

Structural Distortion in Five-Coordinate Nitrosyl Iron Porphyrins. Axial Ligand Tilting and Its Effect on Equatorial Geometry

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Received April 10, 1997

We report that at least some five-coordinate nitrosyliron porphyrin derivatives display a hitherto unexpected structural distortion in both the axial and equatorial directions. The nature of nitric oxide (NO) ligation in hemes has received recent renewed interest because of the recognition of the participation of NO in a wide variety of biological functions.¹ Surprisingly, there are no completely ordered $[\text{Fe}(\text{Porph})(\text{NO})]_2$ complex structures in the literature; the accuracy of the coordination group parameters has been limited by disorder in all four previously reported structures.^{3–5} In three complexes,^{3,4} accurate values of the parameters are obscured by disorder resulting from crystallographically required symmetry higher than the complex can possess. In the fourth structure, there is rotational disorder of the NO ligand that must limit the accuracy of the N and O coordinates.⁵

In the course of recent work on the interaction of nitric oxide (NO) with iron porphyrins, we have isolated high-quality crystals of five-coordinate $[\text{Fe}(\text{OEP})(\text{NO})]$. This complex has an NO stretching frequency of 1666 cm^{-1} in the solid state and 1665 cm^{-1} in methylene chloride solution. A determination of the molecular structure shows the derivative to be well ordered.⁶ Figure 1 shows that the square-pyramidal coordination group has a bent Fe–N–O group as expected for this $\{\text{FeNO}\}$ ⁷ complex with an Fe–N(5)–O(1) angle of $144.4(2)^\circ$.⁸ The axial Fe–N bond distance is $1.722(2)\text{ \AA}$, and the iron is displaced

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(2) Abbreviations: Porph, a generalized porphyrin dianion; OBTPP, dianion of octabromotetraphenylporphyrin; OEP, dianion of octaethylporphyrin; N_p, porphyrinato nitrogen.

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(6) $[\text{Fe}(\text{OEP})(\text{NO})]$ was prepared by reductive nitrosylation of $[\text{Fe}(\text{OEP})\text{OCIO}_3]$ in chloroform. X-ray quality crystals were obtained by vapor diffusion using hexanes as the nonsolvent. The complex crystallizes in the monoclinic space group $P2_1/c$, $a = 14.950(2)\text{ \AA}$, $b = 22.361(2)\text{ \AA}$, $c = 9.6966(3)\text{ \AA}$, $\beta = 104.854(5)^\circ$, $V = 3133.3(4)\text{ \AA}^3$, $Z = 4$. Data collection was carried out on an Enraf-Nonius FAST area-detector diffractometer with a Mo rotating anode source ($\lambda = 0.710\text{ \AA}$) at $130(2)\text{ K}$ (Scheidt, W. R.; Turowska-Tyrk, I. *Inorg. Chem.* **1994**, *33*, 1314). The structure was solved using the direct methods program SHELXS-86 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467); subsequent difference Fourier syntheses led to the location of the remaining non-hydrogen atoms. The structure was refined against F^2 with the program SHELXL-93 (Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation), in which all data collected were used including negative intensities. Hydrogen atoms were idealized with the standard SHELXL-93 idealization methods. All non-hydrogen atoms were refined anisotropically. Final R indices: $R_1 = 0.0421$ ($I > 2\sigma(I)$), $wR_2 = 0.1561$ (all data).⁷ A total of 22 655 reflections were measured; 7890 unique. Complete details are included in the Supporting Information.

(7) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$. The conventional R factors (R_1) are based on F , with F set to zero for negative F^2 . The criterion of $F^2 > 2\sigma(F^2)$ was used only for calculating R_1 . R factors based on F^2 (wR_2) are statistically about twice as large as those based on F , and R factors based on ALL data will be even larger.

(8) The $\{\text{MNO}\}^n$ notation is that of Enemark and Feltham: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(9) The number in parentheses following averaged values is the estimated standard deviation calculated on the assumption that the averaged values are drawn from the same population.

(10) This tilt might be caused by a very modest intermolecular contact of a methylene carbon atom with the nitrosyl nitrogen: $\text{C}(31)\cdots\text{N}(5) = 3.50\text{ \AA}$, $\text{H}(31\text{A})\cdots\text{N}(5) = 2.62\text{ \AA}$. If the Fe–N(5) vector is constrained to be normal to the heme plane, the $\text{C}(31)\cdots\text{N}(5)$ distance would be 3.37 \AA and the $\text{H}(31\text{A})\cdots\text{N}(5)$ would be 2.50 \AA . An ORTEP illustration of the NO surroundings is available in the Supporting Information.

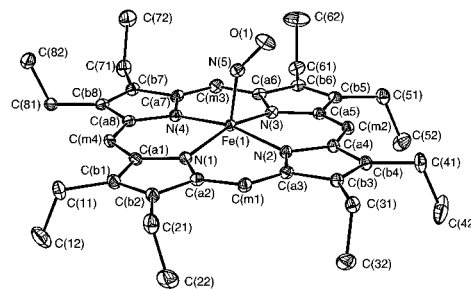


Figure 1. ORTEP diagram of $[\text{Fe}(\text{OEP})(\text{NO})]$ with 50% probability ellipsoids. The atom labeling scheme used in all tables is displayed.

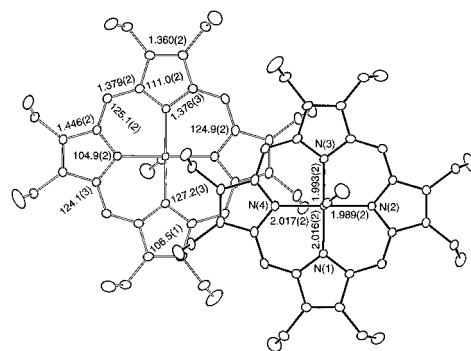


Figure 2. ORTEP diagram (top view) of the two closest molecules that form a weak dimer in the solid state. 50% ellipsoids are shown. On one of the molecules shown, the values of the four unique Fe–N_p distances are shown. On the other molecule, the averaged values of the bond distances and angles are displayed. The Fe \cdots Fe distance is 7.88 \AA , and the mean plane separation is 3.35 \AA .

by 0.29 \AA out of the porphyrin plane. The dihedral angle between the Fe–N–O plane and the closest Fe–N_p vector is 38° . These parameters are similar to those seen in earlier structures^{3–5} but at higher precision. Importantly, the quality of the structure is quite high with exceptionally high internal agreement in bond parameters of the porphyrin core.

However, there are two structural features observed for $[\text{Fe}(\text{OEP})(\text{NO})]$ that have not been previously seen in heme derivatives. As can be seen in Figure 1, the axial Fe–N vector is decidedly not perpendicular to the porphyrin plane but is tilted off-axis (by 6.5°). This corresponds to a 0.19 \AA translation of the nitrosyl nitrogen atom off the heme normal. Second, the four equatorial Fe–N_p bonds show a rather large range of values— $1.989(2)$, $1.993(2)$, $2.016(2)$, and $2.017(2)\text{ \AA}$ —a much larger spread than expected given the internal agreement observed in the porphyrin core. The values do suggest that the Fe–N_p distances are related in pairs. Individual Fe–N_p bond distances and averaged values of bond parameters⁹ in the core have been entered on Figure 2. The Fe–N_p bond distance pattern shown in Figure 2 suggests the possibility that the Fe–N_p differences result from the axial ligand tilting¹⁰ as the two short Fe–N_p distances ($1.991(3)\text{ \AA}$ average) bracket the tilted NO ligand while the two long Fe–N_p distances ($2.016(1)\text{ \AA}$ average) are further from the off-axis NO. The differences in Fe–N_p bonds caused by the off-axis tilt of the NO could be related to the known strong trans influence of the nitrosyl ligand.

To further explore this interesting structural phenomenon, we endeavored to structurally characterize another well-ordered five-coordinate nitrosyl derivative. We have had the fortunate experimental result of obtaining a second crystalline form of $[\text{Fe}(\text{OEP})(\text{NO})]$. This new complex has an NO stretching frequency of 1673 cm^{-1} in the solid state and 1665 cm^{-1} in methylene chloride solution. The EPR spectra (frozen solution) are quite similar to that reported earlier.¹¹ In the finely divided crystalline state, the EPR spectra of the two forms have broad

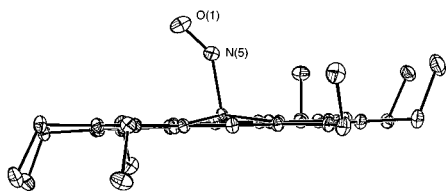


Figure 3. Edge-on view of the second form of [Fe(OEP)(NO)]. The same labeling scheme as that shown in Figure 1 is used.

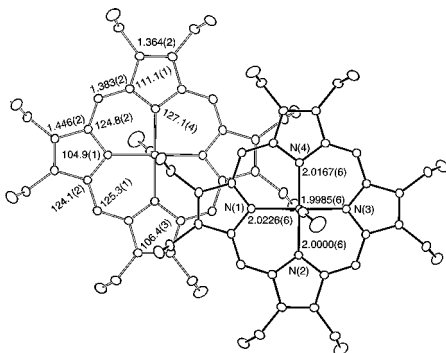


Figure 4. ORTEP diagram (top view) of the two closest molecules of the second form. Note that, although a weak dimer is again formed, the orientations of the two rings are quite distinct. 50% ellipsoids are shown. The same distance and angle information as that given in Figure 2 is displayed. The Fe...Fe distance is 7.67 Å, and the mean plane separation is 3.41 Å.

spectra, with unresolved hyperfine features and display a $\Delta M = 2$ feature consistent with magnetic interactions within a dimer.¹²

This new crystalline form displays even more superlative X-ray diffraction properties and was found to diffract to a remarkably high scattering angle ($2\theta = 89^\circ$ with Mo radiation).¹³ This new complex has a structure quite similar to the previously described form. The displacement of iron out of the porphyrin plane is 0.27 Å, the axial Fe–N distance is 1.7307(7) Å, and the Fe–N(5)–O(1) angle is 142.74 (8)°. Again the NO ligand is tilted off-axis, and this time the tilt angle is 8.2° and the off-axis translation of the nitrogen atom is 0.25 Å. (Figure 3). In both derivatives, the Fe–N–O plane is perpendicular to the porphyrin plane. Again there is remarkable agreement between chemically equivalent bond distances and angles in the porphyrin core. Moreover, there are two long and two short Fe–N_p distances and, as can be seen in Figure 4, the pattern of long and short Fe–N_p bond distances with respect to the tilted axial ligand is the same as in the first derivative (averages = 1.999(1) and 2.020(4) Å). This second structure further strengthens the idea that an off-axis tilt of a heme nitrosyl ligand has a significant effect on the equatorial Fe–N_p distances. Significantly, intermolecular contacts in the crystalline lattice of this second form appear even less likely to have caused the ligand tilt. Thus the off-axis tilt appears to be an intrinsic feature of nitrosyl hemes. Difficulties with disorder, as noted above, limit the possible information on this point from previously determined five-coordinate structures. However, features of the structure of [Fe(OBTPP)(NO)]⁴ are suggestive of a significant ligand tilt. Both the thermal parameter of nitrogen (larger than

oxygen) and the apparently long N–O bond are consistent with a substantial off-axis tilt of the nitrosyl. This derivative might be expected to have a large tilt owing to the extreme nonplanarity of the core demanded by the sterically crowded octabromotetraphenylporphyrin ligand. There are modest off-axis nitrosyl tilts in the three six-coordinate complexes known^{14,15} and suggestive differences in Fe–N_p bond distances, but the structures, all measured at room temperature, are of inadequate precision to allow further comment. Thus the earlier studies, while not conclusively adding to the case for structural distortion in NO binding, are at least modestly supportive. Finally, it is interesting to speculate that the difference in nitric oxide dissociation rates observed⁴ in different iron porphyrin derivatives is related to these structural distortions.

There has been considerable interest in understanding the binding of diatomic ligands to iron in heme proteins and iron porphyrins. A particular point of interest has been the apparent asymmetric binding of CO in the heme proteins that is described as the “tilting” and/or “bending” of the CO group with respect to the heme plane. This binding mode is regarded as the basis for the significant difference in CO affinity between iron porphyrins and the O₂ binding hemoproteins. Although there remains significant controversy about just how distorted the Fe–C–O linkage is,¹⁶ a variety of mechanisms for explaining this distortion has been offered. The traditional explanation offered has been steric effects in the ligand binding pocket.¹⁷ Recent work with a series of myoglobin mutants¹⁸ has emphasized the importance of electrostatic interactions in the distal pocket. More recently, Jewsbury et al.¹⁹ have emphasized the importance of the proximal histidine residue in controlling the distortion. Ghosh and Bocian²⁰ have suggested that the FeCO tilting/bending potential energy surfaces are coupled and relatively soft. The present nitrosyl work offers evidence that a structural distortion of a strongly bonding axial ligand can be a stable one and the distortion supported only by bonding effects. Studies to further confirm these electronic/structural effects in nitrosyl heme derivatives are in prospect.

Acknowledgment. We thank the National Institutes of Health for support of this research under Grant GM-38401. Funds for the purchase of the FAST area detector diffractometer were provided through NIH Grant RR-06709 to the University of Notre Dame.

Supporting Information Available: Figure S1 showing the non-bonded contact for the nitrogen atom of the nitrosyl and Tables S1–S12 giving complete crystallographic details, atomic coordinates, bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions for both derivatives (21 pages). See any current masthead page for ordering and Internet access instructions.

JA971140K

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(13) X-ray quality crystals of this form were prepared by reductive nitrosylation of [Fe(OEP)Cl] in chloroform followed by liquid diffusion using methanol as the nonsolvent. The complex crystallizes in the triclinic space group *P1*, $a = 10.4204(1)$ Å, $b = 10.5562(7)$ Å, $c = 14.0425(7)$ Å, $\alpha = 79.830(5)^\circ$, $\beta = 89.585(4)^\circ$, $\gamma = 80.264(4)^\circ$, $V = 1498.10(13)$ Å³, $Z = 2$. Data collection, structure solution, and refinement are as before except for the more extensive measurement of data to a scattering angle of 2θ of 89° . Final *R* indices: $R_1 = 0.0412$ ($I > 2\sigma(I)$), $wR_2 = 0.1128$ (all data).⁷ A total of 44 013 reflections were measured; 20 616 unique. Complete details are included in the Supporting Information.