

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).

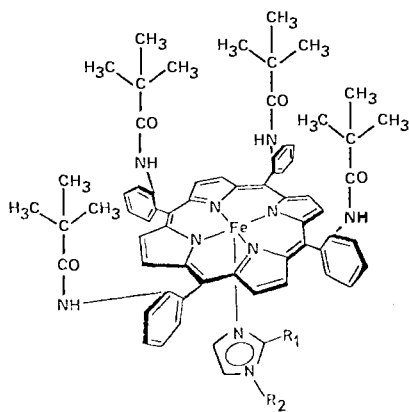


Figure 1. The "picket fence" metalloporphyrin: Fe(TpivPP)(1-Melm), (R<sub>1</sub> = H, R<sub>2</sub> = H); Fe(TpivPP)(2-Melm) (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H).

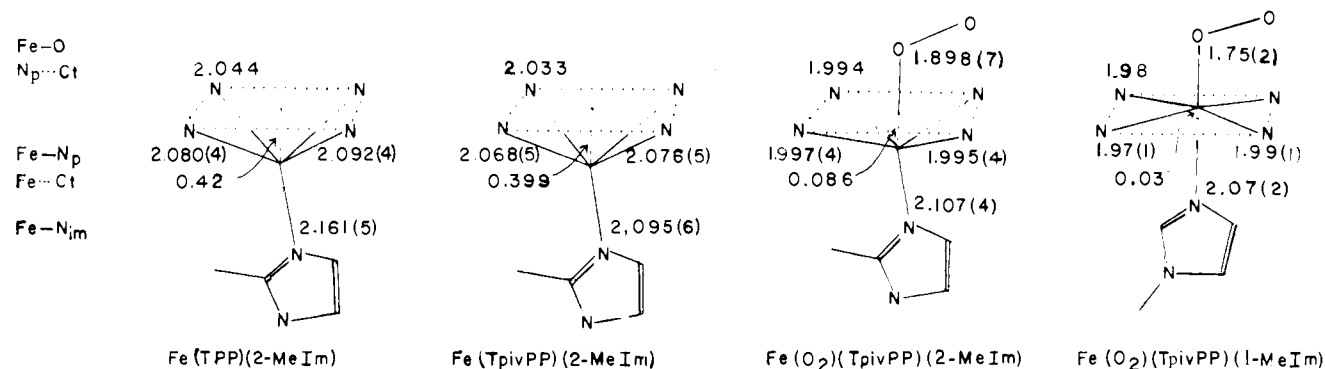


Figure 2. Selected distances (angstroms) in the coordination spheres of Fe(porphyrinato)(imidazole) and Fe(O)(porphyrinato)(imidazole) complexes.

Several differences in the structures of the five-coordinate, high-spin, porphyrinato iron (II) complex I and the related Fe(TPP)(2-MeIm)·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-MeIm).<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-MeIm): 0.03 Å vs. 0.15 Å. There is, instead, considerable buckling of the porphyrinato skeleton to accommodate the 2-MeIm ligand: the mean displacement from the 24-atom least-squares porphyrinato plane is 0.056 Å in I.

The structural accommodation of the 2-MeIm ligand in the O<sub>2</sub> adduct, II, occurs in several ways. The 2-MeIm ligand causes lengthened axial bonds relative to the sterically undemanding 1-MeIm 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-MeIm).<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-MeIm)<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-MeIm).<sup>10</sup> Further adjustment for the steric hindrance of the 2-MeIm 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, irreversible 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-MeIm group adjusts for

this motion by increased tipping: the angles defined by Fe-N<sub>1m</sub>-C<sub>1m2</sub> and by Fe-N<sub>1m</sub>-C<sub>1-5</sub> increase their asymmetry upon oxygenation (in I, 132.1 (8) and 126.3 (7)°, respectively; in II, 135.0 (6) and 123.5 (5)°). The angle made between the Fe-N<sub>1m</sub> vector and the twofold axis normal to the porphyrinato plane decreases from 9.6 to 7.1° upon oxygenation. Small, but complex, changes in the crystal packing also are observed upon oxygenation. In both I and II the solvate ethanol is hydrogen bonded to the N-H part of the 2-MeIm ligand.

Caution must be exercised in making comparisons between these model systems and hemoproteins, particularly with regard to cooperativity in hemoglobin.<sup>6</sup> The "pickets", intermolecular interactions, and, most notably, the hindrance afforded by a 2-MeIm ligand have no exact biological parallel. Nonetheless, the deoxy structure, I, with the sterically demanding 2-MeIm ligand remains a plausible model for the restraint<sup>6</sup> of T state deoxy hemoglobin (the low affinity form). The oxy structure, II, should not be compared with R state oxyhemoglobin (the high affinity form): the 2-MeIm ligand of II can never be unrestrained (as are "relaxed" oxyhemoproteins<sup>6</sup> or Fe(O<sub>2</sub>)(TpivPP)(1-MeIm)<sup>8</sup>). However, complex II may be a simple analogue of T state oxyhemoglobin. The Fe-N<sub>1m</sub> bond length is the same in complexes I, II, and also Fe(O<sub>2</sub>)(TpivPP)(1-MeIm); significantly it is the Fe-O bond length which has lengthened in II, a result of importance in protein stereochemistry. In contrast, the T state NO adduct of hemoglobin has the Fe-N<sub>1m</sub> bond ruptured.<sup>11</sup> This difference between NO and O<sub>2</sub> may reflect their relative binding and trans-labilizing properties.

Recent solid-gas measurements<sup>3,12</sup> on I and its desolvated form show O<sub>2</sub> affinities less than that found for Fe(TpivPP)(1-MeIm), which are consistent with the lengthened Fe-O bond in I and reflect the axial base restraint. Surprisingly the presence of solvate ethanol has a large influence on the solid state O<sub>2</sub> binding of Fe(TpivPP)(2-MeIm); with it, O<sub>2</sub> binds weakly and with no site-site interaction;<sup>12</sup> without it, O<sub>2</sub> binds strongly and with cooperativity.<sup>3</sup> Further structural and ligand binding studies of Fe(TpivPP)(1,2-dimethylimidazole), which has no solvate, may delineate the effects of crystal forces and hydrogen bonding in these systems.

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## References and Notes

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- Abbreviations: TpivPP, *meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrinato; TPP, *meso*-tetraphenylporphyrinato; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole. Following Hoard's notation<sup>1</sup>: N<sub>p</sub>, porphyrinato nitrogen atom; N<sub>im</sub>, coordinated imidazole nitrogen atom; Fe··Ct, displacement of the iron atom from the least-squares plane of the porphyrinate nitrogen atoms; Fe··P<sub>c</sub>, corresponding displacement from the 24-atom porphyrinato plane; Ct··N<sub>p</sub>, radius of the porphyrin "hole". Doring is defined as the difference between Fe··Ct and Fe··P<sub>c</sub>.
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- Compound I crystallizes, as the monoethanol solvate, in space group C<sub>2h</sub><sup>2</sup>-C<sub>2</sub>/c with unit cell parameters a = 18.871 (11), b = 19.425 (13), c = 18.434 (11) Å; β = 91.48 (3)°; V = 6755.0 Å<sup>3</sup>; Z = 4. A total of 4176 unique reflections was collected on a Picker FACS-I automatic diffractometer using graphite-monochromatized Mo Kα radiation. Compound II was obtained by exposure of crystals of I to O<sub>2</sub> saturated with ethanol. The space group is unaltered and unit cell parameters change only slightly (a = 18.864 (5), b = 19.451 (5), c = 18.287 (5) Å; β = 91.45 (2)°; V = 6707.0 Å<sup>3</sup>; Z = 4). Ni-filtered Cu Kα radiation was used to collect 5183 unique reflections. The b axis is normal to the porphyrinato plane. Except for the 2-MeIm ligand and ethanol solvate, which were refined as rigid groups, all nonhydrogen atoms were assigned anisotropic thermal parameters; hydrogen atoms were located and included as fixed contributions to F<sub>o</sub>. The final structural models for I and II assume C<sub>2</sub> molecular symmetry and are described by 373 and 398 variables, respectively; full-matrix least-squares

refinement on all data (including F<sub>o</sub><sup>2</sup> < 0) led to R indices on F<sup>2</sup> of 0.142 and 0.120; conventional R indices on F for data having F<sub>o</sub><sup>2</sup> > 3σ (F<sub>o</sub><sup>2</sup>) are 0.086 and 0.083. The usual solution, refinement, and analysis programs were employed (see, for example, J. M. Waters and J. A. Ibers, *Inorg. Chem.*, **16**, 3273 (1977)).

- Comparison of the structures of the deoxy complex, Fe(TPP)(2-MeIm), with the oxy complex, Fe(TpivPP)(1-MeIm)(O<sub>2</sub>),<sup>8</sup> is necessarily indirect because of the differing axial bases.
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- See, for example, W. T. Robinson and G. A. Rodley, *Nature*, **235**, 438 (1972); G. B. Jameson, W. T. Robinson, and G. A. Rodley, *J. Chem. Soc., Dalton Trans.*, **191** (1978); R. S. Gall and W. P. Schaefer, *Inorg. Chem.*, **15**, 2758 (1976); A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, **98**, 5153 (1976).
- This would tend to dispel the slight reservations expressed<sup>7</sup> about the accuracy of the Fe-O separation for Fe(O<sub>2</sub>)(TpivPP)(1-MeIm).
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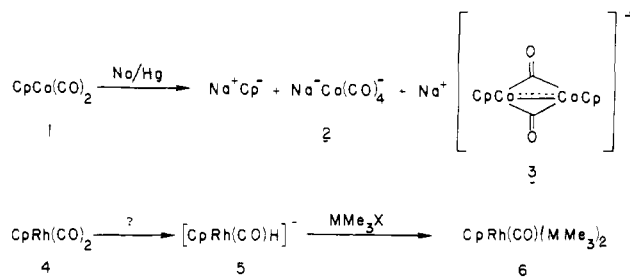
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## Chemical Reduction of η<sup>5</sup>-Cyclopentadienyldicarbonylrhodium. Crystal and Molecular Structure of an Anionic Trinuclear Rhodium Cluster with "Semi-Triple-Bridging" Carbonyl Ligands

Sir:

Reduction of CpCo(CO)<sub>2</sub> (**1**, Cp ≡ η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) with sodium amalgam leads<sup>1</sup> to the formation of sodium tetracarbonylcobaltate (**2**) and the binuclear cobalt radical anion **3**. Reduction



of the rhodium analogue, **4**, takes a different course.<sup>2</sup> In an attempt to understand the differences between these two reactions, we have reexamined the rhodium reduction. We report our results, which include the isolation and X-ray structure determination of an unusual product formed in this process.

Reduction of **4** with sodium amalgam in tetrahydrofuran (THF) was reported<sup>2</sup> to give a solution "with properties characteristic of its containing [η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Rh(CO)H]<sup>-</sup>". This assignment was made on the basis of an IR absorption at 1892 cm<sup>-1</sup> and formation of complexes **6** upon treatment of the reduction solution with MMe<sub>3</sub>X derivatives (M = Ge, Sn). In our hands, treatment of an 0.08 M solution of **4** in THF with 1.5 molar equiv of 0.3% Na/Hg for 3-5 h caused disappear-