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Structural characterization of the μ -Nitrido Complex {[Fe(OEP)]₂N}

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Abstract

The molecular structure of the μ -nitrido dimer, μ -nitrido-bis(2,3,7,8,12,13, 17,18-octaethylporphyrinato)iron, is reported. The axial Fe–N distances average to 1.657 (11) Å and the equatorial distances average to 2.005(5) Å. Although not required by symmetry, the two iron centers appear equivalent and are consistent with an assignment of a low-spin state and a formal oxidation state of +3.5. A comparison of this structure with other nitrido-bridged species is given.

Keywords

iron porphyrin; μ -nitrido dimer; X-ray structure

Introduction

The recent report in this journal [1] of the synthesis and characterization of the nitrido bridged species {[Fe(OEP)]₂N} [2] prompts us to report our synthesis and, more importantly, the X-ray structure determination of molecular {[Fe(OEP)]₂N}. Binuclear nitrido-bridged species of both porphyrin and phthalocyanine macrocycles have been studied for their possible utilization as catalysts in oxidation reactions [3, 4]. We had originally synthesized {[Fe(OEP)]₂N} as part of a program to characterize both the neutral nitrido-bridged species {[Fe(porph)]₂N} and the one electron oxidized relative. This work was part of program to better understand the electronic structure of these species, but we have not been able to obtain crystals of the oxidized OEP species. However, this work has been completed for {[Fe(TPP)]₂N} [5] and {[Fe(TTP)]₂N}⁺ [6], which have formal oxidation states for the iron centers of +3.5 and +4.0, respectively. We compare the details of this new structure with those of earlier nitrido bridged species and other binuclear iron species.

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Supporting Information Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC 973366. Copies can be obtained on request, free of charge, via www.ccdc.cam.ac.uk/datarequest/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or deposit@ccdc.cam.ac.uk).

Experimental Section

General Information

All manipulations were carried out under argon using a double manifold vacuum line, Schlenkware and cannula techniques. Dichloromethane was distilled over CaH_2 , and hexanes were distilled over sodium benzophenone. H_2OEP was purchased from Midcentry Chemical. All other chemicals were used as received from Aldrich or Fisher. $[\text{Fe}(\text{OEP})\text{Cl}]$ and $[\text{Fe}(\text{OEP})(\text{N}_3)]$ were synthesized by literature methods [7, 8]. UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer and IR spectra on a Perkin-Elmer model 883 as KBr pellets. EPR spectra were obtained at 77 K on a Varian E-12 spectrometer operating at X-band.

Synthesis of μ -Nitrido-bis(octaethylporphyrinato)iron

$\{[\text{Fe}(\text{OEP})]_2\text{N}\}$ was prepared by the method of Summerville and Cohen [9]. UV-vis (CH_2Cl_2 solution)(log ϵ): λ_{max} : 368, 554, 586 nm. IR(KBr): $\nu(\text{Fe-N-Fe})$ 931(s) cm^{-1} . EPR (frozen CH_2Cl_2 , 77K) $g_{\perp} = 2.14$, $g_{\parallel} = 2.00$.

X-Ray Structure Determination

Crystals of $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$ suitable to X-ray analysis was obtained by a vapor diffusion of hexanes into a CH_2Cl_2 solution of $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$. X-ray diffraction data were collected on a Nonius FAST area-detector diffractometer with a Mo rotating anode source ($\lambda = 0.71073 \text{ \AA}$) at 130 K. Our detailed methods and procedure for small molecular X-ray data collection have been described previously [10]. A modified version [11] of the absorption correction program DIFABS was applied.

The structure was solved by direct methods [13]. Subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods utilizing all data [13]. Hydrogen atoms of the porphyrin ligand were idealized with the standard SHELXL idealization methods. Brief crystal data are listed in Table 1.

Results and Discussion

The structure of the $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$ molecule is illustrated in the ORTEP diagrams of Figures 1 and 2. As can be seen in Figure 1, the two porphyrin rings approach each other closely and most, but not all, of the peripheral ethyl groups are towards the outside of the dimeric molecule. There is no required symmetry for the molecule, unlike many related derivatives; thus the Fe–N–Fe angle is not required to be linear and indeed is not quite linear at $175.2(2)^\circ$. The two porphyrin planes make a dihedral angle of 7.2° ; and neither porphyrin plane is planar as discussed below. The two axial Fe–N bonds are both very short at 1.649(4) and 1.665(4) $\text{\AA}$, consistent with strong multiple bonds. The average value of the eight equatorial Fe–N_p bonds is 2.005 $\text{\AA}$, consistent with a low-spin state for both iron atoms [14].

Figure 2 provides a top-down view that illustrates the 23.10° twist angle between the two porphyrin rings of $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$. The several structural differences between the

{[Fe(OEP)]₂N} and {[Fe(TPP)]₂N} systems reflect the differing steric factors in bringing the two porphyrin rings in close proximity. These include differences in the iron atom displacements, the interring separation, and the twist angle. Table 2 displays these structural parameters and available equivalent information for several additional monobridged Fe(III) and Fe(IV) porphyrin and phthalocyanine species. The closer approach of the porphyrin rings in the OEP species leads to the very short Fe...Fe distance of 3.311 Å, which has also been observed from EXAFS measurements [1], the 0.3 Å difference in the interplanar spacing, and the smaller twist angle in the OEP derivative.

Figures 3 and 4 display averaged values of the bonding parameters in the two independent porphyrin rings of {[Fe(OEP)]₂N}. As is readily observed from the two diagrams, the structural parameters for the two rings are equivalent to well within the estimated uncertainties. This equivalence between the two rings does not extend to the ring conformations. The two conformations are quite distinct. The conformation of ring 1 (Figure 3) is seen to be a combination of ruffling and saddling, whereas the conformation of ring 2 (Figure 4) is seen to be much more that of a simple ruffled core. Reasons for the differences are not clear; steric factors do not appear to be the cause.

A cell packing diagram in 50% thermal ellipsoid format and including all hydrogen atom is given in Figure 5. The {[Fe(OEP)]₂N} molecules are seen to form a zigzag column along the c-axis with the porphyrin planes approximately parallel to the ab plane. In our experience the inclusion of hexane solvate molecules, especially well-ordered ones, is quite rare. As can be seen in the figure, the six-carbon chains are approximately perpendicular to the pair of porphyrin planes of {[Fe(OEP)]₂N}. The molecule of interest and the solvate molecule have commensurate dimensions. This feature may in fact be responsible for the good ordering of the *n*-hexane chains.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and Notes

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Figure 1.
Side-on ORTEP diagram of $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$. 50% probability ellipsoids are shown.
Hydrogen atoms eliminated for clarity.

Figure 2.

Top-down view of $[\text{Fe}(\text{OEP})]_2\text{N}$. 50% probability ellipsoids are shown. Hydrogen atoms eliminated for clarity. The atom labeling scheme is also shown.

Figure 3.

Formal diagram of the porphinato core of ring **1** of {[Fe(OEP)]₂N} displaying perpendicular displacements, in units of 0.01 Å, of the core atoms from the 24-atom mean plane. Positive values of displacements are towards the bridging nitride. Averaged values of the chemically unique bond distances (in Å) and angles (in deg.) are shown.

Figure 4.

Formal diagram of the porphinato core of ring **1** of $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$ displaying perpendicular displacements, in units of 0.01 Å, of the core atoms from the 24-atom mean plane. Positive values of displacements are towards the bridging nitride. Averaged values of the chemically unique bond distances (in Å) and angles (in deg.) are shown.

Figure 5. Diagram illustrating the packing of the $\{[\text{Fe}(\text{OEP})]_2\text{N}\}$ molecules and the *n*-hexane solvates in the unit cell (50% probabilities shown). Cell axes are labelled.

Table 1Crystallographic details for {[Fe(OEP)]₂N}.

formula	C ₇₂ H ₈₈ Fe ₂ N ₉ ·C ₆ H ₁₄
FW, amu	1277.39
<i>a</i> , Å	13.9256(19)
<i>b</i> , Å	13.8434(14)
<i>c</i> , Å	35.200(2)
β , deg	96.614(10)
<i>V</i> , Å ³	6740.6(12)
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4
<i>D</i> _c , g/cm ³	1.259
<i>F</i> (000)	2740
μ , mm ⁻¹	0.482
crystal dimensions, mm	0.30 × 0.17 × 0.06
radiation	MoK α , λ = 0.71073 Å
goodness-of-fit (based on <i>F</i> ²)	1.031
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0664, <i>wR</i> ₂ = 0.1656
final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0954, <i>wR</i> ₂ = 0.1812

Table 2

Selected Structural Features for Monobridged Binuclear Porphinato Complexes

compound	Fe-N _{sp} ^a , Å	Fe-Y ^b , Å	Fe-Y-Fe, deg.	c, Å	(N _{sp}), ^d Å	mean plane sepn, ^e Å	interplanar angle, ^f deg	twist angle, ^g deg	ref
{[Fe(OEP) ₂ N]}	2.005(5)	1.657(11)	175.2(2)	0.27	0.27	3.83	7.2	23.1	this work
{[Fe(TPP) ₂ N]}	1.991(3)	1.661(7)	180	0.41	0.32	4.15	0	31.7	5
{[Fe(TPP) ₂ N]}	2.010(5)	1.679(4)	177.0(4)						3
{[Fe(TTP) ₂ N]SbCl ₆ }	1.979(5)	1.6280(7)	180	0.37	0.34	4.00	0	30.3	6
{[Fe(TPP)(THF)]-N-}	2.00(5)	1.655(2)	179.0(6)		0.12		2.1	~0	
[Fe(Pc)(H ₂ O)]I ₅	1.95(5)	1.625(2)			0.11				4
{[Fe(Pc)(N ₃) ₂ N]I ₃ }	1.947(5)	1.650(1)	177.4(4)	0.08				38.5	15
{[Fe(Pc)(Br) ₂ N]}	1.945(6)	1.639(2)	180	0		3.25	0	39	16
{[Fe(TPP) ₂ C]}	1.980(8)	1.675	180	-	0.26	3.87	0	31.7	17
{[Fe(OEP) ₂ C]}	1.986(5)	1.6638(9)	179.5	-	0.19	-	-	21.0	18
{[Fe(OEP) ₂ O](A)}	2.077(3)	1.756(3)	172.2(2)	0.50		4.5	7.3	17.0	19
{[Fe(OEP) ₂ O](B)}	2.080(5)	1.755(5)	176.2(2)	0.54		4.6	2.7	16.8	19

^a N_{sp} refers to the pyrrole nitrogen atom in porphyrin ring.

^b Y is the bridging atom.

^c The average displacement of the metal centers from the mean 24-atom core. A positive value indicates that the metal is displaced toward ring center.

^d 4-nitrogen atom plane.

^e The average separation of the individual atom from the other 24-atom core is given.

^f The dihedral angle of two mean planes of the 24-atom core within a dimeric molecule.

^g Average of the four N-M-M'-N' dihedral angles.