

- 10.12. Found: C, 66.10; H, 9.98. Critical micelle concentration =  $4.3 \pm 0.1 \times 10^{-3}$  M (25 °C, surface tension).  
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**Structural Changes upon Oxygenation of an Iron(II)(porphyrinato)(imidazole) Complex**

Sir:

Structural effects of metal ligation are a central theme of metalloporphyrin stereochemistry.<sup>1</sup> Of particular interest in interpreting structure/function relationships of hemoproteins are precisely determined, five-coordinate, imidazole porphyrinato iron(II) complexes and their dioxygen adducts. We report here the structure of such a five-coordinate complex<sup>2,3</sup> Fe(TpivPP)(2-Melm)·C<sub>2</sub>H<sub>5</sub>OH, I (Figure 1), and its six-coordinate dioxygen adduct<sup>3</sup> Fe(O<sub>2</sub>)(TpivPP)(2-Melm)·C<sub>2</sub>H<sub>5</sub>OH, II, which provide the first direct observation of the structural changes occurring upon oxygenation.<sup>4,5</sup> Studies of I and II, which are models for the low affinity, "T", conformation of hemoglobin,<sup>6</sup> reveal the effects of axial base restraint in the binding of O<sub>2</sub> to metalloporphyrins. In solution, axial base restraint leads to decreased O<sub>2</sub> affinities.<sup>7</sup> We now show the structural effects, which include an increase in the Fe-O bond length (Figure 2).

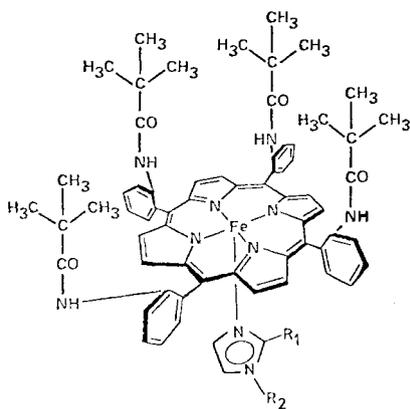


Figure 1. The "picket fence" metalloporphyrin: Fe(TpivPP)(1-Melm). (R<sub>1</sub> = H, R<sub>2</sub> = H); Fe(TpivPP)(2-Melm) (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H).

Several differences in the structures of the five-coordinate, high-spin, porphyrinato iron (II) complex I and the related Fe(TPP)(2-Melm)·EtOH complex<sup>1</sup> are apparent. The Fe-N<sub>Im</sub> separation is considerably shorter (by 0.066 Å) for I than for Fe(TPP)(2-Melm).<sup>1</sup> This is attributable in part to the more nearly eclipsing conformation which the imidazole plane adopts with respect to the Fe-N<sub>p</sub> bonds for the latter complex. In addition, the "doming" of the porphyrinato skeleton is much smaller for I than for Fe(TPP)(2-Melm): 0.03 Å vs. 0.15 Å. There is, instead, considerable buckling of the porphyrinato skeleton to accommodate the 2-Melm ligand: the mean displacement from the 24-atom least-squares porphyrinato plane is 0.056 Å in I.

The structural accommodation of the 2-Melm ligand in the O<sub>2</sub> adduct, II, occurs in several ways. The 2-Melm ligand causes lengthened axial bonds relative to the sterically undemanding 1-Melm ligand; the sum of the Fe-N<sub>Im</sub> and Fe-O separations is 4.005 Å in II, but only 3.813 Å in Fe(O<sub>2</sub>)(TpivPP)(1-Melm).<sup>8</sup> Of this 0.192-Å difference, most (0.150 Å) arises from the lengthening of the Fe-O bond to a value similar to that in unstrained Co-O<sub>2</sub> complexes.<sup>9</sup> This lengthened metal-oxygen distance may be correlated with the decreased O<sub>2</sub> affinities in solution which have been observed in Fe(TpivPP) systems with hindered imidazoles.<sup>7</sup> For II, the compromise between minimum destabilizing nonbonding contacts and maximum bonding results in the iron atom remaining 0.086 Å out of the plane toward the imidazole ligand, in contrast to Fe(O<sub>2</sub>)(TpivPP)(1-Melm)<sup>8</sup> where the Fe atom is displaced a slight 0.030 Å toward the O<sub>2</sub> ligand. The porphyrinato-dioxygen nonbonding contacts are not significantly different between II and Fe(O<sub>2</sub>)(TpivPP)(1-Melm).<sup>10</sup> Further adjustment for the steric hindrance of the 2-Melm group is made by significant buckling of the porphyrinato skeleton: the mean displacement from the least-squares plane is 0.066 Å in II (0.010 Å larger than in I). The O<sub>2</sub> ligand is again<sup>8</sup> found coordinated in the bent, end-on fashion, with fourfold disorder (the occupancy ratio of the two crystallographically independent positions is 0.60:0.40 at room temperature). Lower bounds for the O-O bond lengths and upper bounds for the Fe-O-O bond angles are 1.21 (2) and 1.23 (2) and 129 (1) and 129 (2)°, respectively; these values are uncorrected for the effects of thermal motion and a possible, irresolvable disorder of the coordinated oxygen atom.

Distinct changes in the immediate coordination sphere occur upon oxygenation. There are the expected contractions in Fe-N<sub>p</sub> and Ct-N<sub>p</sub> separations, as well as a general contraction of the porphyrinato core (average change, 0.04 Å), attributable to a high-spin to low-spin transition of the iron atom. The iron atom moves 0.316 Å toward, but not into, the porphyrinato plane, while preserving the Fe-N<sub>Im</sub> separation. Nonbonding porphyrinato-imidazole contacts show decreases of up to 0.27 Å—evidence for strong bonding in low-spin, six-coordinate, iron porphyrinato complexes. The 2-Melm group adjusts for

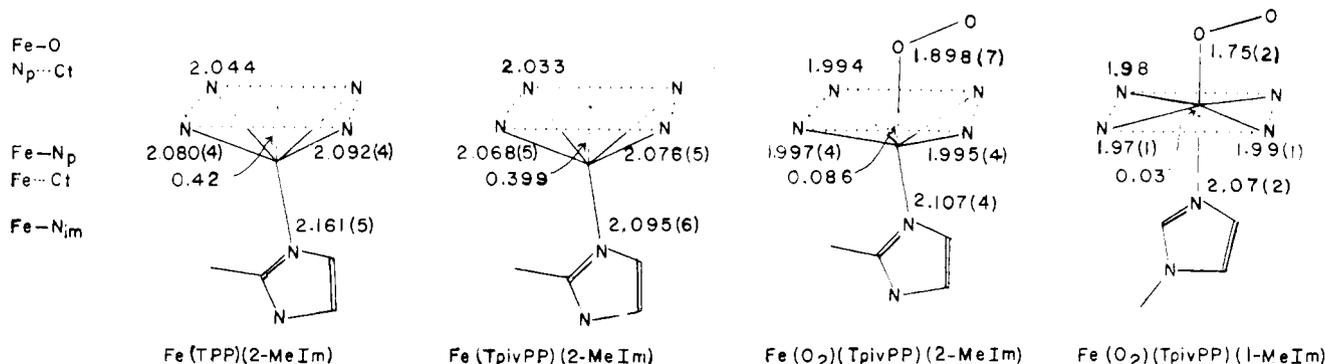


Figure 2. Selected distances (angstroms) in the coordination spheres of Fe(porphyrinato)(imidazole) and Fe(O)(porphyrinato)(imidazole) complexes.

