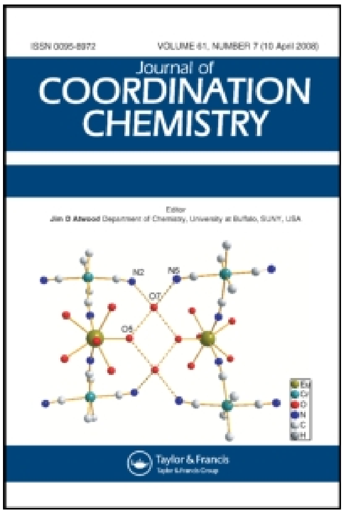

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal Structure and Chemical Reactivity of Heme Phenoxide Adducts

Anna M. Helms[a]; William D. Jones[a]; George L. McLendon[a]
[a] Department of Chemistry, University of Rochester, Rochester, New York, USA

To cite this Article Helms, Anna M. , Jones, William D. and McLendon, George L.(1991) 'Crystal Structure and Chemical Reactivity of Heme Phenoxide Adducts', Journal of Coordination Chemistry, 23: 1, 351 — 359

To link to this Article: DOI: 10.1080/00958979109408264

URL: http://dx.doi.org/10.1080/00958979109408264

J. Coord. Chem. 1991, Vol. 23. pp. 351–359
Reprints available directly from the publisher
Photocopying permitted by license only

CRYSTAL STRUCTURE AND CHEMICAL REACTIVITY OF HEME PHENOXIDE ADDUCTS

ANNA M. HELMS, WILLIAM D. JONES and GEORGE L. McLENDON

Department of Chemistry, University of Rochester, Rochester, New York 14627, U.S.A.

(Received July 24, 1990)

A simple phenoxide heme compound has been fully structurally characterized for the first time. The crystal structure of a 2,6-dichlorophenoxy Fe(III) 5,10,15,20-tetraphenylporphyrin is reported and compared with the structure of simple aliphatic alkoxy aducts of Fe(III) porphyrins. It is further shown that phenoxy Fe porphyrins can promote regiospecific substitution (cyanation) of the bound phenol ring.

Keywords: Heme, iron(III), phenoxide, X-ray structure, reactivity

INTRODUCTION

The coordination chemistry of metal centres in metalloproteins has been widely investigated for many years. Much of the attention given to model systems has been focussed on porphyrin complexes due to the ubiquitous nature of heme-containing proteins. A number of metalloproteins with phenolate coordination have been reported.[1–5] Two types of heme proteins with phenolate coordination have been characterized, the mutant hemoglobins and catalase. In the mutant hemoglobins, tyrosine replaces either the proximal or distal histidine. This substitution *in vivo* permanently oxidizes the iron centre to Fe(III). The redox potential of the mutants are so negative that neither ascorbate nor hemoglobin reductase can reduce the iron centre.[4,6] Catalase is found in almost all respiring organisms; it catalyzes the disproportionation of H_2O_2 to H_2O. X-ray crystallographic studies on beef liver catalase have determined the sole axial ligand on the Fe to be tyrosine,[7] but just how the tyrosine is involved in the disproportionation reaction has not been resolved.[8] However, although spectroscopic data for model Fe phenoxy porphyrins have been reported, high resolution structural data are not available for corresponding monomeric model compounds (a dimeric complex, (Fe_2TTOP_2), has been characterized). Therefore, in this paper, we report the structure of an iron porphyrin phenoxide complex, 2,6-dichlorophenoxyiron(III)5,10,15,20-tetraphenylporphyrin. Furthermore, the reaction chemistry of this compound has been investigated, focussing on the regiospecific cyanation reaction of the unsubstituted parent compound phenoxy-Fe(III)TPP.

EXPERIMENTAL

Materials

Pyrrole, phenol, benzaldehyde, and deuterated solvents were obtained from Aldrich Chemicals. Other solvents were obtained from Fisher and used without further

---

* Author for correspondence.

purification unless noted. Mass spectral determinations were performed by tl Midwest Center for Mass Spectrometry, a National Science Foundation Region Instrument Facility (Grant No. CHE 8211164). Proton Fourier transform NM spectra were obtained at 300 MHz on a QE-300 GE NMR instrument.

Synthesis

'Chlorin free' 5,10,15,20-tetraphenyl porphyrin (H_2TPP) was prepared by tl method of Barnett.[9] (5,10,15,20-tetraphenylporphyrinato)iron(III) chloric (Fe(TPP)Cl) was prepared as described by Smith.[10] Tetramethylammonium cyanic was prepared by the method of Andreades.[11]

(5,10,15,20-tetraphenyl porphyrinato)iron(III) 2,6-dichlorophenoxide, (Fe(TPP)(O-2,6-$C_6H_3Cl_2$))

A mixture of 250 mg (0.35 mmol) of Fe(TPP)Cl and 100 mg (1.06 mmol) of 2, dichlorophenol in 150 cm^3 of CH_2Cl_2 was stirred under N_2. Three drops of fresh distilled triethyl amine were added and the mixture stirred for two hours.[12] Tl solvent was removed under reduced pressure and the product crystallized from eth actetate/hexanes to give 200 mg (0.26 mmol) of the product in 75% yield. Electron spectrum in CH_2Cl_2, λ, nm, (log ε): 610.0 (4.31), 514.0 (4.48), 421.0 (5.11), 337 (4.75). All other phenoxide complexes were prepared in the same manner.

Electrochemistry

All electrochemical techniques were carried out in dry, degassed CH_2Cl_2. A potentials are reported *vs* Ag/AgCl and are uncorrected. The electrolysis cell w constructed from a 150 cm^3 heavy-walled beaker and covered with a Teflon li Anode and cathode were concentric platinum gauze cylinders. The reference ele trode, Ag/AgCl (B.A.S.), was connected *via* a salt bridge to the cell. A Par 17 instrument was used to maintain a constant potential.

Cyanation of Fe(TPP)OC_6H_5

Some 840 mg (1.10 mmol) of Fe(TPP)(OC_6H_5) was dissolved in 70 cm^3 of dr degassed CH_2Cl_2 with stirring under N_2. Some 6.4 gm. (64 mmol) of $(CH_3)_4NC$ along with a minimal amount of dry, degassed CH_3OH (to dissolve the electrolyt was added. The potential was maintained at +1.5 V for 20 hrs. The reaction mixtu was then poured into distilled water and shaken to remove excess $(CH_3)_4NCN$. Tl organic layer was separated and dried with Na_2SO_4 and the solvent removed und reduced pressure. The precipitate was dissolved in 50 cm^3 of HCl-saturated CH_2C and stirred for 15 mins to remove ligand from porphyrin. The mixture was th shaken with 100 cm^3 4M KOH and the organic layer removed. The aqueous lay was then acidified with HCl and extracted with CH_2Cl_2. The organic layer was dri with Na_2SO_4 and the solvent removed under reduced pressure. Yield of substitut products by NMR: 20%. Product distribution determination by GC (20M Carbow column): 93.1% 4-cyanophenol, 6.8% 2-cyanophenol, >0.1% 3-cyanophenol.

Structure determination

The dark purple crystals of Fe(TPP)(O-2,6-$C_6H_3Cl_2$) were examined on an Enr

Nonius CAD4 automated diffractometer. The lattice constants were obtained from 25 centred reflections with values of χ between 5 and 70°. Cell reduction with the program TRACER revealed only a primitive triclinic system. The crystal showed marked decomposition in the beam at room temperature which necessitated data collection at low temperature (−75°C).[13] A two molecule unit cell was established with cell parameters as listed in Table I. Data were corrected for the observed 8.5% decay and also for the effects of absorption by the DIFABS empirical method (average correction of 0.974). The structure was solved in the centric space group $P\bar{1}$ using Patterson and difference Fourier methods. All non-hydrogen atoms were anisotropically refined by full matrix least-squares with hydrogen atoms placed in idealized positions. At convergence, R was 0.038 and R_w was 0.055 with a goodness of fit indicator of 1.78. The final difference Fourier map had its largest peak of 0.45e/Å^3 and the maximum parameter shift was 0.25 in the final cycle. Values of atomic coordinates are given in Table II.

TABLE I
Summary of crystal data for Fe(TPP)(O-2,6-$C_6H_3Cl_2$).

formula	$C_{50}H_{31}Cl_2FeN_4O$
fw	830.57
lattice parameters	a/Å = 10.95(1) b/Å = 12.220(5) c/Å = 16.371(7) alpha/deg = 102.25(4) beta/deg = 99.96(5) gamma/deg = 108.24(6) V/Å^3 = 1965(5)
space group	$P\bar{1}$(#2)
Z	2
D_c/g cm^{-3}	1.40
F(000)	854
μ_{Mo}/cm^{-1}	5.78
radiation	Mo K-alpha (lambda = 0.71069), graphite-monochromated
temp/°C	−75
$2\theta_{max}$/deg	49.9
$N_o(I > 3.00(\mathrm{sig}(I)))$	5697
ind var	523
R; R_w	0.038; 0.055

RESULTS AND DISCUSSION

Structural Data

A detailed study of phenolic binding to an iron porphyrin was reported by Sugimoto, Udea, and Mori.[14] Initial visible spectra of Fe(TPP)(OC_6H_5) obtained in our lab (Fig. 1) did not agree with the literature. In order to resolve this discrepancy an effort was made to fully characterize the compound.

High resolution mass spectroscopy confirmed the parent ion at 761.2023 ± 0.002 amu. The ^{1}HNMR spectrum in $CDCl_3$ was assigned through the

TABLE II
Positional parameters and *B*(*eq*) for Fe(TPP)(O-2,6-$C_6H_3Cl_2$) at −75°C .

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(*eq*)
Fe	0.19629(3)	0.12409(3)	0.18998(2)	1.49(1)
Cl1	0.30922(9)	−0.06298(8)	0.34049(6)	4.88(3)
Cl2	0.5095(1)	0.39637(8)	0.33545(7)	5.80(3)
O1	0.3562(2)	0.1372(2)	0.2612(1)	2.35(5)
N1	0.0637(2)	0.0411(2)	0.2526(1)	1.68(6)
N2	0.1754(2)	0.2825(2)	0.2463(1)	1.73(6)
N3	0.2556(2)	0.2026(2)	0.0966(1)	1.62(5)
N4	0.1298(2)	−0.0387(2)	0.0966(1)	1.61(6)
C1	0.0838(2)	0.2213(2)	0.3644(1)	1.86(7)
C2	0.1336(2)	0.3054(2)	0.3215(1)	1.80(7)
C3	0.1486(3)	0.4297(2)	0.3479(2)	2.34(8)
C4	0.1991(3)	0.4819(2)	0.2913(2)	2.24(8)
C5	0.2197(2)	0.3915(2)	0.2281(1)	1.78(7)
C6	0.2832(2)	0.4134(2)	0.1634(1)	1.74(7)
C7	0.3042(2)	0.3241(2)	0.1043(1)	1.68(6)
C8	0.3787(2)	0.3461(2)	0.0420(1)	1.95(7)
C9	0.3735(2)	0.2377(2)	−0.0046(1)	2.00(7)
C10	0.2939(2)	0.1480(2)	0.0271(1)	1.65(6)
C11	0.2510(2)	0.0238(2)	−0.0098(1)	1.64(7)
C12	0.1649(2)	−0.0608(2)	0.0190(1)	1.64(6)
C13	0.0963(2)	−0.1854(2)	−0.0290(1)	1.96(7)
C14	0.0232(2)	−0.2383(2)	0.0195(2)	2.02(7)
C15	0.0465(2)	−0.1486(2)	0.0987(1)	1.73(7)
C16	−0.0052(2)	−0.1714(2)	0.1686(1)	1.71(7)
C17	0.0089(2)	−0.0805(2)	0.2425(1)	1.79(7)
C18	−0.0350(3)	−0.1009(2)	0.3174(2)	2.29(8)
C19	−0.0079(3)	0.0087(2)	0.3726(2)	2.22(8)
C20	0.0511(2)	0.0973(2)	0.3318(1)	1.81(7)
C21	0.0595(3)	0.2679(2)	0.4501(1)	2.03(7)
C22	−0.0679(3)	0.2490(3)	0.4595(2)	3.13(9)
C23	−0.0874(3)	0.2958(3)	0.5391(2)	3.7(1)
C24	0.0197(3)	0.3620(2)	0.6090(2)	3.2(1)
C25	0.1454(3)	0.3809(3)	0.6003(2)	3.6(1)
C26	0.1662(3)	0.3340(3)	0.5209(2)	3.01(9)
C27	0.3327(2)	0.5396(2)	0.1578(1)	1.91(7)
C28	0.4301(3)	0.6299(2)	0.2254(2)	2.75(8)
C29	0.4698(3)	0.7488(2)	0.2227(2)	3.5(1)
C30	0.4131(3)	0.7787(2)	0.1522(2)	3.00(9)
C31	0.3201(3)	0.6886(2)	0.0835(2)	2.88(9)
C32	0.2802(3)	0.5699(2)	0.0857(2)	2.40(8)
C33	0.2935(2)	−0.0224(2)	−0.0884(1)	1.65(6)
C34	0.2565(2)	0.0058(2)	−0.1644(1)	2.08(7)
C35	0.2914(3)	−0.0412(2)	−0.2382(2)	2.45(8)
C36	0.3651(3)	−0.1145(2)	−0.2352(2)	2.65(8)
C37	0.4047(3)	−0.1416(2)	−0.1596(2)	2.48(8)
C38	0.3682(2)	−0.0965(2)	−0.0860(1)	1.98(7)
C39	−0.0758(2)	−0.2990(2)	0.1644(1)	1.89(7)
C40	−0.0102(3)	−0.3805(2)	0.1556(2)	2.34(8)
C41	−0.0742(3)	−0.5001(2)	0.1504(2)	3.01(9)
C42	−0.2045(3)	−0.5397(2)	0.1549(2)	3.4(1)

TABLE II (continued)

atom	*x/a*	*y/b*	*z/c*	*B(eq)*
C43	−0.2707(3)	−0.4599(3)	0.1642(2)	3.08(9)
C44	−0.2073(3)	−0.3404(2)	0.1688(2)	2.43(8)
C45	0.4036(2)	0.1709(2)	0.3462(2)	2.42(8)
C46	0.3888(3)	0.0878(3)	0.3952(2)	3.3(1)
C47	0.4399(4)	0.1234(4)	0.4836(2)	5.2(1)
C48	0.5102(5)	0.2440(4)	0.5265(2)	6.0(2)
C49	0.5306(4)	0.3277(4)	0.4813(2)	5.2(1)
C50	0.4787(3)	0.2916(3)	0.3928(2)	3.5(1)
H1	0.1264	0.4681	0.3970	2.8
H2	0.2182	0.5636	0.2922	2.7
H3	0.4234	0.4222	0.3346	2.3
H4	0.4153	0.2243	−0.0501	2.4
H5	0.1017	−0.2231	−0.0847	2.4
H6	−0.0336	−0.3203	0.0040	2.4
H7	−0.0755	−0.1767	0.3266	2.7
H8	−0.0248	0.0239	0.4281	2.7
H9	−0.1423	0.2040	0.4112	3.8
H10	−0.1752	0.2819	0.5453	4.5
H11	0.0060	0.3945	0.6633	3.9
H12	0.2195	0.4265	0.6486	4.3
H13	0.2543	0.3475	0.5154	3.6
H14	0.4701	0.6108	0.2740	3.3
H15	0.5364	0.8101	0.2695	4.2
H16	0.4382	0.8602	0.1514	3.6
H17	0.2827	0.7079	0.0340	3.5
H18	0.2163	0.5086	0.0375	2.9
H19	0.2071	0.0572	−0.1662	2.5
H20	0.2648	−0.0229	−0.2905	2.9
H21	0.3886	−0.1467	−0.2857	3.2
H22	0.4568	−0.1907	−0.1578	3.0
H23	0.3939	−0.1161	−0.0342	2.4
H24	0.0801	−0.3534	0.1532	2.8
H25	−0.0284	−0.5545	0.1437	3.6
H26	−0.2488	−0.6215	0.1515	4.1
H27	−0.3605	−0.4874	0.1676	3.7
H28	−0.2539	−0.2866	0.1750	2.9
H29	0.4272	0.0654	0.5150	6.2
H30	0.5442	0.2687	0.5876	7.2
H31	0.5802	0.4102	0.5107	6.2

use of mono- and dichloro derivatives of phenol. The assignments were found to be in agreement with those of Goff[15] with the exception that the *ortho* protons were not resolved. An attempt was made at solving the crystal structure of Fe(TPP)OC_6H_5 but the ligand was found to be disordered over eight positions. In order to overcome this problem, we investigated the structure of a substituted derivative, Fe(TPP)(O-2,6-$C_6H_3Cl_2$). An ORTEP projection of the molecular structure is presented in Figure 2. The porphyrin core, metal, and ligand geometries are detailed in Table III.

Since the visible spectrum in Figure 1 corresponds to the compound whose structur is shown in Figure 2, it is clear that the previously reported spectrum[14] does *no* correspond to the phenoxy Fe porphyrin.

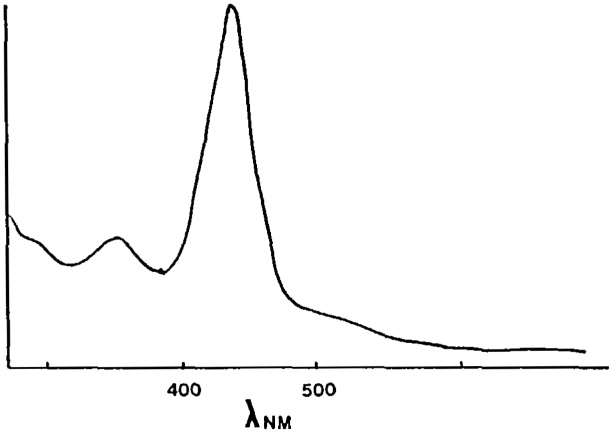

FIGURE 1 The electronic spectrum of the complex.

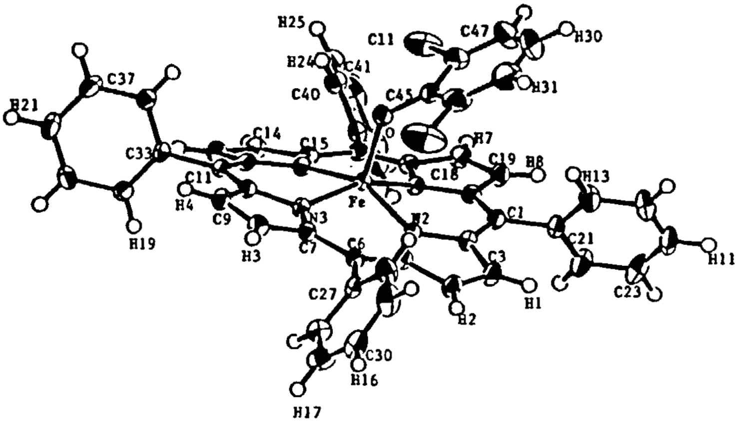

FIGURE 2 ORTEP projection of Fe(TPP)(O-2,6-$C_6H_3Cl_2$). Hydrogen atoms have an arbitrary radi of 1 Å. Thermal envelopes are at the 50% probability level. Most atoms are left unlabelled for clarity.

The average Fe–N distance of 2.060(4) Å and Fe atom displacements from bo the N core (0.4667 Å) and the mean porphyrin plane (0.5089 Å) are consistent wi observed values for high spin Fe(III) porphyrinates.[16] A relatively short Fe– distance (1.86 Å) was observed, similar to values for Fe alkoxides. A formal diagra of the porphinato core with perpendicular displacements of the 24 atoms whic determine the mean plane are presented in Figure 3. The crystallographic structur of three related Fe(III) compounds, Fe(TPP)OCH_3,[17] ((TTOP)Fe)$_2$),[15] and tl dimethyl ester of (mesoporphyrin IX)Fe(OCH_3),[18] have been reported. A compai son between relative bond distances and angles of these three compounds can l

TABLE III
Distance and angle data for the iron atom environment.

Fe displacement from N core	0.467 Å		
Distances (Å)			
Fe–N1	2.055(2)		
Fe–N2	2.060(2)		
Fe–N3	2.063(2)		
Fe–N4	2.060(2)		
Fe–O	1.869(2)		
O–C45	1.323(3)		
Cl1–C46	1.727(4)		
Cl2–C50	1.727(3)		
Angles (deg)			
O–Fe–N1	100.2(1)	N2–Fe–N4	151.34(8)
O–Fe–N2	102.1(1)	N4–Fe–N3	86.99(8)
O–Fe–N3	103.6(1)	C45–O–Fe	132.6(2)
O–Fe–N4	106.5(1)	C45–C46–Cl1	118.0(2)
N1–Fe–N2	87.68(9)	C47–C46–Cl1	120.0(3)
N1–Fe–N3	156.21(8)	C45–C50–Cl2	118.0(2)
N1–Fe–N4	87.0(1)	C49–C50–Cl2	119.6(3)
N2–Fe–N3	86.62(8)		

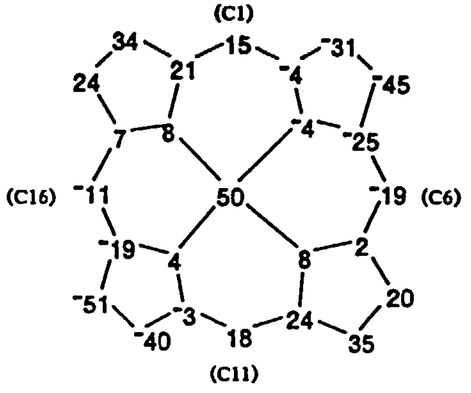

FIGURE 3 Formal diagram of the porphinato core with perpendicular displacements of the atoms in units of 0.01 Å.

found in Table IV. The present compound provides the best currently available structural model for phenoxy heme proteins like catalase.

REACTION CHEMISTRY

Metalloporphyrins have been widely employed as shape selective reagents; regiospecific reactions have been observed in epoxidations of olefins[19] and in hydroxylations of alkanes.[20] Space filling models generated from the crystal structure of Fe(TPP)(O-2,6-$C_6H_3Cl_2$) led us to investigate the cyanation of Fe(TPP)OPh. Anodic cyanations of aromatic compounds occur through a one-electron oxidation of the aromatic to the corresponding cation radical followed by attack of cyanide ion. The observed product distributions follow the known patterns for electrophilic substitution. The space filling models clearly show that attack at the *para* position should be preferred over the more hindered *ortho* positions.

TABLE IV
Crystallographic comparisons.

Compound	Fe displacement from N core (Å)	Fe–O (Å)	O–Cl (Å)	Fe–O–C (°)
Fe(TPP)diClOPh	0.4667	1.869(2)	1.323(3)	132.6(2)
Fe(TPP)OMe	0.484	1.816(2)	1.393(2)	129.10(9)
Fe(meso)OMe	0.455	1.842(4)	1.367(12)	125.9(6)
((TTOP)Fe)$_2$	0.46	1.847(2)	1.333(5)	135.11(25)

It has previously been shown that cyanation occurs only at potentials in the region of the oxidation halfwave potential of the organic substrate.[11] The cyclic voltammogram of Fe(TPP)(OC_6H_5) showed an oxidation halfwave at +1.35 V which we have assigned to both the Fe^{III}/Fe^{IV} porphyrin and the phenoxy ligand oxidation. This assignment is supported by previous workers who have found this overlap to occur in catecholate and substituted phenoxide complexes of Fe(III)porphyrins.[14,21] A potential of +1.5 V was chosen to ensure complete oxidation of the organic substrate during the electrolysis. Clearly, cyanide ion is oxidized well below this potential; the fact that the organic substrate can compete with cyanide ion oxidation indicates electrode absorption of the aromatic.[22]

Phenol is oxidized irreversibly in acidic, neutral, or basic solutions to quinones, polyphenyl ethers, and polymeric films.[23] A control reaction, using phenol in place of Fe(TPP)OPh, resulted in an insoluble black polymeric material. Ronlan has demonstrated that the large differences in halfwave potentials between phenols and phenol ethers result from very fast deprotonation of phenols following oxidation.[23] The binding constant for phenol to FeIII(TPP), determined by spectrophotometry, is large ($>10^5\ M^{-1}$). This led us to use the cyanation of anisole, rather than phenol, as a comparison for the porphyrin system. The substitution with anisole resulted in a product distribution of 50.7% *ortho* and 49.3% *para* in 5% overall yield.[11] The porphyrin-mediated reaction showed clear preference for the *para* position.

The regioselectivity evidenced in this reaction could be extendable to other electrophilic substitutions.

ACKNOWLEDGEMENTS

This work is dedicated to Arthur Martell on his 75th birthday.

This work was supported by the National Science Foundation.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables SI and SII, listing bond lengths and bond angles (8 pages), Table SIII listing hydrogen atom coordinates (1 page), Tables SIV and SV, listing U values and least square planes (4 pages), Figures S1 and S2, showing crystal packing and space filling model (2 pages), Table SVI, listing structure factor amplitudes (39 pages) and Table SVII listing a summary of crystal data (1 page) are available from the authors on request.

REFERENCES

1. I. Aisenard and I. Listowsky, *Ann. Rev. Biochem.*, **49**, 357 (1980.
2. J.C. Davis, S.S. Lingard and B.A. Averill, *Biochem.*, **20**, 4062 (1981).
3. M. Nozaki, *Topics Curr. Chem.*, **78**, 145 (1978).
4. P.D. Pulsinelli, M.F. Perutz and R.L. Nagel, *Proc. Natl. Acad Sci. USA.*, **70**, 3870 (1973).
5. T.C. Reid III, M.R.N. Murthy, A. Sicignana, T. Tanaka, W.D.L. Musick and M.G. Rossmann, *Proc. Natl. Acad. Sci. USA.*, **78**, 4767 (1981).
6. E.W. Ainscough, A.W. Addison, D. Dolphin and B.R. James, *J. Am. Chem. Soc.*, **100**, 7585 (1978).
7. M.R.N. Murthy, T.C. Reid III, A. Sicignano, T. Tanaka, W.D.L. Musick and M.G. Rossmann, *J. Mol. Bio.*, **152**, 965 (1985).
8. L. Que Jr., *Coor. Chem. Rev.*, **50**, 73 (1983).
9. G.H. Barnett, M.F. Hudson and K.M. Smith, *Tett. Lett.*, 2887 (1973).
10. K.M. Smith (ed), *Porphyrins and Metalloporphyrins*, Elsevier Scientific Pub. Co., Washington, 1975, pg. 180.
11. S. Andreades and E.W. Zahnow, *J. Am. Chem. Soc.*, **91**, 4181 (1969).
12. Note: If the CH_2Cl_2 is acidic there is no reaction; if too much $(Et)_3N$ is added μ-oxo dimer is formed rather than $Fe(TPP)OC_6H_5$.
13. Dr. Michael O'Neil constructed the low temperature X-ray system. We are grateful for his help with frigidity.
14. H. Sugimoto, N. Ueda and M. Mori, *Bull. Chem. Soc. Jpn.*, **55**, 3468 (1982).
15. H.M. Goff, E.T. Shimomura, Y.J. Lee and W.R. Scheidt, *Inorg. Chem.*, **23**, 315 (1984).
16. W.R. Scheidt and C.A. Reed, *Chem. Rev.*, **81**, 543 (1981).
17. C. Lecomte, D.L. Chadwick, P. Coppens and E.D. Stevens, *Inorg. Chem.*, **22**, 2982 (1983).
18. J.L. Hoard, M.J. Hamor and W.S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).
19. M.E. De Carvalho and B. Meunier, *New J. Chem.*, **10**, 223 (1986).
20. B.R. Cook, T.J. Reinert and K.S. Suslick, *J. Am. Chem. Soc.*, **108**, 7281 (1986).
21. H. Sugimoto, N. Ueda and M. Mori, *Chem. Lett.*, 449 (1982).
22. N.L. Weinberg and H.R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).
23. A. Ronlan, *Encyclopedia of Electrochemistry of the Elements* (A.J. Bard and H. Lund (eds)), Marcel Dekker, Inc., NY, 1978, pg. 242.