Inorganica Chimica Acta, *123* (1986) 91–97

Effects of Steric Crowding on Porphyrin Conformation. Synthesis, Crystal Structure and Molecular Stereochemistry of μ-Oxo-bis[(5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphinato)iron(III)]

KIONG-LAM LAY, JOHANN W. BUCHLER*

Institut für Anorganische Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt, F.R.G.

JONATHAN E. KENNY and W. ROBERT SCHEIDT

Department of Chemistry, University of Notre Dame, Notre Dame, Ind. 46556, U.S.A.

Received October 1, 1985

Abstract

The preparation and structural characterization of $[Fe(ODM)]_2O$ is described. This μ-oxo iron(III) derivative has a nearly eclipsed arrangement of the two porphinato cores when viewed along the nearly linear Fe–O–Fe spine. This feature and the pronounced nonplanarity of the porphinato core are the consequence of significant steric congestion in the periphery of the molecule. The steric congestion also appears to have affected bond parameters in the core. However, the coordination group bond parameters are that expected for a high-spin iron(III) porphyrinate with Fe–N(ave) = 2.065 Å, Fe–O = 1.752(1) Å and a Fe–O–Fe angle of 178.6(6)°. The iron(III) atom is displaced 0.53 Å from the quasi D_{2d} ruffled core. Crystal data: monoclinic, $a = 22.593(10)$, $b = 15.138(5)$, $c = 20.368(6)$ Å and $\beta = 103.04(2)°$, $Z = 4$, space group $C2/c$, 4199 observed data collected on an automated four-circle diffractometer.

Introduction

In the course of his famous synthesis of vitamin B_{12}, Woodward developed the concept of the 'overcrowded molecular plane' [2]. He stated that in a porphyrin, four peripheral alkyl substituents at two adjacent pyrrole rings and a fifth one in a *meso* position between these pyrrole rings would suffer severely from mutual steric compression. During our work on metal porphodimethenes [3] (5,15-dialkyl-octaethyl-5H,15H-porphyrins), we have found many further examples proving this concept [3e,f,h,i]. In particular, the existence of air-stable porphodimethene complexes is a consequence of the build-up of steric hindrance that would arise for dehydrogenation and concomitant rehybridization of the alkylated 5,15 positions. However, the metal-free porphodimethene, 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5H,15H-porphyrin, can be dehydrogenated in acetic acid to yield the corresponding 5,15-dimethyl-octaethylporphyrin, $H_2(ODM)$ [3a]. Several observations indicate some internal strain within this porphyrin: a notable Brunings–Corwin effect on the optical spectra, increased basicity and increased ease of *meso*-deuteriation as compared with octaethylporphyrin [3a].

Sterically hindered porphyrins are presently being investigated in many laboratories and it seemed worthwhile to prepare an iron derivative of $H_2(ODM)$. This was easily achieved by short boiling of $H_2(ODM)$ with iron(II) acetylacetonate in phenol. Stirring of the reaction product with aqueous sodium hydroxide and chromatography on alumina produced the μ-oxo complex, $[Fe(ODM)]_2O$. The magnetic moment (1.9 μ_B per Fe^{III} at 293 K) and the Mössbauer spectrum ($\delta = 0.39$ mm/s and $\Delta E_q = 0.52$ mm/s at 78 K) were typical for a μ-oxo iron(III) porphyrinate [3f].

Steric congestion led to several surprising observations in the series of porphodimethenes and their iron complexes [3e,h]. A general feature of the porphodimethene complexes is a roof-like folding of the macrocycle [3b–e,g]. A likely stereochemical solution to the anticipated congestion in $[Fe(ODM)]_2O$ would be a similar folding of the porphinato core along the line joining the two methyl-substituted methine carbon atoms, with the overall result defining a derivative with a 'domed' porphinato core. Such conformationally well-defined deriva-

---

*Paper 39 on 'Metal Complexes of Tetrapyrrole Ligands'. Paper 38 is ref. 1.

0020-1693/86/$3.50

tives [4]* appear useful for spectroscopic studies, in particular, for studies of the possible effects of the protein on heme conformation.

Accordingly, we have determined the molecular stereochemistry of μ-oxo-bis[(5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphinato)iron(III)], hereinafter written as $[Fe(ODM)]_2O$, which was expected to have a folded porphinato core. The porphinato cores in $[Fe(ODM)]_2O$ are indeed quite nonplanar. However, contrary to our *a priori* expectations, the porphinato rings are not simply folded along a line joining opposite methine carbon atoms but rather folded along both sets of opposing methine carbon atoms. The resulting overall conformation is rather similar to an D_{2d} ruffling. This ruffling accommodates the steric congestion of the peripheral substituents. Another significant effect of the steric crowding is the essentially eclipsed pair of porphinato rings when viewed along the Fe–O–Fe axis.

Experimental

Preparation of [Fe(ODM)]₂O

401 mg (0.71 mmol) $H_2(ODM)$, 2 g $Fe(acac)_2$ and 2 g of phenol were refluxed for 10 min with stirring. After cooling, the mixture was taken up in dichloromethane and stirred for 30 min with 100 ml of 10% aqueous NaOH, the organic layer separated, washed with water until neutral, filtered and taken to dryness *in vacuo*. The residue was dissolved in dichloromethane and chromatographed on alumina (grade III, neutral). The red main fraction was evaporated and the residue recrystallized from dichloromethane/n-hexane: 278 mg (63%) violet crystals of $[Fe(ODM)]_2O$. UV-Vis: λ_{max} (log ϵ), 580(4.07), 414(5.18) nm, IR (KBr): 860 (FeOFe), 681 cm^{-1}, $\mu_{eff}(CDCl_3$, ext. TMS, 293 K), 1.9 μ_B, Mössbauer: $\delta = 0.388$ (78 K), 0.453 (4.2 K) mm/s (*vs.* iron metal), ΔE_q = 0.523 (78 K), 0.529 (4.2 K) [3f]. *Anal.* Calcd. for $C_{76}H_{96}N_8OFe_2$: C, 73.06; H, 7.75; N, 8.97; O, 1.28. Found: C, 72.62; H, 7.68; N, 9.20; O, 1.53%.

Structure Determination

Crystals of $[Fe(ODM)]_2O$ were obtained by slow evaporation of benzene solutions of the complex. Preliminary X-ray examination established a four-molecule monoclinic unit cell with *Cc* or *C2/c* as the possible space groups. Lattice constants, a = 22.593(10), b = 15.138(5), c = 20.368(6) Å, and β = 103.04(2)°, came from a least-squares refinement of 60 automatically centered reflections on a Nicolet P$\bar{1}$ diffractometer using Mo Kα radiation (λ = 0.71073 Å). The calculated density was 1.21 g/cm^3 compared to the experimental density of 1.20 g/cm^3. Intensity data were collected using graphite-monochromated Mo Kα radiation using a crystal specimen of dimensions 0.63 × 0.30 × 0.13 mm. All independent data to 2θ of 50.7° were measured by $\theta-2\theta$ scanning; a variable scan rate of 0.5 to 6.0°/min was employed. Backgrounds were estimated from the reflection profiles [5]. No absorption correction was applied; $\mu = 0.47$ mm^{-1}. All intensity data were reduced as described previously [6]. Data having $F_o > 3\sigma(F_o)$ were retained as observed; a total of 4199 data were retained and used in the solution and refinement of structure.

The choice of *C2/c* required that the $[Fe(ODM)]_2O$ molecule have a twofold symmetry axis. This initial choice was confirmed by all subsequent developments during the solution and refinement of structure. The structure was solved by the heavy-atom method**. Refinements were carried to convergence using anisotropic temperature factors for all atoms. The final value of R_1 was 0.096 and that of R_2 was 0.11. ($R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$). Final parameter shifts were less than 25% of the estimated standard deviations during the last cycle. A final difference Fourier synthesis was judged to be significantly free of features with no peaks greater than 0.36 e/Å^3, less than 20% of the height of a typical carbon atom. A listing of the final observed and calculated structure amplitudes is available from the authors. Atomic coordinates are listed in Table I. The associated anisotropic thermal parameters are given in Table IS, see 'Supplementary Material'.

Results and Discussion

The numbering scheme employed is displayed in Fig. 1 which shows the unique half of the molecule. Figure 1 also displays bond distances in the peripheral ethyl groups. Bond parameters for the macrocycle are listed in Tables II and III. Figure 2 is a perspective view of the entire $[Fe(ODM)]_2O$ molecule (ethyl groups removed for clarity) illustrating the relative orientations of the two porphinato rings. The molecule has approximate D_{2d} symmetry; the crystallographically required twofold axis (indicated on

---

*Pb(TPrP) has a 'domed' porphyrin conformation as a result of a roof-like folding along an opposite pair of methine carbon atoms. However, this conformational feature is the apparent result of the coordination requirements of the lead(II) ion and not of the tetra-n-propylporphinato core itself.

**Locally modified versions of the programs listed in ref. 7a were employed. Atomic form factors were taken from ref. 7b. Real and imaginary corrections for anomalous dispersion in the form factor of the iron atom were taken from ref. 7c.

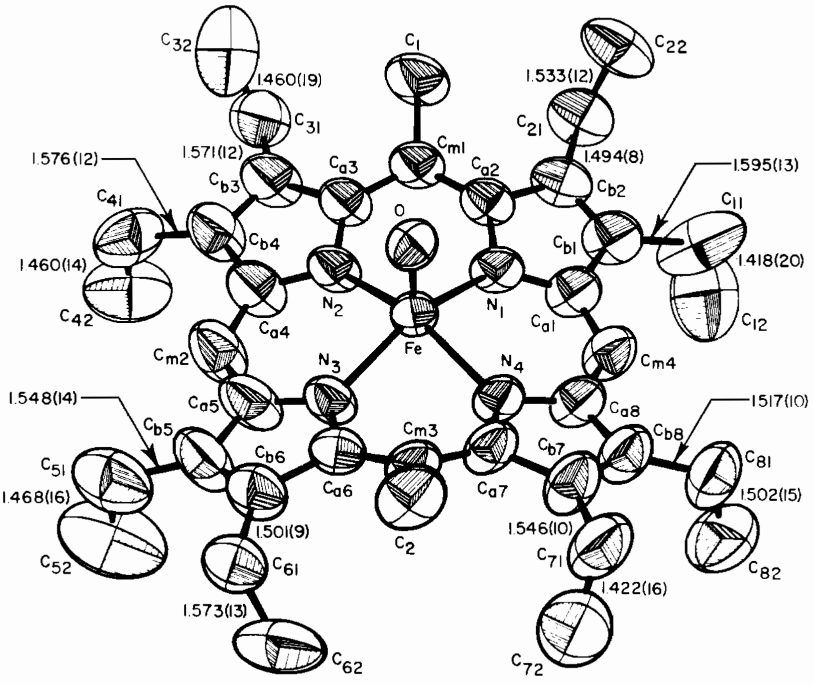

Fig. 1. Computer-drawn model of the crystallographically unique half of the [Fe(ODM)]$_2$O molecule illustrating the atom labeling scheme. Also shown are the observed C–C bond distances in the peripheral ethyl groups. Ellipsoids are scaled at the 50% probability level.

TABLE I. Atomic Coordinates in the Unit Cell

Atom type	Coordinates[a]		
	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
Fe[b]	276(0)	1174(0)	3376(0)
O	0	1160(3)	1/4
N_1	1217(2)	1172(3)	3534(3)
N_2	389(2)	–139(3)	3639(3)
N_3	–504(2)	1196(3)	3740(3)
N_4	323(2)	2501(3)	3613(3)
C_{a1}	1596(2)	1889(4)	3655(4)
C_{a2}	1542(3)	478(4)	3357(3)
C_{a3}	807(3)	–672(4)	3454(4)
C_{a4}	–28(4)	–668(4)	3842(4)
C_{a5}	–800(4)	482(5)	3934(4)
C_{a6}	–910(3)	1875(4)	3634(3)
C_{a7}	–176(3)	3039(4)	3494(4)
C_{a8}	821(3)	3041(4)	3704(3)
C_{m1}	1320(3)	–374(4)	3238(4)
C_{m2}	–569(4)	–375(5)	3997(5)
C_{m3}	–779(2)	2722(4)	3413(3)
C_{m4}	1413(3)	2735(4)	3753(4)
C_1	1615(4)	–987(5)	2811(5)
C_2	–1304(3)	3299(5)	3051(4)
C_{b1}	2198(3)	1638(5)	3593(4)
C_{b2}	2169(3)	785(5)	3387(4)
C_{b3}	659(4)	–1600(5)	3577(5)
C_{b4}	128(4)	–1591(5)	3795(5)
C_{b5}	–1409(4)	724(6)	3987(5)
C_{b6}	–1480(3)	1586(5)	3808(4)
C_{b7}	26(3)	3963(4)	3512(4)
C_{b8}	651(3)	3957(4)	3659(4)
C_{11}	2749(3)	2318(8)	3671(7)
C_{21}	2704(3)	288(6)	3261(4)
C_{31}	1072(6)	–2433(6)	3569(6)
C_{41}	–238(5)	–2385(5)	4011(5)
C_{51}	–1865(4)	101(8)	4220(6)
C_{61}	–2029(3)	2123(5)	3849(5)
C_{71}	–347(4)	4828(5)	3413(6)
C_{81}	1094(4)	4723(5)	3786(5)
C_{12}	3011(7)	2383(12)	4371(9)
C_{22}	2796(4)	399(7)	2542(5)
C_{32}	834(6)	–2875(9)	2926(7)
C_{42}	–40(6)	–2449(9)	4743(5)
C_{52}	–1702(7)	108(12)	4959(6)
C_{62}	–1883(4)	2816(8)	4438(5)
C_{72}	–540(5)	5018(7)	4016(6)
C_{82}	1328(5)	4914(8)	4523(6)

[a] Numbers in parentheses are the estimated standard deviations in the last significant figure. [b] For Fe $10^5 \times x = 2.765(3)$, $10^5 \times y = 11.744(5)$, $10^5 \times z = 33.755(4)$.

TABLE II. Bond Lengths in the Coordination Group, in the Porphinato Skeleton, and to the Methyl Substituents[a]

Type	Length (Å)	Type	Length (Å)	Type	Length (Å)
$Fe-O$	1.752(1)	N_4-C_{a7}	1.368(7)	$C_{a1}-C_{b1}$	1.447(8)
$Fe-N_1$	2.077(4)	N_4-C_{a8}	1.369(8)	$C_{a2}-C_{b2}$	1.479(9)
$Fe-N_2$	2.060(4)	$C_{m1}-C_{a2}$	1.385(9)	$C_{a3}-C_{b3}$	1.478(10)
$Fe-N_3$	2.061(4)	$C_{m1}-C_{a3}$	1.405(9)	$C_{a4}-C_{b4}$	1.448(10)
$Fe-N_4$	2.063(4)	$C_{m2}-C_{a4}$	1.402(10)	$C_{a5}-C_{b5}$	1.451(10)
N_1-C_{a1}	1.369(8)	$C_{m2}-C_{a5}$	1.394(10)	$C_{a6}-C_{b6}$	1.477(9)
N_1-C_{a2}	1.376(7)	$C_{m3}-C_{a6}$	1.413(8)	$C_{a7}-C_{b7}$	1.468(8)
N_2-C_{a3}	1.357(7)	$C_{m3}-C_{a7}$	1.418(8)	$C_{a8}-C_{b8}$	1.436(9)
N_2-C_{a4}	1.371(8)	$C_{m4}-C_{a8}$	1.398(8)	$C_{b1}-C_{b2}$	1.356(11)
N_3-C_{a5}	1.376(9)	$C_{m4}-C_{a1}$	1.373(9)	$C_{b3}-C_{b4}$	1.371(10)
N_3-C_{a6}	1.362(7)	$C_{m1}-C_1$	1.525(9)	$C_{b5}-C_{b6}$	1.354(11)
		$C_{m3}-C_2$	1.522(8)	$C_{b7}-C_{b8}$	1.375(10)

[a] Numbers in parentheses are the estimated standard deviations.

TABLE III. Bond Angles in the Oxo Bridge, the Coordination Group, and the Porphinato Skeleton[a]

Angle	Value (deg)	Angle	Value (deg)	Angle	Value (deg)
$Fe-O-Fe$	178.5(6)	$C_{a7}-N_4-C_{a8}$	106.7(5)	$N_4-C_{a7}-C_{b7}$	108.9(5)
N_1-Fe-O	106.0(1)	$N_1-C_{a1}-C_{m4}$	124.7(5)	$C_{m3}-C_{a7}-C_{b7}$	127.6(5)
N_2-Fe-O	104.3(2)	$N_1-C_{a1}-C_{b1}$	109.7(5)	$N_4-C_{a8}-C_{b8}$	111.6(5)
N_3-Fe-O	103.3(2)	$C_{m4}-C_{a1}-C_{b1}$	125.3(6)	$N_4-C_{a8}-C_{m4}$	123.8(5)
N_4-Fe-O	103.8(2)	$N_1-C_{a2}-C_{b2}$	108.2(5)	$C_{b8}-C_{a8}-C_{m4}$	124.2(6)
N_1-Fe-N_2	84.0(2)	$N_1-C_{a2}-C_{m1}$	124.2(5)	$C_{a2}-C_{m1}-C_{a3}$	122.5(5)
N_2-Fe-N_3	89.3(2)	$C_{b2}-C_{a2}-C_{m1}$	127.3(5)	$C_{a2}-C_{m1}-C_1$	118.6(6)
N_3-Fe-N_4	84.4(2)	$N_2-C_{a3}-C_{m1}$	124.8(5)	$C_1-C_{m1}-C_{a3}$	118.8(6)
N_4-Fe-N_1	88.2(2)	$N_2-C_{a3}-C_{b3}$	108.7(5)	$C_{a4}-C_{m2}-C_{a5}$	127.0(6)
$Fe-N_1-C_{a1}$	127.0(3)	$C_{m1}-C_{a3}-C_{b3}$	126.3(5)	$C_{a6}-C_{m3}-C_{a7}$	122.3(5)
$Fe-N_1-C_{a2}$	123.3(4)	$N_2-C_{a4}-C_{b4}$	110.5(5)	$C_{a6}-C_{m3}-C_2$	118.6(5)
$C_{a1}-N_1-C_{a2}$	107.7(5)	$N_2-C_{a4}-C_{m2}$	125.2(6)	$C_2-C_{m3}-C_{a7}$	119.0(6)
$Fe-N_2-C_{a3}$	123.7(4)	$C_{b4}-C_{a4}-C_{m2}$	123.9(7)	$C_{a8}-C_{m4}-C_{a1}$	127.8(6)
$Fe-N_2-C_{a4}$	126.2(4)	$N_3-C_{a5}-C_{m2}$	124.1(6)	$C_{a1}-C_{b1}-C_{b2}$	107.3(6)
$C_{a3}-N_2-C_{a4}$	107.7(5)	$N_3-C_{a5}-C_{b5}$	110.8(6)	$C_{b1}-C_{b2}-C_{a2}$	106.9(5)
$Fe-N_3-C_{a5}$	127.0(4)	$C_{m2}-C_{a5}-C_{b5}$	124.8(7)	$C_{a3}-C_{b3}-C_{b4}$	107.1(6)
$Fe-N_3-C_{a6}$	123.7(4)	$N_3-C_{a6}-C_{b6}$	109.3(5)	$C_{b3}-C_{b4}-C_{a4}$	105.9(6)
$C_{a5}-N_3-C_{a6}$	106.5(5)	$N_3-C_{a6}-C_{m3}$	123.6(5)	$C_{a5}-C_{b5}-C_{b6}$	106.2(6)
$Fe-N_4-C_{a7}$	122.8(4)	$C_{b6}-C_{a6}-C_{m3}$	127.0(5)	$C_{b5}-C_{b6}-C_{a6}$	107.1(5)
$Fe-N_4-C_{a8}$	127.6(3)	$N_4-C_{a7}-C_{m3}$	123.4(5)	$C_{a7}-C_{b7}-C_{b8}$	107.3(5)
				$C_{b7}-C_{b8}-C_{a8}$	105.5(5)

[a] Numbers in parentheses are the estimated standard deviations.

Fig. 2) is one of the dihedral twofolds of the group. The Fe–O–Fe angle is 178.5(6)° rather than the 180° value required for exact D_{2d} symmetry. The angle of twisting about the S_4 axis for exact eclipsing would be 0°; the observed twist angle is 3.8°.

The porphinato cores in $[Fe(ODM)]_2O$ are markedly ruffled as shown in the formal diagram of Fig. 3 which displays the displacement of the skeletal atoms (in units of 0.01 Å) from the mean plane of the 24-atom core. In addition to the D_{2d} description, the ruffling can be quantitatively described by noting the angles between the normals to the pyrrole rings (as usual, the pyrrole rings themselves are planar to within 0.02 Å). The angles between the pyrrole rings bridged by the methyl-substituted methine carbons are 25.2 and 23.8° (N_1, N_2; N_3, N_4, respectively); those between the pyrrole rings bridged by unsubstituted methine carbon atoms are 22.3 and 17.9° (N_1, N_4; N_2, N_3, respectively). (The pyrrole rings are specified by naming the nitrogen atom of the ring.)

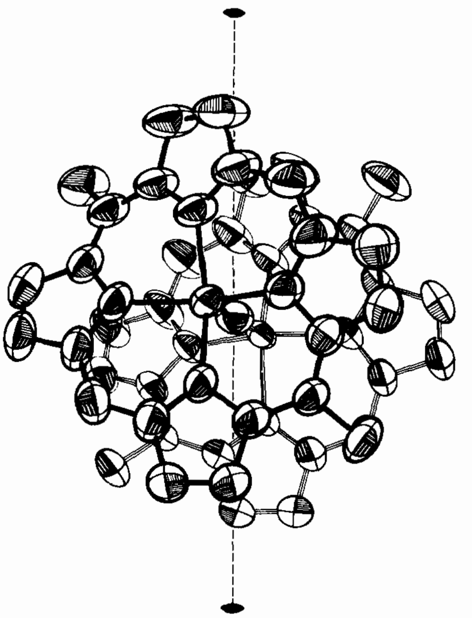

Fig. 2. Perspective view of [Fe(ODM)]$_2$O showing the relative orientation of the two porphinato cores. The position of the crystallographically required twofold axis is also displayed.

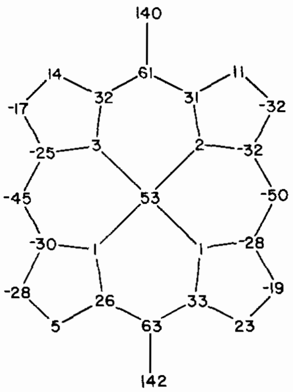

Fig. 3. Formal diagram of the porphinato skeleton, with the same relative orientation as Fig. 1, and including the two methyl groups bonded to the methine carbon atoms. The perpendicular displacement of each atom, in units of 0.01 Å, from the 24-atom mean plane is illustrated.

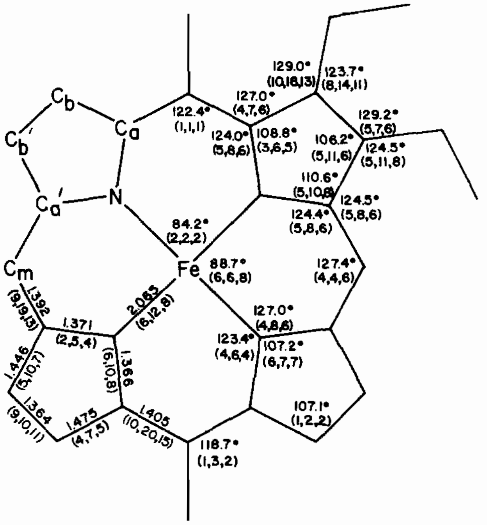

Fig. 4. Formal diagram of the porphinato skeleton in [Fe(ODM)]$_2$O. Bond lengths and angles in the porphinato skeleton, averaged in agreement with C_{2v} symmetry, are entered on the diagram. Average values for bond angles involving the peripheral ethyl groups (only two of the eight are shown) are also entered on the diagram. The first figure in parentheses following an averaged value is the mean deviation from the average, the second is the maximum deviation from the average, and the third is the estimated standard deviation calculated on the assumption that the values averaged are drawn from the same population.

Thus in terms of the folding description, it is seen that there is a slightly larger folding between the halves bridged by the substituted methine carbon atoms compared to the halves bridged by the unsubstituted methine carbon atoms. The angles between opposite pyrrole rings are 32.4 and 31.2° (N_1, N_3; N_2, N_4). It is worth noting that although many metalloporphyrin derivatives with substantially ruffled cores have been characterized previously [8], this is the first derivative wherein the metal atom is displaced considerably out of plane. The ruffling of the core is the direct result of steric congestion between the methyl substituents and the methylene groups of the adjacent peripheral ethyl groups. These contacts are remarkably tight with $C_1 \cdots C_{21}$ = 3.10(1) Å, $C_1 \cdots C_{31}$ = 3.09(1) Å, $C_2 \cdots C_{61}$ = 3.11(1) Å, and $C_2 \cdots C_{71}$ = 3.14(1) Å; the nominal value* of the sum of the van der Waals radii of these two groups is 3.4 Å.

The bond parameters of the porphinato core appear to deviate significantly from fourfold geometry to accommodate this steric congestion. Figure 4 displays values of bond distances and angles in the porphinato core, averaged in agreement with C_{2v} symmetry. The numbers given in parentheses following each averaged parameter are, in order; the mean deviation from the average, the maximum deviation from the average, and the estimated standard deviation calculated on the assumption that the values averaged are from the same population. An examination of Fig. 4 reveals that bond parameters involving the C_a carbon atoms of the pyrrole rings are

---

*The value suggested by Bondi [9a] is less than the value of 4.0 Å suggested by Pauling [9b].

rationally divided into two sets: one set comprised by the four C_a carbon atoms adjacent to the methyl-substituted methine carbon bridges and the other by the four C_a carbon atoms adjacent to the unsubstituted bridges (labeled as C_a'). The values of bond parameters for the C_a and C_a' sets appear to differ in a way that maximizes the $C_1 \cdots C_{n1}$ non-bonded distances. The 5.0° difference in the C_a–C_m–C_a angles (and the concomitant differences in the N–Fe–N angles), the 2.5° difference in the C_m–C_a–C_b angles and the 4.5° difference in the C_a–C_b–C_{n1} angles all vary in the direction appropriate for increasing the $C_1 \cdots C_{n1}$ (n = 2, 3, 6, and 7) nonbonded contacts. Bond angles are, of course, more adaptable to changes needed to relieve stress than are bond lengths. Nonetheless, values of bond lengths for the two classes of C_a–C_b bonds appear to reflect such a change. The C_a'–C_b' bond class averages to 1.466 Å, a normal length for this chemical type [8, 10]. The C_a–C_b bond class is lengthened by 0.029 Å (to 1.475 Å) and is a long bond. The values for the other class of bonds for which a lengthening might be anticipated, the C_a–C_m sets, are not different at a statistically significant level, although the average values for the two sets differ in the direction expected. The $Ct \cdots C_m$ distances, where Ct represents the center of the macrocycle, are also significantly different with $Ct \cdots C_{m1}$ (C_{m3}) = 3.43 Å and $Ct \cdots C_{m2}$ (C_{m4}) = 3.330 Å.

A D_{2d} ruffling of the quasi-rigid porphinato core usually affords a means for obtaining shorter M–N bonds than those found in analogous derivatives with planar cores [10]. In [Fe(ODM)]$_2$O, despite the considerable ruffling of the core, the average Fe–N bond distance of 2.065 Å is not significantly shorter than those found for several high-spin iron(III) porphyrinates studied previously [11]. The iron atom is displaced 0.53 Å from the mean plane of the porphyrin core (Fig. 3) and 0.51 Å from the mean plane of the four porphinato nitrogen atoms. The values of these displacements are comparable to those of other high-spin iron(III) porphyrinates [11]. Other features of the coordination group (*vide infra*) are also typical of other μ-oxo derivatives. Thus the observed porphyrin conformation relieves the steric congestion of the peripheral groups but is ineffective in substantially modifying the coordination group parameters. We conclude that the observed conformation is not caused by the coordination requirements of the high-spin iron(III) ion. Since the observed conformation is however the most probable one for species with relatively short metal–nitrogen bond distances, we further conclude that the quasi-D_{2d} ruffled conformation will generally be found for all derivatives of H_2(ODM).

The Fe–O bond length of 1.752(1) Å is quite comparable to the 1.763(1) Å value observed for [Fe(TPP)]$_2$O [12], the 1.787(17) Å average value found for [Fe$_2$(μ-O)(FF)]·H_2O [13]*, and the 1.73 Å value found for [Fe(ProtoMe$_2$)]$_2$O [14]**. The Fe–O–Fe angle in [Fe(ODM)]$_2$O is 178.5(6)°, much closer to a linear bridge bond than the 174.5° value in [Fe(TPP)]$_2$O or the 172.5° angle in [Fe(ProtoMe$_2$)]$_2$O. Concomitant with the more nearly linear link in [Fe(ODM)]$_2$O is a slight increase in the separation (4.55 Å) between the two mean porphinato planes from the 4.50 Å value in [Fe(TPP)]$_2$O and the 4.40 Å value in [Fe(ProtoMe$_2$)]$_2$O.

The orientation of the two porphyrin rings in [Fe(ODM)]$_2$O is essentially eclipsed when viewed along the Fe–O–Fe bond. This is quite different from the orientation observed in other μ-oxo-iron(III) porphyrinates. An eclipsed orientation in [Fe-TPP)]$_2$O is presumably precluded by the bulky phenyl substituents; the observed N–Fe–Fe–N dihedral angle of 54.6° is close to the ideal 45° value for a staggered arrangement; this dihedral angle in [Fe(ODM)]$_2$O is 3.8°. The analogous angle in [Fe$_2$(μ-O)(FF)]·H_2O is 24°. Such substituent interactions are not present in [Fe(ProtoMe$_2$)]$_2$O; however the observed dihedral angle is 62°. It is, therefore, a rational conclusion that the observed eclipsed conformation results from a minimization of nonbonded contacts between the methyl groups and other peripheral substituents of the two rings. The closest observed intramolecular, *inter*-ring contact is a 3.72 Å distance between a methine carbon atom and a methyl carbon atom. The hypothetical staggered conformation would lead to closer contacts because of the substantial ruffling of the cores.

The packing of the [Fe(ODM)]$_2$O molecules in the unit cell is illustrated in Fig. 5. There are no unusually short intermolecular contacts; the closest approaches range from 3.5 Å upwards.

Supplementary Material

Anisotropic thermal parameters are available from the authors on request.

Acknowledgements

Financial support from the National Institutes of Health (Grant HL-15627, to W.R.S.), the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Vereinigung von Freunden der Technischen Hochschule Darmstadt is gratefully acknowledged.

---

*FF is confacial biporphyrin.

**ProtoMe$_2$ is protoporphyrin IX dimethyl ester.

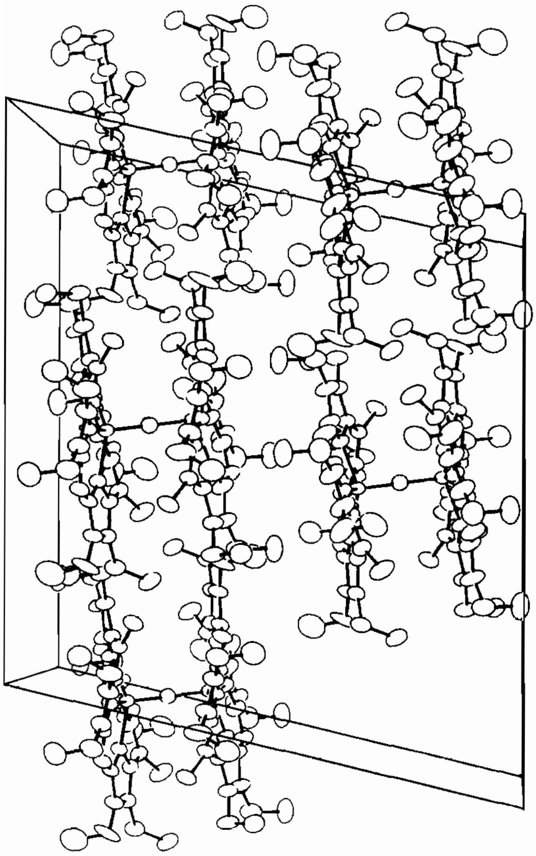

Fig. 5. Diagram illustrating the packing of the [Fe(ODM)]$_2$O molecules in the unit cell.

References

1 J. W. Buchler and S. Pfeifer, *Z. Naturforsch., Teil B, 40,* 1362 (1985).

2 R. B. Woodward, *Angew. Chem., 72,* 651 (1960).

3 (a) J. W. Buchler and L. Puppe, *Liebigs Ann. Chem., 740,* 142 (1970); (b) P. N. Dwyer, J. W. Buchler and W. R. Scheidt, *J. Am. Chem. Soc., 96,* 2789 (1974); (c) P. N. Dwyer, L. Puppe, J. W. Buchler and W. R. Scheidt, *Inorg. Chem., 14,* 1782 (1975); (d) J. W. Buchler, K.-L. Lay, P. D. Smith, W. R. Scheidt, G. A. Ruprecht and J. E. Kenny, *J. Organomet. Chem., 110,* 109 (1976); (e) J. W. Buchler, K.-L. Lay, P. D. Smith, Y. J. Lee and W. R. Scheidt, *Angew. Chem., Int. Ed. Engl., 21,* 432 (1982); (f) A. Botulinski, J. W. Buchler, K.-L. Lay, J. Ensling, H. Twilfer, J. Billecke, H. Lueken and B. Tonn, *Adv. Chem. Ser., 201,* 254 (1982); (g) J. W. Buchler, C. Dreher, K.-L. Lay, Y. J. Lee and W. R. Scheidt, *Inorg. Chem., 22,* 888 (1983); (h) A. Botulinski, J. W. Buchler, K.-L. Lay and H. Stoppa, *Liebigs Ann. Chem.,* 1259 (1984); (i) A. Botulinski, J. W. Buchler, B. Tonn and M. Wicholas, *Inorg. Chem., 24,* 3239 (1985).

4 K. M. Barkigia, J. Fajer, A. D. Adler and G. J. B. Williams, *Inorg. Chem., 19,* 2057 (1980).

5 R. Blessing, P. Coppens and P. Becker, *J. Appl. Crystallogr., 7,* 488 (1974).

6 W. R. Scheidt, *J. Am. Chem. Soc., 96,* 84 (1974).

7 (a) C. R. Hübbard, C. O. Quicksal and A. R. Jacobson, 'ALFF'; W. R. Busing, K. O. Martin and H. A. Levy, 'ORFFE'; C. K. Johnson, 'ORTEP'; J. J. Park, 'Refine'; (for further details see ref. 6); (b) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 24,* 321 (1968); (c) D. T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1891 (1970).

8 W. R. Scheidt, in D. Dolphin (ed.), 'The porphyrins', Vol. III, 1978, pp. 463–511; J. L. Hoard in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, Chap. 8.

9 (a) A. Bondi, *J. Chem. Phys., 68,* 441 (1964); (b) L. Pauling, 'The Nature of the Chemical Bond', 3rd edn., Cornell University Press, Ithaca, N.Y., 1960.

10 (a) J. L. Hoard, *Ann. N.Y. Acad. Sci., 206,* 18 (1973); (b) D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc., 96,* 2095 (1974); (c) J. A. Kaduk and W. R. Scheidt, *Inorg. Chem., 13,* 1875 (1974).

11 W. R. Scheidt and C. A. Reed, *Chem. Rev., 81,* 543 (1981).

12 A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, R. S. Srivastava and J. L. Hoard, *J. Am. Chem. Soc., 94,* 3620 (1972).

13 J. T. Landrum, D. Grimmett, K. J. Haller, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc., 103,* 2640 (1981).

14 L. J. Radonovich, W. S. Caughey and J. L. Hoard, unpublished results.