

- 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).
 (7) Levene, P. A.; Rothen, A. J. *J. Org. Chem.* **1936**, *1*, 76.
 (8) Mislow, K. *J. Am. Chem. Soc.* **1951**, *73*, 3855.
 (9) MacLeod, R.; Welch, F. J.; Mosher, H. S. *J. Am. Chem. Soc.* **1960**, *82*, 876.

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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.¹ 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^{2,3} Fe(TpivPP)(2-Melm)·C₂H₅OH, I (Figure 1), and its six-coordinate dioxygen adduct³ Fe(O₂)(TpivPP)(2-Melm)·C₂H₅OH, II, which provide the first direct observation of the structural changes occurring upon oxygenation.^{4,5} Studies of I and II, which are models for the low affinity, "T", conformation of hemoglobin,⁶ reveal the effects of axial base restraint in the binding of O₂ to metalloporphyrins. In solution, axial base restraint leads to decreased O₂ affinities.⁷ We now show the structural effects, which include an increase in the Fe–O bond length (Figure 2).

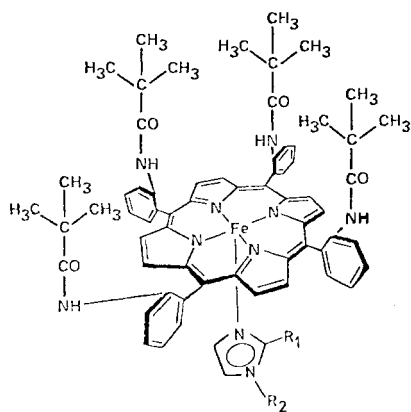


Figure 1. The "picket fence" metalloporphyrin: Fe(TpivPP)(1-Melm). (R₁ = H, R₂ = H); Fe(TpivPP)(2-Melm) (R₁ = CH₃, R₂ = H).

Several differences in the structures of the five-coordinate, high-spin, porphyrinato iron (II) complex I and the related Fe(TPP)(2-Melm)·EtOH complex¹ are apparent. The Fe–N_{Im} separation is considerably shorter (by 0.066 Å) for I than for Fe(TPP)(2-Melm).¹ This is attributable in part to the more nearly eclipsing conformation which the imidazole plane adopts with respect to the Fe–N_p 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 O₂ 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_{Im} and Fe–O separations is 4.005 Å in II, but only 3.813 Å in Fe(O₂)(TpivPP)(1-Melm).⁸ 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–O₂ complexes.⁹ This lengthened metal–oxygen distance may be correlated with the decreased O₂ affinities in solution which have been observed in Fe(TpivPP) systems with hindered imidazoles.⁷ 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(O₂)(TpivPP)(1-Melm)⁸ where the Fe atom is displaced a slight 0.030 Å toward the O₂ ligand. The porphyrinato–dioxygen nonbonding contacts are not significantly different between II and Fe(O₂)(TpivPP)(1-Melm).¹⁰ 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 O₂ ligand is again⁸ 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_p and Ct–N_p 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_{Im} 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

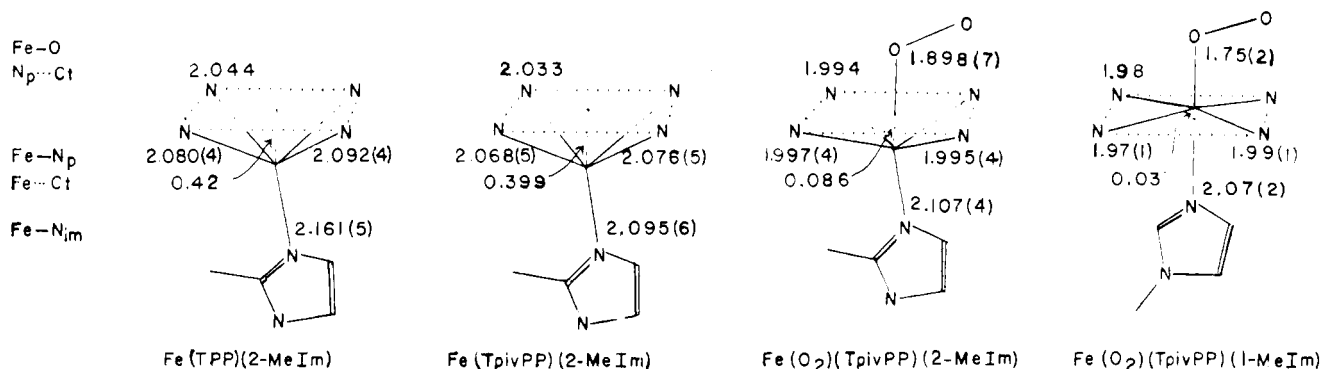


Figure 2. Selected distances (angstroms) in the coordination spheres of Fe(porphyrinato)(imidazole) and Fe(O)(porphyrinato)(imidazole) complexes.

this motion by increased tipping: the angles defined by Fe-N_{1m}-C_{1m2} and by Fe-N_{1m}-C₁₋₅ 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_{1m} 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.⁶ 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 restraint⁶ 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" oxyhemoproteins⁶ or Fe(O₂)(TpivPP)(1-MeIm)⁸). However, complex II may be a simple analogue of T state oxyhemoglobin. The Fe-N_{1m} bond length is the same in complexes I, II, and also Fe(O₂)(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_{1m} bond ruptured.¹¹ This difference between NO and O₂ may reflect their relative binding and trans-labilizing properties.

Recent solid-gas measurements^{3,12} on I and its desolvated form show O₂ 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 O₂ binding of Fe(TpivPP)(2-MeIm): with it, O₂ binds weakly and with no site-site interaction;¹² without it, O₂ binds strongly and with cooperativity.³ 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

- J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, pp 317-380; J. L. Hoard, personal communication.
- Abbreviations: TpivPP, *meso*-tetra(α,α,α,α-o-pivalamidophenyl)porphyrinato; TPP, *meso*-tetraphenylporphinato; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole. Following Hoard's notation¹: N_p, porphyrinato nitrogen atom, N_m, coordinated imidazole nitrogen atom; Fe-Ct, displacement of the iron atom from the least-squares plane of the porphyrinate nitrogen atoms; Fe-P_c, corresponding displacement from the 24-atom porphyrinato plane; Ct-N_p, radius of the porphyrin "hole". Doping is defined as the difference between Fe-Ct and Fe-P_c.
- J. P. Collman, J. I. Brauman, E. Rose, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 1052 (1978).
- Compound I crystallizes, as the monoethanol solvate, in space group C_{2h}⁶-C2/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 Å³; *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 O₂ 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 Å³; *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_c. The final structural models for I and II assume C₂ molecular symmetry and are described by 373 and 396 variables, respectively; full-matrix least-squares

refinement on all data (including $F_o^2 < 0$) led to *R* indices on F^2 of 0.142 and 0.120; conventional *R* indices on *F* for data having $F_o^2 > 3\sigma(F_o^2)$ 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)(O₂),⁶ is necessarily indirect because of the differing axial bases.
- For a recent review, see M. F. Perutz, *Br. Med. Bull.*, **32**, 195 (1976).
- J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 564 (1978); J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, S. E. Hayes, and K. S. Suslick, *J. Am. Chem. Soc.*, **100**, 2761 (1978).
- G. B. Jameson, G. A. Rodley, W. T. Robinson, R. R. Gagne, C. A. Reed, and J. P. Collman, *Inorg. Chem.*, **17**, 850 (1978); J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci., U.S.A.*, **71**, 1326 (1974).
- 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 expressed⁷ about the accuracy of the Fe-O separation for Fe(O₂)(TpivPP)(1-MeIm).
- M. F. Perutz, S. V. Kilmartin, K. Nagai, A. Szabo, and S. R. Simon, *Biochemistry*, **15**, 378 (1976); J. C. Maxwell and W. S. Caughey, *ibid.*, **15**, 388 (1976).
- K. S. Suslick, Ph.D. Thesis, Stanford University, 1978.

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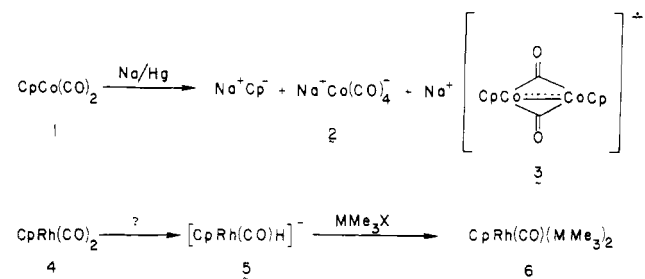
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Chemical Reduction of η⁵-Cyclopentadienyldicarbonylrhodium. Crystal and Molecular Structure of an Anionic Trinuclear Rhodium Cluster with "Semi-Triple-Bridging" Carbonyl Ligands

Sir:

Reduction of CpCo(CO)₂ (**1**, Cp ≡ η⁵-C₅H₅) with sodium amalgam leads¹ to the formation of sodium tetracarbonylcobaltate (**2**) and the binuclear cobalt radical anion **3**. Reduction



of the rhodium analogue, **4**, takes a different course.² 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 reported² to give a solution "with properties characteristic of its containing [η⁵-C₅H₅Rh(CO)H]⁻". This assignment was made on the basis of an IR absorption at 1892 cm⁻¹ and formation of complexes **6** upon treatment of the reduction solution with MMe₃X 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-