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Preparation and Molecular Structure of (Methoxo)-(octaethylporphinato)iron (III)

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Synopsis. The X-ray structure of Fe(OEP)(OMe) is reported: $\mathrm{Fe(C_{36}H_{44}N_4)(CH_3O)}$, *F.W.*=619.7, monoclinic, $P2_1/c$, a=13.412(5) Å, b=13.751(2) Å, c=18.912(8) Å, β=106.28(3)° and V=3348(4) Å^3, Z=4. A methoxide-coordinated iron(III) porphyrinate with π-π dimeric porphyrin interaction in the solid state was revealed. The facile formation of the methoxide is briefly discussed.

The hydroxide-coordinate iron(III) porphyrins, Fe(P)(OH),[1] and related macrocycles have a tendency to form μ-oxo-bridged dimers in a variety of solvents.[2–10] However, recent studies utilizing sterically protected porphyrins have demonstrated the possibility of isolation of the high-spin hydroxide iron porphyrinate monomers.[11–14] It is also reported that the conversion of an unhindered porphyrin hydroxide complex, Fe(TTP)(OH), to the μ-oxo dimer is significantly slow at ambient room temperature.[15] The magneto-spectroscopic investigations of the antiferromagnetically coupled $\mathrm{(Fe(P))_2O}$ complexes were frequently hampered, probably by this kind of high-spin complex as impurities.[3,8,16] In the course of our attempts to prepare $\mathrm{(Fe(OEP))_2O}$ crystals, well formed single crystals of the Fe(OEP) alkoxides were produced in the presence of alcohols, despite the fact that a similar treatment of Fe(TPP) gave the μ-oxo dimer. This report deals with the X-ray crystal structure of Fe(OEP)(OMe) and the facile formation of the alkoxide complexes of Fe(OEP) from the hydroxide complex.

Experimental

Fe(OEP)Cl was purchased from Aldrich and purified by recrystallization several times from chloroform-methanol. Fe(OEP)(OH) was prepared from Fe(OEP)Cl by analogous methods reported for a variety of binuclear oxo-bridged iron(III) porphyrins;[2,7,8] a chloroform solution of Fe(OEP)-Cl was vigorously shaken in a separatory funnel with an aqueous KOH solution three times; the chloroform layer was then evapolated to dryness, yielding a crude solid product. A solution of the crude product in chloroform was allowed to vapor diffusion of pentane for recrystallization; however, a brown powder was recovered. Methanol was added into the solution, and slow evaporation of the solution afforded crystals of the methoxide complex. Anal. Calcd for $\mathrm{FeC_{37}H_{47}N_4O}$, Fe(OEP)(OMe): C, 71.72; H, 7.65; N, 9.04%. Found: C, 71.66; H, 7.42; N, 9.16%. IR(KBr) cm^{-1}: ($\mathrm{Fe\text{-}OCH_3}$) 542, ($\mathrm{Fe\text{-}OCD_3}$) 533.

Rhombic crystals suitable for X-ray analysis were obtained by slow evaporation of the chloroform-methanol solution of Fe(OEP)(OMe). A preliminary examination of a crystal with dimensions of 0.48×0.18×0.57 mm^3 on Enraf-Nonius CAD4 diffractometer indicated a monoclinic unit cell. Systematic absences were consistent with the space group $P2_1/c$. A least-squares refinement of the setting angles of 25 reflections, collected in the range of 22°< 2θ<34°, led to the cell constants shown in Synopsis. For Z=4 and FW=619.7, the calculated density is 1.225 g cm^{-3} and the experimental density is 1.220 g cm^{-3}.

Diffracted intensities were measured by ω−2θ scanning with graphite-monochromated Mo$K\alpha$ radiation. A total of 8327 reflections up to 2θ=55° were measured. Net intensities were reduced to a set of relative structure factors by the application of the standard Lorentz and polarization factors. No absorption correction was made (μ=0.48 mm^{-1}). A

Table 1. Fractional Coordinates and Isotropic Equivalent Temperature Factors

Atom	x	y	z	B_{eq}*
Fe	0.33505(5)	0.49160(6)	0.57070(4)	2.85(1)
O	0.2918(3)	0.4341(3)	0.6451(2)	4.19(9)
$\mathrm{N_1}$	0.4347(3)	0.5990(3)	0.6255(2)	3.27(9)
$\mathrm{N_2}$	0.4666(3)	0.4146(3)	0.5668(2)	3.27(9)
$\mathrm{N_3}$	0.2544(3)	0.4155(3)	0.4776(2)	3.09(9)
$\mathrm{N_4}$	0.2232(3)	0.5996(3)	0.5368(2)	2.90(9)
$\mathrm{C_{Me}}$	0.2428(5)	0.4825(6)	0.6923(3)	5.6(2)
$\mathrm{C_{a1}}$	0.4068(4)	0.6885(4)	0.6481(3)	3.4(1)
$\mathrm{C_{a2}}$	0.5387(4)	0.5887(4)	0.6624(3)	3.4(1)
$\mathrm{C_{a3}}$	0.5659(4)	0.4295(4)	0.6084(3)	3.4(1)
$\mathrm{C_{a4}}$	0.4673(4)	0.3256(4)	0.5319(3)	3.6(1)
$\mathrm{C_{a5}}$	0.2843(4)	0.3269(4)	0.4536(3)	3.3(1)
$\mathrm{C_{a6}}$	0.1547(4)	0.4295(4)	0.4366(3)	3.1(1)
$\mathrm{C_{a7}}$	0.1269(4)	0.5890(4)	0.4896(3)	3.0(1)
$\mathrm{C_{a8}}$	0.2235(4)	0.6900(4)	0.5692(3)	3.2(1)
$\mathrm{C_{b1}}$	0.4940(4)	0.7315(5)	0.7014(3)	3.8(1)
$\mathrm{C_{b2}}$	0.5750(4)	0.6705(5)	0.7110(3)	3.9(1)
$\mathrm{C_{b3}}$	0.6317(4)	0.3490(5)	0.6002(3)	3.7(1)
$\mathrm{C_{b4}}$	0.5710(4)	0.2858(5)	0.5541(3)	3.8(1)
$\mathrm{C_{b5}}$	0.1998(4)	0.2884(4)	0.3957(3)	3.5(1)
$\mathrm{C_{b6}}$	0.1203(4)	0.3517(4)	0.3842(3)	3.6(1)
$\mathrm{C_{b7}}$	0.0640(4)	0.6747(4)	0.4911(3)	3.1(1)
$\mathrm{C_{b8}}$	0.1243(4)	0.7355(4)	0.5408(3)	3.3(1)
$\mathrm{C_{m1}}$	0.5990(4)	0.5098(5)	0.6529(3)	3.7(1)
$\mathrm{C_{m2}}$	0.3816(4)	0.2873(4)	0.4808(3)	3.6(1)
$\mathrm{C_{m3}}$	0.0944(4)	0.5096(4)	0.4439(3)	3.2(1)
$\mathrm{C_{m4}}$	0.3081(4)	0.7271(4)	0.6221(3)	3.5(1)
$\mathrm{C_{11}}$	0.4931(5)	0.8299(5)	0.7363(4)	5.0(2)
$\mathrm{C_{12}}$	0.5050(6)	0.9131(5)	0.6872(4)	6.2(2)
$\mathrm{C_{21}}$	0.6818(5)	0.6801(6)	0.7638(4)	4.8(2)
$\mathrm{C_{22}}$	0.6949(7)	0.6284(9)	0.8374(5)	9.6(3)
$\mathrm{C_{31}}$	0.7469(4)	0.3424(5)	0.6367(3)	4.7(2)
$\mathrm{C_{32}}$	0.7751(6)	0.3039(9)	0.7138(5)	9.3(3)
$\mathrm{C_{41}}$	0.6000(5)	0.1879(5)	0.5296(4)	5.0(1)
$\mathrm{C_{42}}$	0.5785(8)	0.1042(7)	0.5749(6)	9.3(3)
$\mathrm{C_{51}}$	0.2046(5)	0.1916(5)	0.3583(4)	4.5(1)
$\mathrm{C_{52}}$	0.1872(6)	0.1044(5)	0.4012(5)	6.7(2)
$\mathrm{C_{61}}$	0.0176(5)	0.3477(5)	0.3275(4)	4.6(1)
$\mathrm{C_{62}}$	0.0085(7)	0.4196(6)	0.2641(4)	6.1(2)
$\mathrm{C_{71}}$	−0.0435(4)	0.6899(5)	0.4427(3)	3.9(1)
$\mathrm{C_{72}}$	−0.0452(6)	0.7264(7)	0.3660(4)	6.2(2)
$\mathrm{C_{81}}$	0.0974(5)	0.8356(5)	0.5620(4)	4.6(1)
$\mathrm{C_{82}}$	0.1349(8)	0.9176(6)	0.5225(6)	8.0(3)

* $B_{\mathrm{eq}}=(4/3)\ (B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab(\cos\gamma)+B_{13}ac(\cos\beta)+B_{23}bc(\cos\alpha))$.

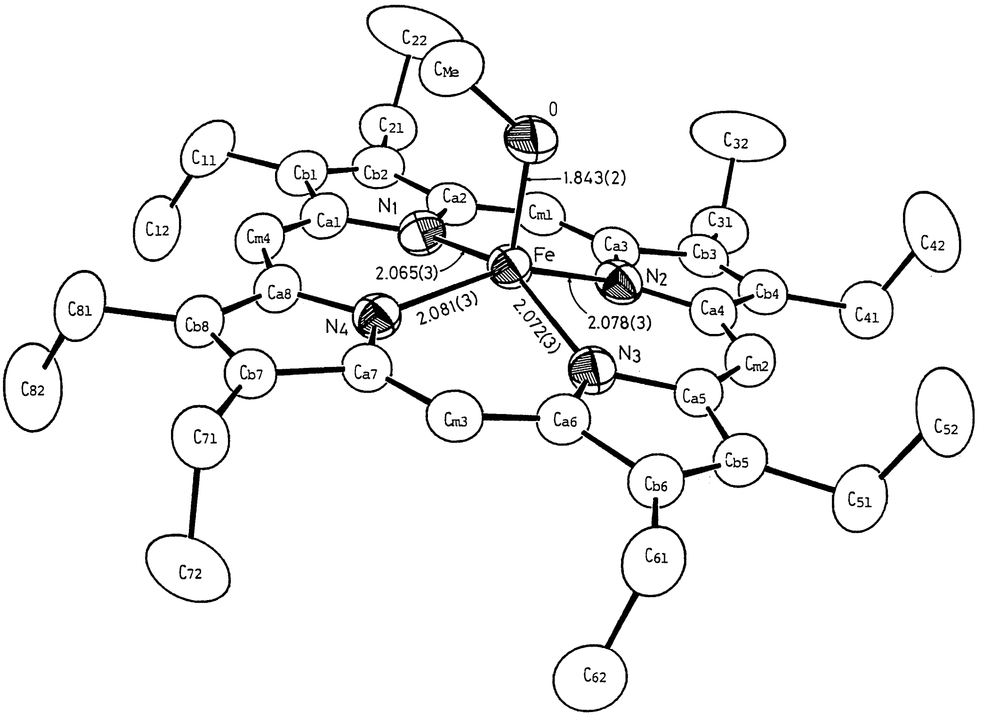

Fig. 1. ORTEP diagram(Johnson, 1976) and labeling scheme for all non-hydrogen atoms of the Fe(OEP)(OMe) molecule. Bond lengths of the coordination sphere of iron are entered in units of Å.

total of 5323 unique reflections having $|F_o|>3\sigma(|F_o|)$ were retained as observed and used in the solution and refinement of the structure.

The structure was solved by the direct method and refined by full-matrix least-squares methods.17a) Final cycles of least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and fixed idealized hydrogen atoms were carried to convergence. The final values for the discrepancy indices were $R=0.077$ and $R_w=0.088$.17b) The atomic coordinates for non-hydrogen atoms with the isotropic equivalent thermal factors are given in Table 1.17c)

Results and Discussion

Description of the Molecular Structure. A perspective view of Fe(OEP)(OMe) with the atomic labeling is given in Fig. 1. Also entered in Fig. 1 are the bond lengths of the iron(III) coordination sphere. These bond lengths and out of plane localization of iron are those expected for a five-coordinate high-spin iron(III) porphyrinate.18) The π-π dimeric nature of the complexes in the crystal is shown in Fig. 2. The figure displays a flat porphinato core. The maximum perpendicular displacement from the 24-atom mean plane was 0.10 Å at the C_{b3} carbon. Two Fe(OEP)(OMe) molecules of the dimer are centrosymmetrically related by the center lying on the Fe-Fe vector. The Fe-Fe separation is 5.78 Å and the separation of two mean planes of the 24-atom core is 3.54 Å. The lateral shift defined by Scheidt and Lee19) is calculated to be 3.09 Å in a direction approximately parallel to the Fe-C_{a3} vector. These dimeric characteristics are categorized into the moderate π-π interaction of Group I.19)

The molecular structure of Fe(OEP)(OMe), including the dimeric nature, is essentially identical with that of Fe(MesoDME)(OMe),20) although we did not encounter the disorder problem in this space group choice. The average Fe-N_p bond distance, 2.074(4) Å, iron(III) atom displacement from the mean plane of the 24-atom core, 0.53 Å, Fe-O bond distance, 1.843(2) Å, Fe-O-CH_3 bond angle, 125.5(3)°, are comparable with 2.073(6) Å, 0.49 Å, 1.842(4) Å and 125.9(6)° of Fe(MesoDME)(OMe), respectively. The orientation of methanol, determined by the dihedral angle between the coordination plane(N_2,N_4,Fe,O) and methanol plane(C_{Me},O,Fe), is 32.7°, is slightly smaller than the bisection angle (~45°) in the disordered Fe(MesoDME)(OMe). The significantly longer

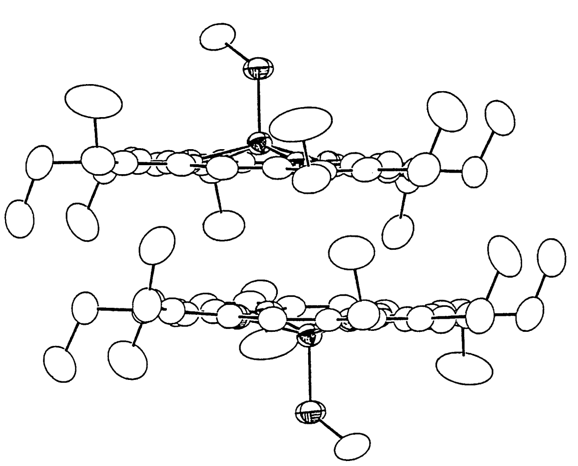

Fig. 2. An overall view of the π-π dimer in the lattice of Fe(OEP)(OMe). The porphinato planes are approximately perpendicular to the plane of the plot.

C_{Me}-O bond length, 1.415(5) Å than 1.367(12) Å in Fe(MesoDME)(OMe) is associated with this orientation. This orientation is in contrast to the eclipsed configuration reported for Fe(TPP)(OMe).[21] The difference in the methoxide orientation between the OEP and the TPP moiety can be interpreted in terms of the steric factor of the peripheral parts, i.e., the ethyl groups at the β-pyrrole position (OEP) and the phenyl groups at the meso position (TPP). There is no other unusual structural feature compared with the low-temperature structure of Fe(TPP)(OMe), except for the dimer formation of Fe(OEP)(OMe).

Facile Formation of the Methoxide Complex of Fe(OEP). Fe(OEP)(OMe) is apparently produced from the iron hydroxide porphyrinate by a dehydration reaction,

$$\mathrm{Fe(OEP)(OH)} + \mathrm{CH_3OH} \longrightarrow \mathrm{Fe(OEP)(OMe)} + \mathrm{H_2O}. \quad (1)$$

The formation of μ-oxo-bridged species, $(\mathrm{Fe(OEP)})_2\mathrm{O}$, from the two hyroxide molecules was also postulated[7,16] according to a general hydration-dehydration equilibrium,

$$2\,\mathrm{Fe(P)(OH)} \rightleftarrows (\mathrm{Fe(P)})_2\mathrm{O} + \mathrm{H_2O}. \quad (2)$$

Few reports have been concerned with the characterization of Fe(OEP)(OH) or $(\mathrm{Fe(OEP)})_2\mathrm{O}$ as the precursor of Fe(OEP)(OMe), although a facile alkoxide formation has recently been reported in other ironporphyrin-alcohol systems.[22] Such a facile formation of Fe(OEP)(OMe) from Fe(OEP)(OH) provokes a question as to whether it is possible to generate a pure μ-oxo bridged species in the absence of alcohols. The IR spectrum of the powder Fe(OEP)(OH) product prepared in the absence of alcohol showed strong absorption at 880 cm^{-1} in a KBr pellet. The absorption around this region has been assigned to antisymmetric Fe-O-Fe stretching of the μ-oxo-bridged species.[2,3,8] However, to our surprise, the same strong absorption has also been seen in the IR spectrum of Fe(OEP)(OMe) in a KBr pellet along with some absorptions assignable to the methoxide ligand, e.g., at 542 cm^{-1} of the Fe-$\mathrm{OCH_3}$ stretching. The intensity of the IR absorption at 880 cm^{-1} in the Fe(OEP)(OMe) sample was too distinct to be explained by the partial conversion of Fe(OEP)(OMe) to $((\mathrm{Fe(OEP)})_2\mathrm{O}$, even though it would occur in the solid state. This absorption makes it difficult to uniquely identify $(\mathrm{Fe(OEP)})_2\mathrm{O}$ in the powder product, since it is possible for Fe(OEP)(OH) and Fe(OEP)(OMe) to possess some unidentified IR absorption in this region. On the other hand, a direct conversion of $(\mathrm{Fe(OEP)})_2\mathrm{O}$ to Fe(OEP)(OMe) is unlikely in a chloroform solution, since there has been no optical spectral change attributable to the cleavage of Fe-O-Fe by the addition of alcohols into a solution of the crude product. However, the powder product has been completely converted to methoxide by the addition of methanol, as mentioned above. These facts suggest that the formation of the μ-oxo dimer is limited in the Fe(OEP) moiety, and that most of the powder solid produced under the conditions of this work must be Fe(OEP)(OH), which converts easily to the methoxide according to Eq. 1.

Isolation and characterization of $(\mathrm{Fe(OEP)})_2\mathrm{O}$ or Fe(OEP)(OH) of high chemical purity remains to be investigated for establishing Eq. 2 in the Fe(OEP) system.

References

1) Abbreviations: P=generalized porphyrin dianion; TTP=tetra-*p*-tolylporphyrin dianion; OEP=octaethylporphyrin dianion; TPP=tetraphenylporphyrin dianion; MesoDME=Mesoporphyrin-IX dimethyl ester dianion; OMe, methoxide.

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17) a) The ENRAF-NONIUS SDP package for MICRO VAXII was used. The equipped atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974). b) $R=\sum||F_o|-|F_c||/\sum|F_o|$, $R_w=[\sum w(F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$ where $w=1/\sigma^2(F_o)$. c) Tables of the anisotropic temperature factors for non-hydrogen atoms, the idealized atomic coordinates for hydrogen atoms, individual bond distance and angles, and the observed and calculated structure factors (27 pages) are deposited as Document No. 8921 at the Office of the Editor of BCSJ.

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