{III}(S

= $1/2$)-O₂-(S = $1/2$) species or an Fe^{II}(S = 1)-O₂(S = 1)²⁶ partially spin-paired species.

Recently, difficulties in synthesizing and studying iron(II) model systems have been circumvented. By using low temperatures,²⁷ or by creating a protected binding site for dioxygen,^{28,29} the facile and irreversible oxidation that occurs at ambient temperature through bimolecular contact of Fe-O₂ and Fe^{II} species can be avoided. The latter approach, utilizing the atropisomerism of *meso*-tetra(ortho-substituted phenyl)porphyrins, has led to the "picket fence" porphyrins of which an iron-dioxygen derivative has been prepared²⁹ and structurally characterized in a preliminary manner.³⁰

In this paper we present the full structural characterization of this "picket fence" porphyrin derivative mono(1-methylimidazole)(dioxygen)-*meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphinatoiron(II), Fe(TpivPP)(1-Me-imid)(O₂). At the time of the preliminary communication³⁰ there were unresolved problems associated with the solvate species and with the methyl carbon atoms of the pivalamide "pickets".

Collection and Reduction of Intensity Data

Dark red-black crystals of the title compound were prepared,²⁹ recrystallized from benzene, and examined by precession photography using Cu K α x radiation. Symmetry and systematic absences consistent with the monoclinic space groups C2/c (No. 15) and Cc (No. 9) were observed.³¹ All crystals exhibited twinning or very poor mosaicity. Single-crystal intensity data were collected by a scintillation counter on a Hilger and Watts four-circle computer-controlled diffractometer using Zr-filtered Mo K α (λ 0.7107 Å) x radiation. The ten-faced crystal used was irregularly shaped with maximum and minimum dimensions of 0.40 and 0.20 mm and volume of 0.0145 mm³. It was aligned with the *c* axis and spindle axis approximately coincident. Its mosaicity (peak width at half peak height), as determined by open-counter ω scans at a takeoff angle of 3°, ranged from 0.12 to 0.19° for strong low angle reflections. For some reflections a minor maximum of intensity, at worst less than 9% of the total integrated intensity, was observed. This was the best crystal available.

Crystal orientation and unit cell dimensions at 24 °C were obtained by least-squares refinement of the setting angles of 12 reflections accurately centered in the receiving aperture of a 5-mm diameter diffracted beam collimator which was 230 mm from the crystal. The dimensions obtained were *a* = 18.690 (3) Å, *b* = 19.514 (3) Å, *c* = 18.638 (3) Å, and β = 91.00 (1)°. Here and elsewhere in this paper the estimated standard deviation in the last figure is quoted in parentheses; it is conventionally derived from the inverse of the least-squares matrix. The linear absorption coefficient calculated for four [FeC₆₈N₁₀O₆H₇₀· $1/2$ (C₆H₆)· $1/2$ (N₂C₄H₆)] formula units in the cell and Mo K α x radiation was 2.93 cm⁻¹ and, since the maximum likely error due to neglect of absorption was less than 3%, absorption corrections were not applied. The preservation of the very limited number of crystals for other analyses precluded the sacrifice of a crystal for density measurements.

Excluding systematic absences, 3155 unique reflections, for which $2\theta \leq 40^\circ$, were collected by the θ - 2θ scan technique. A symmetric scan range of 1.20° in 2θ , centered on the calculated peak position, comprised 60 steps each of 4-s duration. Stationary counter, stationary crystal background counts at each end of the scan were recorded for 12 s. Reflections with peak count rates greater than 8000 per second were rerecorded with a copper foil attenuator placed in the path of the diffracted beam to bring the count rate within the linear response range of the scintillation counter. Three standard reflections monitored every 100 reflections showed no systematic variation in intensity. The data were scaled and corrected for Lorentz and polarization effects.³² Due to a computer mishap half the *Ok*l were collected later under changed experimental conditions (orientation, incident beam intensity). Accordingly, two scale factors were applied in final refinements of the structure.

Solution and Refinement of Structure

Throughout this work, full-matrix least-squares refinements were based on *F*, and the function minimized was $\sum w(|F_o| - |F_c|)^2$.³³ The weights *w* were assigned as $4I/\sigma_I^2$, where σ_I is the standard deviation in the observed intensity *I*, estimated from counting statistics.³⁴ *F*_o and *F*_c are the observed and calculated structure factor amplitudes, respectively.

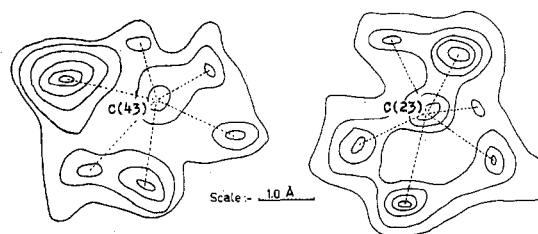


Figure 1. Section of a Fourier synthesis calculated over the plane of the pivalamide methyl carbon atoms, showing the disorder.

Agreement factors were defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. Atomic scattering factor tables were taken from Cromer and Mann.³⁵ The effects of anomalous dispersion for iron were included in *F*_c³⁶ using Cromer's values.³⁷

Analysis of the three-dimensional Patterson synthesis established coordinates for the iron atom on special position 2e in space group C2/c. Successful least-squares refinements of the structure were carried out in this space group which imposes twofold rotational symmetry on the molecular species. Atoms in phenyl and pyrrole rings were initially constrained in rigid groups each with a single isotropic temperature factor.³⁸ The initial model assumed that the two crystallographically independent pivalamide nitrogen atoms were ortho substituents on two phenyl rings which were oriented so as to give the α,α -atropisomer. Application of the twofold symmetry operation generates the $\alpha,\alpha,\alpha,\alpha$ -atropisomer for the molecule. It was also assumed that nitrogen (from 1-methylimidazole) and oxygen (from dioxygen) atoms occupied the unhindered and hindered axial coordination sites, respectively. This partial model was refined using 1105 reflections with $I > 3\sigma_I$, so that *R* and *R*_w had values 0.28 and 0.36, respectively.

From weighted *F*_o Fourier syntheses,³⁹ interspersed with cycles of least-squares refinements, positions were obtained for the remaining atoms of the 1-methylimidazole ligand and the pivalamidophenyl "pickets" (except for the terminal methyl groups). Twofold rotational disorder is imposed on the 1-methylimidazole ligand; in particular, this leads to a hybrid carbon-nitrogen position ($1/2$ (C + N) scattering factor) and to half-occupancy of the methyl group position. Further least-squares refinement led to values for *R* and *R*_w of 0.20 and 0.28, respectively.

*F*_o Fourier syntheses calculated over sections parallel to the presumed mean planes of the pivalamide methyl carbon atoms indicated that for each "picket" these atoms were disordered into two sets as illustrated in Figure 1. Fourier syntheses over the asymmetric unit using *F*_o coefficients confirmed this disorder. Hence, for each "picket", six half-carbon atoms with individual isotropic temperature factors were included in the model which, on refinement, led to agreement values for *R* and *R*_w of 0.16 and 0.22, respectively.

At this stage a difference Fourier synthesis over the asymmetric unit showed that the terminal oxygen atom of the dioxygen ligand was disordered over four positions of which two are crystallographically independent. A portion of this synthesis showing the disorder is depicted in Figure 2. A solvate species was also detected, and one section of a difference Fourier synthesis calculated parallel to the plane of maximum electron density for the solvate species is shown in Figure 3. The terminal oxygen atom, apportioned equally between the two crystallographically independent positions, and the solvate species, tentatively presumed to be a benzene molecule, were added to the model. Two cycles of least-squares refinement led to values for *R* and *R*_w of 0.106 and 0.130, respectively.

The high thermal motions of some atoms and the positions of residual electron density (revealed in a difference Fourier synthesis) indicated that relaxation of the constraints on some atoms was necessary. Accordingly, atoms in phenyl groups were allowed individual temperature factors, rigid group constraints on the pyrrole rings were relaxed, and anisotropic thermal parameters were applied to the iron, porphinato nitrogen, imidazole ligand, and pivalamide atoms. This model was refined in two blocks but the benzene solvate molecule refined poorly. A closer examination of Fourier syntheses indicated that the solvate species was best described as an equal mixture of 1-methylimidazole and benzene molecules, as indicated in Figure 3.

Because of the near-superposition of atoms of the 1-methylimidazole and benzene molecules, refinement of a single atom model would have

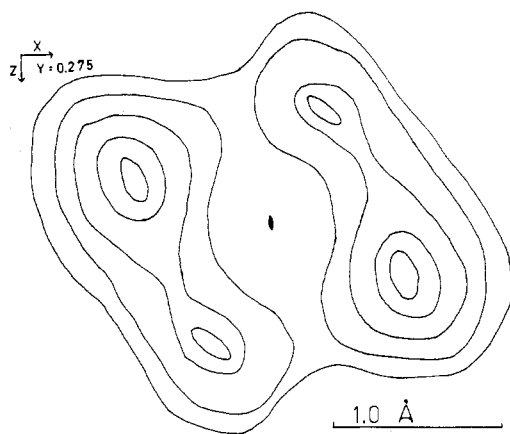


Figure 2. Section of a Fourier synthesis calculated parallel to the xz plane showing the terminal oxygen atom position.

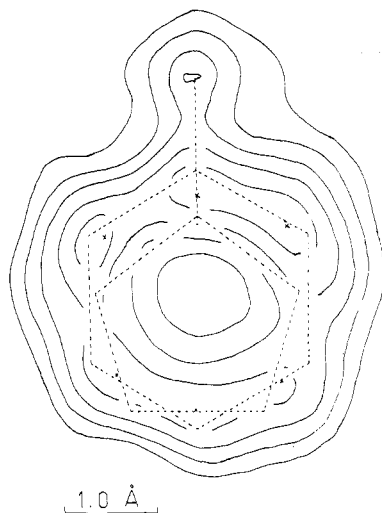


Figure 3. Section of a Fourier synthesis calculated over the plane of maximum electron density for the solvate species. The best model for the solvate is superimposed.

been inappropriate. Consequently for the final cycles of refinement, the geometry, relative proportions, and relative disposition of the two species, as indicated in Figure 3, were held constant in a rigid group.^{38d} In view of the large number of parameters (312) needed to adequately describe the positions and thermal motions of the 60 nonhydrogen atoms, it was considered essential to utilize more data. Consequently, the final cycles of full-matrix least-squares refinement used 1784 reflections with $I > \sigma_I$. Refinement converged with values for R and R_w of 0.109 and 0.116, respectively. The standard error in an observation of unit weight was 1.324. For the portion of data having $I > 3\sigma_I$ the agreement factors were 0.076 and 0.096, respectively.

In the final cycle the ratios of the change in a parameter to its estimated standard deviation were less than 0.10 and 0.20 for all positional and thermal parameters, respectively, except for those describing the pivalamide methyl carbon atoms where the respective ratios were 0.50 and 0.60. There was no evidence for secondary extinction among intense low-angle reflections. A final difference Fourier synthesis had no prominent features although residual electron density was concentrated, as expected, near the solvate moiety and pivalamide methyl carbon atoms. The electron density associated with the top peak was $0.39 \text{ e}/\text{\AA}^3$; that associated with the terminal oxygen atom positions, in earlier Fourier syntheses, was 0.50 and $0.57 \text{ e}/\text{\AA}^3$; that associated with the pivalamide methyl carbon atoms ranged from 0.62 to $1.0 \text{ e}/\text{\AA}^3$. These values are on approximately the same relative scale.

Since the averaged values of the minimized function appeared to be generally independent of $|F_o|$ or $(\sin \theta)/\lambda$, the weighting scheme was judged satisfactory, although low-angle reflections ($(\sin \theta)/\lambda < 0.23 \text{ \AA}^{-1}$) returned a slightly higher value for the minimized function than did the rest of the data. The p factor³⁴ for the optimal weighting

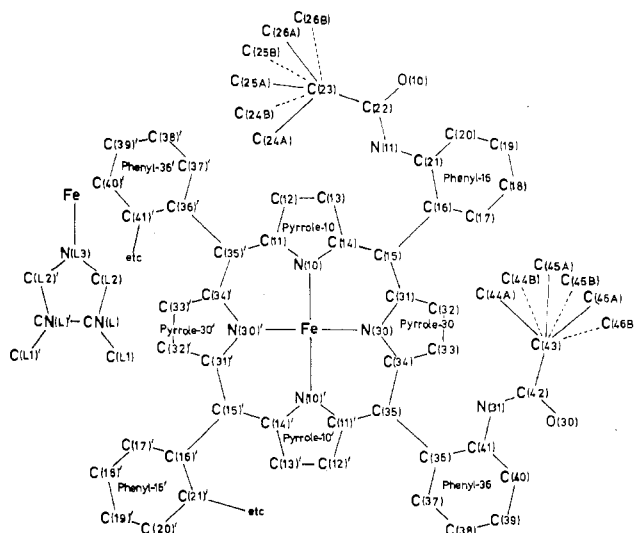


Figure 4. Atom labeling scheme for $\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)$.

scheme is unusually high ($p = 0.11$) but this is attributable to several factors, including (i) the twinned nature of the crystal, (ii) the deficiencies unavoidably inherent in this (or any other) description for the high thermal motion and/or disorder of many parts of the structure, and (iii) the noninclusion of the 76 hydrogen atoms, but not including instrumental instabilities. All atoms refined with anisotropic thermal parameters had physically meaningful thermal ellipsoid parameters. While there is gross eccentricity in the thermal motion of the pivalamide methyl carbon atoms, the earlier Fourier syntheses did not indicate complete rotational disorder. It is generally true that the refinement of structures with limited data causes ellipsoid eccentricity to be over-accentuated.

The usual statistical analyses on normalized structure factors were in close agreement with those predicted for a centrosymmetric space group.³³ Moreover, refinements in the alternative noncentric space group Cc (no point symmetry imposed) did not result in a better model.

A table of $|F_o|$ and $|F_c|$ for all data is contained in the supplementary material in the microfilm edition. Final atomic and thermal parameters and their associated standard deviations are contained in Table I. Figure 4 defines the atom and group labeling systems used throughout this paper.

General Description of the Structure

The crystal structure consists of neutral monomeric molecules of mono(1-methylimidazole)(dioxygen)-*meso*-tetra-($\alpha,\alpha,\alpha,\alpha$ -*p*-pivalamidophenyl)porphinatoiron, $\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)$, as illustrated in Figures 5 and 6, and a mixture of 1-methylimidazole and benzene solvate molecules, as illustrated in Figure 3. There is a crystallographic twofold rotational axis passing through the coordinated oxygen, the iron and the coordinated nitrogen atoms of the axially bound 1-methylimidazole ligand. Hence, C_2 point symmetry is imposed on the molecular species. In particular the 1-methylimidazole ligand can be considered statistically disordered between the two symmetry related sites, as illustrated in Figure 1.

The complex has four pivalamide "pickets" on one side of the porphyrin (the $\alpha,\alpha,\alpha,\alpha$ -atropisomer), thereby forming a protective pocket wherein dioxygen is coordinated in the end-on bent bond mode predicted by Pauling.² 1-Methylimidazole occupies the unhindered coordination site. The coordination geometry is approximately octahedral. The terminal oxygen atom occupies two crystallographically independent positions and thus it exhibits fourfold positional disorder. Bond distances and angles for the complex are accumulated in Tables II and III.

The porphinato skeleton, comprising four pyrrole groups and four linking methine carbon atoms, is ruffled in quasi- D_{2d} fashion, as illustrated in Figure 7. This plane, and the plane

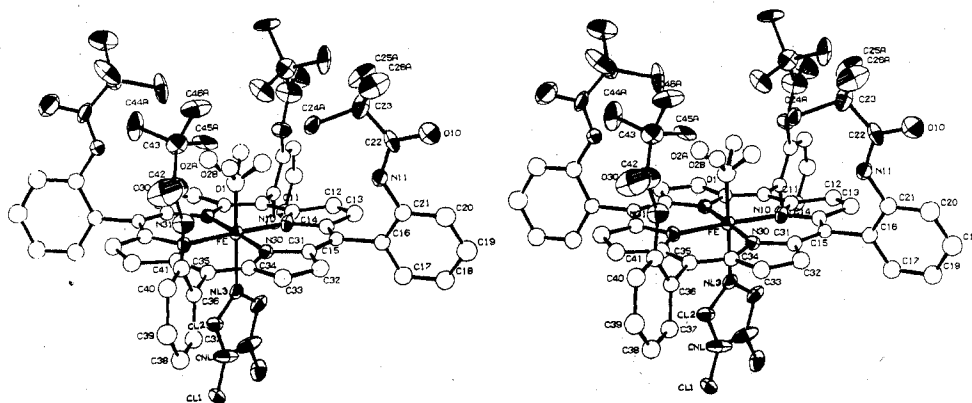


Figure 5. A stereoscopic diagram of $\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)$, showing the disorder of the terminal oxygen atom and the *N*-methyl carbon atom but, for clarity, not of the pivalamide methyl carbon atoms. The atom labeling is illustrated. Probability ellipsoids are drawn at the 20% level.

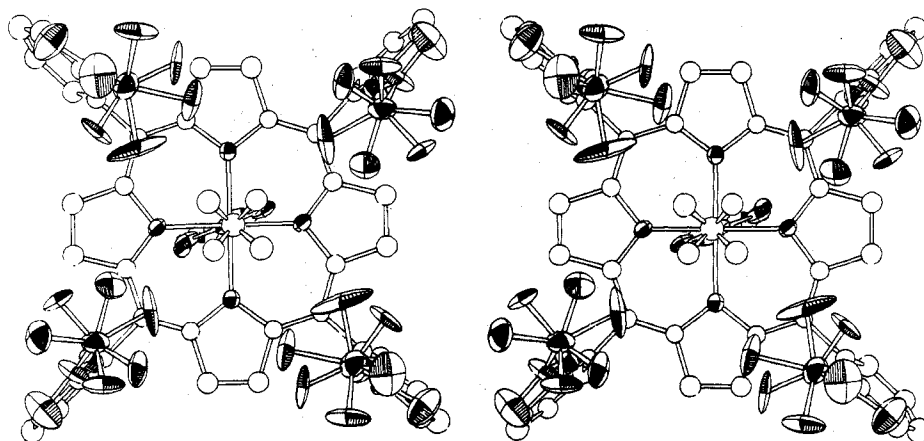


Figure 6. A stereoscopic diagram of $\text{Fe}(\text{TpivPP})(1\text{-Me-imid})(\text{O}_2)$ looking down the $C_2(b^-)$ axis of symmetry. The disorder of the terminal oxygen atom, *N*-methyl carbon atom, and pivalamide methyl carbon atoms is shown. Probability ellipsoids are drawn at the 20% level.

formed by the porphinato nitrogen atoms, is constrained by the crystallographic twofold axis to be normal to the crystallographic *y* axis. The iron atom is displaced toward the dioxygen ligand by 0.015 (3) Å from the former plane and by 0.030 (3) Å from the latter plane. The pyrrole-10 group is tilted from coplanarity with the porphinato plane by 4.8° and pyrrole-30 by 3.0°. The pyrrole groups are essentially planar. Chemically equivalent bond lengths and angles in the porphinato core do not display statistically significant differences (Tables II and III). The internal consistency is reassuring.

The phenyl groups and the porphinato plane are not orthogonal; the dihedral angles between, respectively, phenyl-16 and phenyl-36 and the porphinato plane at 77.9 and 83.2°. The two amide groups (N(11), C(22), O(10), and C(23); N(31), C(42), O(30), and C(43)) are approximately planar. They are tilted by 17.1 and 5.6° to their host phenyl groups phenyl-16 and phenyl-36, respectively.

For both pickets, alternative positions are available for the pivalamide methyl carbon atoms. High thermal motions are associated with the half-carbon atom positions (Figures 5 and 6) and there is considerable scatter of bond lengths involving these terminal methyl groups about the mean value (Table II). Some of the conformations which can be inferred from the disordered pivalamide methyl groups and the terminal oxygen atom are chemically unreasonable. For example there is a separation of only 2.68 Å between the atom sites C(45A) and O(2B).

The close contacts of 2.90 and 3.24 Å which the pivalamide oxygen atoms make with the atoms of the axial base and solvate species are not considered abnormal in view of the high

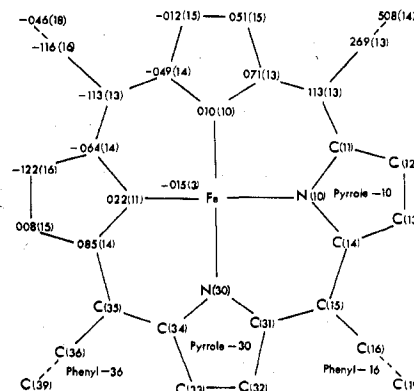


Figure 7. Displacements of atoms from the mean 24-atom porphinato plane. This plane is constrained by the C_2 axis of symmetry to lie in the *xz* crystal plane. Displacements are, therefore, the component parallel to the *y* axis from the centroid of the 24-atom porphinato skeleton. Atom and group labeling for the porphyrin is also illustrated.

thermal motion of these atoms; slight positional disorder such that these contacts are alleviated is inferred. The arrangement of molecular species with respect to the unit cell is illustrated in Figure 8.

Discussion

(1) The Short O–O Separations. The O(1)–O(2) separations of 1.17 (4) and 1.15 (4) Å⁴⁰ are unrealistically short when compared to the molecular oxygen O–O separation of 1.21 Å.⁴¹ An off-axis displacement of the bonded oxygen atom, similar to that inferred for some Co–NO complexes,^{23,24} seems

Table I. Final Positional and Thermal Parameters^a

(a) Individually Refined Atoms									
Atom	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0	0.13975 (15)	1/4	0.00310 (11)	0.00280 (11)	0.00280 (10)	0	-0.00013 (7)	0
O(1)	0	0.2292 (10)	1/4	7.2 (4)					
O(2A)	-0.046 (3)	0.267 (2)	0.235 (3)	7.0 (10)					
O(2B)	-0.013 (2)	0.269 (2)	0.293 (2)	6.2 (10)					
N(L3)	0	0.0337 (9)	1/4	0.0032 (7)	0.0030 (7)	0.0054 (8)	0	-0.0017 (6)	0
C(L2)	-0.0435 (8)	-0.0074 (9)	0.2941 (9)	0.0050 (7)	0.0031 (7)	0.0058 (8)	-0.0012 (6)	-0.0027 (6)	0.0011 (6)
CN(L) ^b	-0.0230 (12)	-0.0745 (8)	0.2746 (8)	0.0111 (16)	0.0026 (5)	0.0052 (11)	-0.0017 (7)	-0.0037 (8)	0.0011 (5)
C(L1)	-0.0426 (16)	-0.1358 (18)	0.3037 (17)	0.0043 (13)	0.0049 (15)	0.0067 (15)	-0.0012 (12)	0.0006 (11)	0.0024 (13)
N(10)	0.0952 (5)	0.1379 (6)	0.2065 (5)	0.0027 (4)	0.0038 (4)	0.0036 (4)	0.0005 (4)	-0.0006 (3)	-0.0007 (4)
C(11)	0.1119 (7)	0.1347 (7)	0.1342 (8)	5.3 (3)					
C(12)	0.1895 (8)	0.1386 (8)	0.1225 (8)	6.2 (3)					
C(13)	0.2199 (8)	0.1452 (8)	0.1907 (8)	6.3 (4)					
C(14)	0.1624 (7)	0.1423 (7)	0.2433 (7)	5.1 (3)					
N(30)	0.0448 (5)	0.1385 (5)	0.3475 (5)	0.0031 (4)	0.0027 (4)	0.0034 (4)	-0.0000 (3)	0.0003 (3)	0.0002 (4)
C(31)	0.1179 (7)	0.1415 (7)	0.3648 (7)	4.7 (3)					
C(32)	0.1288 (7)	0.1396 (8)	0.4422 (7)	6.0 (3)					
C(33)	0.0619 (8)	0.1364 (8)	0.4722 (8)	6.3 (4)					
C(34)	0.0096 (7)	0.1354 (7)	0.4129 (7)	4.6 (3)					
C(15)	0.1712 (6)	0.1448 (7)	0.3160 (6)	4.1 (3)					
C(35)	-0.0618 (7)	0.1332 (7)	0.4216 (7)	4.9 (3)					
N(11)	0.2401 (7)	0.2655 (7)	0.3661 (7)	0.0036 (5)	0.0035 (5)	0.0063 (6)	0.0002 (4)	-0.0005 (4)	-0.0006 (4)
C(22)	0.2601 (12)	0.3289 (12)	0.3672 (10)	0.0036 (9)	0.0062 (11)	0.0071 (9)	-0.0023 (8)	-0.0001 (7)	-0.0009 (7)
O(10)	0.3235 (9)	0.3424 (7)	0.3766 (9)	0.0074 (8)	0.0062 (7)	0.0149 (11)	-0.0014 (6)	-0.0025 (7)	0.0007 (6)
C(23)	0.2075 (14)	0.3884 (12)	0.3591 (13)	0.0044 (10)	0.0071 (12)	0.0072 (12)	0.0017 (9)	-0.0005 (9)	-0.0017 (8)
C(24A)	0.122 (3)	0.364 (4)	0.377 (5)	0.003 (2)	0.008 (3)	0.014 (4)	0.001 (2)	0.002 (2)	0.008 (3)
C(25A)	0.218 (4)	0.420 (3)	0.289 (2)	0.010 (3)	0.008 (3)	0.0018 (14)	0.005 (2)	0.0026 (17)	0.0011 (5)
C(26A)	0.221 (4)	0.440 (3)	0.423 (3)	0.014 (4)	0.007 (2)	0.0041 (17)	0.002 (2)	-0.004 (2)	-0.0027 (17)
C(24B)	0.163 (6)	0.375 (4)	0.290 (5)	0.019 (6)	0.010 (4)	0.017 (6)	0.009 (4)	-0.016 (6)	-0.005 (4)
C(25B)	0.243 (3)	0.456 (2)	0.352 (5)	0.012 (3)	0.0034 (17)	0.015 (5)	-0.0034 (18)	0.002 (3)	0.001 (2)
C(26B)	0.160 (3)	0.382 (4)	0.412 (5)	0.002 (2)	0.007 (3)	0.014 (5)	0.001 (2)	0.004 (2)	0.000 (3)
N(31)	-0.1057 (7)	0.2453 (8)	0.4976 (7)	0.0067 (7)	0.0043 (6)	0.0042 (6)	0.000 (5)	-0.0010 (5)	-0.0008 (5)
C(42)	0.1215 (13)	0.3098 (13)	0.5158 (11)	0.0113 (13)	0.0067 (11)	0.0024 (7)	0.0008 (9)	0.0015 (7)	0.0003 (8)
O(30)	-0.1380 (11)	0.3237 (9)	0.5772 (10)	0.0163 (13)	0.0096 (9)	0.0079 (9)	0.0036 (8)	0.0042 (9)	0.0010 (7)
C(43)	-0.1116 (12)	0.3674 (11)	0.4640 (10)	0.0067 (11)	0.0061 (9)	0.0040 (8)	-0.0000 (9)	-0.0010 (7)	0.0012 (8)
C(44A)	-0.178 (3)	0.389 (3)	0.431 (3)	0.004 (2)	0.012 (3)	0.007 (3)	0.000 (2)	-0.004 (2)	0.000 (2)
C(45A)	-0.061 (4)	0.348 (3)	0.399 (5)	0.008 (3)	0.0045 (20)	0.016 (4)	0.0009 (19)	0.010 (3)	0.005 (2)
C(46A)	-0.081 (3)	0.437 (2)	0.505 (2)	0.013 (4)	0.0028 (15)	0.0045 (19)	-0.0002 (19)	-0.004 (2)	-0.0016 (12)
C(44B)	-0.123 (4)	0.339 (3)	0.389 (3)	0.009 (3)	0.011 (3)	0.005 (2)	0.002 (3)	0.000 (2)	0.005 (2)
C(45B)	-0.048 (3)	0.406 (3)	0.472 (3)	0.0039 (18)	0.006 (3)	0.010 (3)	-0.0006 (19)	0.0022 (19)	0.003 (2)
C(46B)	-0.181 (3)	0.418 (3)	0.482 (3)	0.006 (2)	0.007 (2)	0.009 (3)	0.0029 (18)	0.001 (2)	0.000 (2)

(b) Derived Parameters for Atoms Constrained in Rigid Groups

Atom	x	y	z	B, Å ²	Atom	x	y	z	B, Å ²
C(16)	0.2484 (5)	0.1449 (8)	0.3435 (7)	5.3 (3) ^e	C(40)	-0.1381 (7)	0.1772 (6)	0.6037 (7)	6.2 (4)
C(17)	0.2865 (8)	0.0836 (6)	0.3429 (7)	6.9 (4)	C(41)	-0.1118 (7)	0.1833 (5)	0.5346 (7)	5.4 (3)
C(18)	0.3570 (8)	0.0818 (7)	0.3683 (8)	7.3 (4)	C(S1B)	0	0.637 (1)	1/4	12.0266
C(19)	0.3894 (5)	0.1414 (9)	0.3943 (8)	8.5 (4)	C(S2B)	0.0453 (9)	0.601 (1)	0.2972 (8)	12.0266
C(20)	0.3512 (8)	0.2027 (7)	0.3949 (7)	8.1 (5)	C(S3B)	0.0453 (9)	0.530 (1)	0.2972 (8)	12.0266
C(21)	0.2808 (8)	0.2045 (6)	0.3695 (7)	5.9 (4)	C(S4B)	0	0.494 (1)	1/4	12.0266
C(36)	-0.0895 (6)	0.1252 (7)	0.4978 (5)	4.8 (3)	C(S1A)	0	0.688 (1)	1/4	14.0266
C(37)	-0.0936 (6)	0.0610 (5)	0.5301 (7)	6.0 (4)	N(S1A)	0	0.612 (1)	1/4	12.0266
C(38)	-0.1199 (7)	0.0549 (5)	0.5991 (7)	6.2 (4)	C(S2A)	0.0412 (8)	0.570 (1)	0.2929 (7)	12.0266
C(39)	-0.1422 (7)	0.1130 (7)	0.6359 (5)	7.6 (4)	CN(SA)	0.0259 (5)	0.505 (1)	0.2769 (5)	12.0266

(c) Group Parameters^c

Group	x	y	z	φ^d	σ	ρ	B_{group}
Phenyl-16	0.3189 (4)	0.1432 (4)	0.3689 (3)	0.053 (7)	0.218 (6)	-0.340 (6)	- ^e
Phenyl-36	-0.1158 (3)	0.1191 (4)	0.5669 (3)	0.143 (6)	0.039 (6)	-1.944 (6)	- ^e
Solvate	0	0.612 (1)	1/4	π	π	2.35 (1)	12.0 (5)

^a The form of the anisotropic thermal ellipsoid is $\exp[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. ^b CN(L), half carbon/half nitrogen atom. ^c Group orientation defined by Doedens.^{38a} ^d Angles in radians. ^e Atoms allowed individual temperature factors.

probable, especially since Co-NO and Fe-O₂ systems are formally isoelectronic. A quite small displacement (with respect to the thermal motion observed) of 0.1 Å would lead to more realistic O-O separations and a tighter Fe-O-O bond angle. Pauling's formulation² for the Fe-O₂ linkage invokes an Fe-O double bond and an O-O single bond. As such an O-O separation of approximately 1.46 Å is expected. Notwithstanding the probable disorder of the bonded oxygen atom, our results appear to be incompatible with this limiting case.

Moreover, in contrast to Hoard,⁴² and noting that oxyhemoglobin is *not* diamagnetic above 50 K,²⁵ we do not expect the O-O separation for end-on, angularly bonded Fe-O₂ species to be significantly greater than 1.34 Å—the separation observed for the superoxide anion.¹⁵

(2) **Relative Orientations of 1-Methylimidazole, Fe-O-O and Solvate Planes.** It is convenient to define an orientation angle Φ , this being the dihedral angle between the plane of an axial ligand and the plane O(1)-Fe-N(10). In this structure these

Table II. Bond Distances (in Å)

Atom	Distance	Average ^a	Atom	Distance	Average ^a
Fe-O(1)	1.745 (18)		C(15)-C(16)	1.52 ^c	
Fe-N(L3)	2.068 (18)		C(35)-C(36)	1.53	1.53
Fe-N(10)	1.969 (10)		N(11)-C(21)	1.41	
Fe-N(30)	1.988 (10)	1.979 (10)	N(31)-C(41)	1.40	1.41
O(1)-O(2A)	1.17 (4)		N(11)-C(22)	1.29 (2)	
O(1)-O(2B)	1.15 (4)	1.16 (4)	N(31)-C(42)	1.34 (2)	1.32 (2)
N(L3)-C(L2)	1.41 (2)		C(22)-O(10)	1.22 (2)	
C(L2)-CN(L)	1.41 (2)		C(42)-O(30)	1.22 (2)	1.22 (2)
CN(L)-CN(L)	1.29 (3)		C(22)-C(23)	1.53 (3)	
CN(L)-C(L1)	1.36 (3)		C(42)-C(43)	1.50 (3)	1.52 (3)
N(10)-C(11)	1.390 (15)		C(23)-C(24A)	1.70 (6)	
N(10)-C(14)	1.423 (15)		C(23)-C(25A)	1.47 (4)	
N(30)-C(31)	1.398 (15)		C(23)-C(26A)	1.58 (4)	
N(30)-C(34)	1.397 (14)	1.402 (14)	C(23)-C(24B)	1.54 (5)	
C(11)-C(12)	1.473 (17)		C(23)-C(25B)	1.48 (4)	
C(13)-C(14)	1.469 (17)		C(23)-C(26B)	1.35 (7)	1.52 (12)
C(31)-C(32)	1.455 (16)		C(43)-C(44A)	1.43 (5)	
C(33)-C(34)	1.462 (17)	1.465 (8)	C(43)-C(45A)	1.59 (5)	
C(12)-C(13)	1.388 (17)		C(43)-C(46A)	1.65 (4)	
C(32)-C(33)	1.380 (17)	1.384 (17)	C(43)-C(44B)	1.52 (6)	
C(15)-C(14)	1.364 (15)		C(43)-C(45B)	1.42 (5)	
C(15)-C(31)	1.363 (15)		C(43)-C(46B)	1.66 (5)	1.53 (11)
C(35)-C(34)	1.348 (15)				
C(35)-C(11) ^b	1.388 (16)	1.366 (17)			

^a The esd for the average is conventionally derived from the dispersion of chemically equivalent bond lengths about their mean, except where only the average is calculated over only two chemically equivalent bonds in which case the esd is the longer of the esd's calculated for an individual bond length. ^b A prime denotes an atom whose position is generated by the C_2 symmetry. ^c CORFFE³⁵ does not calculate estimated standard deviations (esd) in bond parameters for atoms constrained in rigid groups. However an esd of 0.02 Å is reasonable.

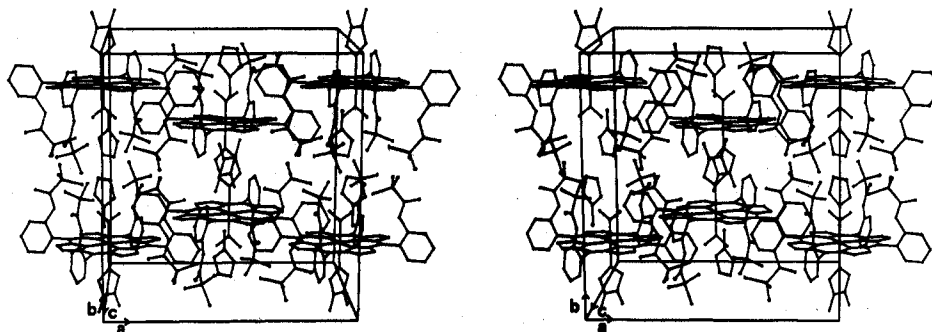


Figure 8. An ORTEP stereoscopic diagram of the unit cell contents.

planes are constrained by the C_2 axis to be perpendicular to the porphinato plane.

For the Fe-O(1)-O(2A) and Fe-O(1)-O(2B) planes, Φ is 43 and -48° respectively, that is these planes nearly bisect the $N_{\text{porph}}\text{-Fe-N}_{\text{porph}}$ right angles. In the bisecting orientation O(2)··· N_{porph} contacts are minimized. However, for the axial base Φ is 20° . Hence, since the dihedral angles between the imidazole plane and the Fe-O(1)-O(2) planes are 27.5 and 62.9° , the terminal oxygen atom positions are chemically different. This may account for the distinctive temperature dependence of the nuclear quadrupole splitting observed in the Mössbauer spectra of both this model compound^{29b,43} and oxyhemoglobin.⁴⁴ At room temperature a population ratio of 0.6 was postulated for the occupancy of the two terminal oxygen atom sites;⁴³ the x-ray data, although indicating a ratio of 1.0, are inadequate to exclude a 0.6 ratio.

The solvate moiety, which is at right angles to the imidazole plane, has numerous contacts of around van der Waals separations. This relative orientation prevents unduly close solvate-axial base contacts. Thus the orientation of the axial base is largely determined by packing effects rather than by intrinsic electronic properties of the porphinato-iron-dioxygen component.

(3) **Bond Lengths in the FeL₆ Core.** The Fe- N_{porph} separations which average 1.98 (1) Å are insignificantly different from those obtained for the structures of the essentially

diamagnetic complexes Fe(TPP)(pip)₂ (2.004 (3) Å)⁴⁵ and Fe(TPP)(1-Me-imid)₂ (1.999 (4) Å).⁴⁶

The Fe-O(1) separation (1.75 (2) Å) is considerably shorter than the corresponding separations (in the range 1.88 (2)-1.889 (2) Å) which are observed for dioxygen adducts of cobalt-Schiff species.⁷⁻¹² Hoard observed, for the nearly isostructural carbonyl analogue of Fe(TpivPP)(1-Me-imid)(O₂), an Fe-C separation in the range 1.59-1.63 Å.⁴² However, that this abbreviated Fe-C separation (and possibly the Fe-O separation we have observed) could be an artifact is indicated by the concordant and much longer Fe-C separations of 1.77 (2) and 1.751 (5) Å obtained for the structures of Fe(TPP)(py)(CO)⁴⁷ and Fe(N₄-annulene)(py)(CO),⁴⁸ respectively.

By comparison with the Fe- N_{imid} separations of 2.016 (5) Å observed in the structure of Fe(TPP)(1-Me-imid),⁴⁶ the corresponding separation of 2.07 (2) Å in the structure of Fe(TpivPP)(1-Me-imid)(O₂) is significantly longer. This lengthening is paralleled in the three iron-carbonyl complexes (vide supra). Thus a trans effect appears to be associated with the coordination of dioxygen.

The dimensions of the binding pocket (depth \approx 5.1 Å, $r(N(11)\text{-}N(11)') \approx$ 10 Å) and the flexibility of the "pickets", as evidenced by the isolation of the six-coordinate species Fe(TpivPP)(1-Me-imid)₂, preclude the possibility that the geometry of dioxygen coordination is influenced by the pickets.

Table III. Bond Angles (deg)^a

Atoms	Angle	Average	Atoms	Angle	Average
N(10)-Fe-N(10)'	177.9 (7)		C(15)-C(16)-C(17)	118.5	
N(30)-Fe-N(30)'	178.6 (6)	178.3 (7)	C(15)-C(16)-C(21)	121.5	
N(10)-Fe-N(30)	90.4 (4)		C(35)-C(36)-C(37)	121.0	
N(10)-Fe-N(30)'	89.5 (4)	90.0 (4)	C(35)-C(36)-C(41)	119.0	120.0 (15)
O(1)-Fe-N(10)	91.1 (3)		N(11)-C(21)-C(20)	122.8	
O(1)-Fe-N(30)	90.7 (3)	90.9 (3)	N(31)-C(41)-C(40)	124.3	
N(L3)-Fe-N(10)	88.9 (3)		N(11)-C(21)-C(16)	117.2	
N(L3)-Fe-N(30)	89.3 (3)	89.1 (3)	N(31)-C(41)-C(36)	115.7	120.0 (42)
O(1)-Fe-N(L3)	180		C(21)-N(11)-C(22)	130.5	
Fe-O(1)-O(2A)	129 (2)		C(41)-N(31)-C(42)	131.9	131.2
Fe-O(1)-O(2B)	133 (2)	131 (2)	N(11)-C(22)-O(10)	119 (2)	
Fe-N(L3)-C(L2)	124.5 (10)		N(31)-C(42)-O(30)	121 (2)	120 (2)
C(L2)-N(L3)-C(L2)'	111.0 (20)		N(11)-C(22)-C(23)	122.7 (18)	
N(L3)-C(L2)-CN(L)	102.4 (17)		N(31)-C(42)-C(43)	120.0 (18)	121.4 (18)
C(L2)-CN(L)-CN(L)'	112.1 (10)		O(10)-C(22)-C(23)	118 (2)	
C(L2)-CN(L)-C(L1)	129 (2)		O(30)-C(42)-C(43)	118 (2)	118 (2)
CN(L)'-CN(L)-C(L1)	118.5 (17)		C(22)-C(23)-C(24A)	112 (3)	
Fe-N(10)-C(11)	128.3 (8)		C(22)-C(23)-C(25A)	108 (2)	
Fe-N(10)-C(14)	126.6 (8)		C(22)-C(23)-C(26A)	108 (2)	
Fe-N(30)-C(31)	127.1 (8)		C(22)-C(23)-C(24B)	107 (3)	
Fe-N(30)-C(34)	127.0 (8)	127.3 (7)	C(22)-C(23)-C(25B)	114 (3)	
N(10)-C(14)-C(15)	124.8 (12)		C(22)-C(23)-C(26B)	107 (3)	
N(10)-C(11)-C(35)'	124.6 (12)		C(42)-C(43)-C(44A)	113 (2)	
N(30)-C(34)-C(35)	126.1 (11)		C(42)-C(43)-C(45A)	113 (2)	
N(30)-C(31)-C(15)	124.9 (11)	125.1 (7)	C(42)-C(43)-C(46A)	112 (2)	
C(13)-C(14)-C(15)	125.9 (12)		C(42)-C(43)-C(44B)	108 (3)	
C(12)-C(11)-C(35)'	122.9 (12)		C(42)-C(43)-C(45B)	117 (3)	
C(33)-C(34)-C(35)	124.0 (12)		C(42)-C(43)-C(46B)	102 (3)	110 (4)
C(32)-C(31)-C(15)	124.9 (12)	124.4 (13)	C(24A)-C(23)-C(25A)	116 (3)	
C(11)-N(10)-C(14)	105.0 (11)		C(24A)-C(23)-C(26A)	100 (5)	
C(31)-N(30)-C(34)	105.9 (10)	105.5 (11)	C(25A)-C(23)-C(26A)	113 (4)	
N(10)-C(11)-C(12)	112.3 (12)		C(24B)-C(23)-C(25B)	108 (5)	
N(10)-C(14)-C(13)	109.3 (11)		C(24B)-C(23)-C(26B)	104 (6)	
N(30)-C(31)-C(32)	110.2 (11)		C(25B)-C(23)-C(26B)	117 (4)	
N(30)-C(34)-C(33)	109.9 (11)	110.4 (13)	C(44A)-C(43)-C(45A)	105 (4)	
C(11)-C(12)-C(13)	104.9 (12)		C(44A)-C(43)-C(46A)	104 (3)	
C(12)-C(13)-C(14)	108.4 (12)		C(45A)-C(43)-C(46A)	109 (4)	
C(31)-C(32)-C(33)	106.9 (12)		C(44B)-C(43)-C(45B)	113 (4)	
C(32)-C(33)-C(34)	107.0 (12)	106.8 (14)	C(44B)-C(43)-C(46B)	108 (4)	
C(14)-C(15)-C(31)	125.8 (11)		C(45B)-C(43)-C(46B)	109 (4)	109 (5)
C(34)-C(35)-C(11)'	124.4 (12)	125.1 (12)			
C(14)-C(15)-C(16)	115.6 ^b				
C(31)-C(15)-C(16)	118.4				
C(34)-C(35)-C(36)	117.9				
C(11)'-C(35)-C(36)	117.7	117.4 (12)			

^a See footnotes for Table II. In this case an esd of 1.2–2.0° is reasonable for atoms constrained in rigid groups.

Table IV. Selected Intermolecular Distances Less Than 3.75 Å

C(L1)-O(10)	2.90 (3)	C(38)-CN(L)	3.55
C(26A)-C(46B)	3.37 (7)	C(38)-C(L2)	3.73
C(18)-N(S1A)	3.54	C(39)-CN(L)	3.56
C(18)-C(S2A)	3.59	C(39)-C(44A)	3.57
C(18)-C(S2B)	3.63	C(19)-C(S1B)	3.42
C(18)-C(S1B)	3.66	C(19)-N(S1A)	3.47
C(18)-C(S2A)'	3.75	C(19)-C(S1A)	3.54
C(18)-C(S3B)	3.75	C(19)-C(S2B)	3.55
O(10)-C(32)	3.50 (2)	C(19)-C(S2A)	3.71
O(10)-C(33)	3.53 (2)	C(S2B)-O(30)	3.24
O(30)-C(12)	3.43 (2)	C(S3B)-C(24B)	3.75
O(30)-C(13)	3.48 (2)	C(S1A)-C(L1)	3.67
C(38)-CN(L)	3.73	C(S2A)-O(30)	3.64
C(39)-CN(L)	3.46	CN(SA)-C(24B)	3.60
C(39)-C(L1)	3.64	CN(SA)-C(24A)	3.75

The possibility of side-on coordination for porphinatoiron(II) derivatives has been rejected as sterically unlikely.²⁴ However, in view of the extraordinarily close O...N_{porph} separations of 2.46 Å observed in the crystal structure of Mo(*p*-CH₃TPP)(O₂)₂⁴⁹ the possibility of side-on coordination cannot be dismissed on steric grounds alone.

Conclusion

Although structural precision is severely compromised by limited data, by high thermal motion, and by disorder in many

parts of the structure, end-on coordination of dioxygen to an iron(II)-porphyrin derivative has been unequivocally established.

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Registry No. [Fe(TpivPP)(1-Me-imid)(O₂)]^{1/2}(C₆H₆)^{1/2}·N₂C₄H₆, 65045-57-0.

Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Abbreviations: 3-F-saltmen, *N,N'*-(1,1,2,2-tetramethyl)ethylene-bis(3-fluorosalicylideneimino); TpivPP, *meso*-tetrakis(α,α,α,α-*p*-ivalamidophenyl)porphinato; TPP, *meso*-tetraphenylporphinato; *p*-CH₃TPP, tetra-*p*-tolylporphinato; N₄-annulene, 7,16-dihydro-6,8-, 15,17-tetramethyldibenzo[*b,f*][1,4,8,11]tetraazacyclotetradecimato ligand; 1-Me-imid, 1-methylimidazole; pip, piperidine; py = pyridine. (b) University of Canterbury. (c) Stanford University.

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