be transmitted through this system and would not affect the coupling of ^{13}C-2 to H-5''. The large amount of electron density in the C-2–O-2 bond of **2** is extended in this direction as seen on the difference map. The decrease in the residual electron density of the C-2–N-1 and N-1–C-1' bonds in **2** as compared to that in **1** can account for the anomalously low value for **2** of $^3J_{^{13}C\text{-}2,H\text{-}1'}$ (6.6 Hz for a torsional angle of $-175°$). The residual electron density is decreased in the C-2–N-1 bond but is increased in the N-1–C-6 bond of **2** from that of **1** and the $^3J_{^{13}C\text{-}2,H\text{-}6}$ for **2** of 7.2 Hz for a torsion angle of $-174°$ falls closer to the Karplus curve.

The comparison of the residual electron density between compounds **2** and **1** has been made with only one of the independent molecules in the asymmetric unit of **1**. The reason for this particular comparison is that the second independent molecule of **1** forms a hydrogen bond with N-3 of the uracil ring. The formation of this hydrogen bond distorts the electron density in the ring in the manner shown in Figure 3. In this map the only significant change in the electron density distribution involves atom N-3 of the molecule forming a hydrogen bond. Electron density is withdrawn from the bonds N-3–C-2 and N-3–C-4 and resides in the remaining sp^2 orbital on N-3 and is directed toward the proton of the hydrogen bond donor. This work thus also gives evidence of a shift in electron density, from the bonding orbitals of a nitrogen atom to a nonbonding orbital of this atom, as a result of the formation of a hydrogen bond.

These combined results from X-ray diffraction and nmr studies indicate that anomalous bonding electron density can account for non-Karplus-type behavior relating torsional angles to observed coupling constants and therefore care should be exercised in the interpretation of nmr results in cases where anomalous bonding is concerned.

(11) F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, "World List of Crystallographic Computer Programs," 2nd ed, D. P. Shoemaker, Ed., National Research Council Crystallographic Programs for the IBM/360 System, Bronder-Offset, Rotterdam, Holland, 1966, Appendix, p 52.

L. T. J. Delbaere, M. N. G. James*

Department of Biochemistry, University of Alberta
Edmonton, Alberta, Canada

R. U. Lemieux

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Reversible Oxygen Adduct Formation in Ferrous Complexes Derived from a "Picket Fence" Porphyrin. A Model for Oxymyoglobin

Sir:

The synthetic challenge of preparing oxymyoglobin and oxyhemoglobin models has both fascinated and

frustrated chemists for decades. Many claims of ferrous complexes that reversibly bind molecular oxygen have been made,[1-9] but none have been fully substantiated, some have later proved to be invalid,[10,11] and most have rested on the observation of a single physical parameter, often a change in the visible spectrum, as a criterion of oxygen uptake and reversibility. Low temperature seems to sufficiently retard irreversible oxidation in some systems[8,9,12] to permit the observation of some reversible oxygenation. However, in view of the now well-recognized facile ligand redox reactions of iron complexes,[13] claims of reversible oxygenation which rely solely on the criterion of solution spectral change must be treated with utmost caution. We communicate here the synthesis and full characterization of a crystalline dioxygen[14] complex derived from a specifically designed ferrous porphyrin complex.

Reversible oxygenation of myoglobin and hemoglobin appears to result from a five-coordinate high-spin iron(II) porphyrin immobilized within a hydrophobic pocket.[15] Apparently irreversible oxidation of iron results from either a bimolecular interaction involving two Fe(II) complexes with one O_2 molecule[16] or protonation affording H_2O_2 which subsequently reacts with the Fe(II). Exploiting the concept of biphenyl-type atropisomerism[17] in ortho-substituted meso-tetraphenylporphyrins, we have constructed a "picket fence" porphyrin whose steric bulk on one side creates a nonprotic cavity for the coordination of small ligands while also protecting such ligands from bimolecular reactions.

meso-Tetra(*o*-aminophenyl)porphyrin (H_2TamPP)[18a,b] was prepared by $SnCl_2$ reduction of *meso*-tetra(*o*-nitrophenyl)porphyrin and separated (silica gel chromatography) into its four atropisomers.[19] The slowest

(1) A. H. Corwin and Z. Reyes, *J. Amer. Chem. Soc.*, **78**, 2437 (1956).
(2) J. H. Wang, *ibid.*, **80**, 3168 (1958).
(3) J. F. Drake and R. J. P. Williams, *Nature (London)*, **182**, 1084 (1958).
(4) W. R. McClellan and R. E. Benson, *J. Amer. Chem. Soc.*, **88**, 5165 (1966).
(5) J. O. Alben, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *Biochemistry*, **7**, 624 (1968).
(6) D. Vonderschmitt, K. Bernauer, and S. Fallab, *Helv. Chim. Acta*, **48**, 951 (1965).
(7) L. Marchant, M. Sharrock, B. M. Hoffman, and E. Munck, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2396 (1972).
(8) J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, **95**, 5757 (1973).
(9) L. K. Chang and T. G. Traylor, et al., *ibid.*, **95**, 5810 (1973).
(10) M. J. Cowan, J. M. F. Drake, and R. J. P. Williams, *Discuss. Faraday Soc.*, **27**, 217 (1959); Ph.D. Thesis of R. C. Davies, Wadham College, Oxford, 1963.
(11) D. R. Eaton, W. R. McClellan, and J. F. Weiher, *Inorg. Chem.*, **7**, 2040 (1968).
(12) J. Sibert, personal communication.
(13) Piperidine spontaneously reduces FeCl(TPP) to the ferrous state: L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967). For other facile ligand oxidations see also V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
(14) Coordinated molecular oxygen is referred to as the dioxygen ligand.
(15) (a) J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973); (b) C. L. Nobbs, H. C. Watson, and J. C. Kendrew, *Nature (London)*, **209**, 339 (1966); (c) M. F. Perutz, H. Muirhead, J. M. Cox, and L. C. G. Goaman, *ibid.*, **219**, 139 (1968); (d) J. L. Hoard, *Science*, **174**, 1295 (1971).
(16) G. S. Hammond and C. S. Wu, *Advan. Chem. Ser.*, No. 77, 186 (1968).
(17) L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.*, 3071 (1969).
(18) (a) Characterized by complete elemental analysis. (b) Characterized by its pmr spectrum. (c) Analysis by the method of E. W. Lard and R. C. Horn, *Anal. Chem.*, **32**, 878 (1960).
(19) Interconversion of the atropisomers of H_2TamPP is sufficiently slow at room temperature to allow a clean separation of the $\alpha,\alpha,\alpha,\alpha$-

moving isomer, $\alpha,\alpha,\alpha,\alpha$-H$_2$TamPP (**1**), was isolated in 12% yield (statistical abundance) and its configuration frozen by formation of the amide, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidephenyl)porphyrin[18a,b] ($\alpha,\alpha,\alpha,\alpha$-H$_2$TpivPP), **2** (eq 1). Treatment with FeBr$_2$ (THF, 7 hr at reflux)

$\alpha,\alpha,\alpha,\alpha$-H$_2$TamPP

1

(1)

$\alpha,\alpha,\alpha,\alpha$-H$_2$TpivPP

2
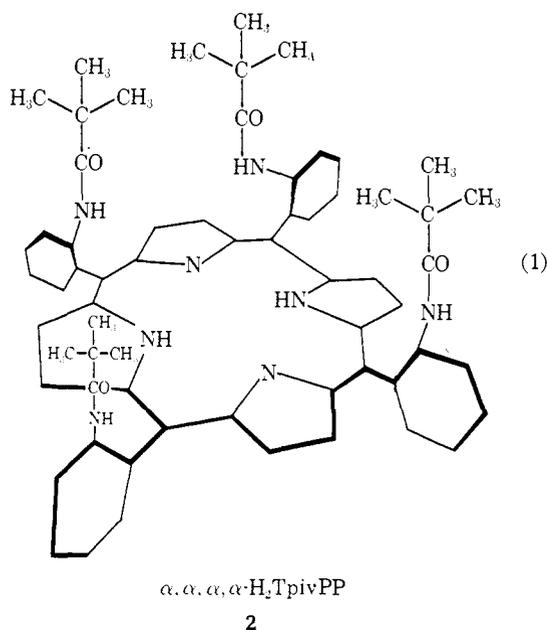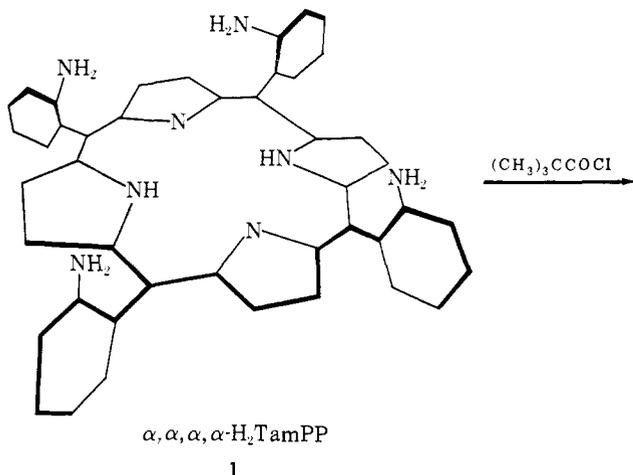
followed by recrystallization (HBr–CH$_2$Cl$_2$–CH$_3$OH–heptane) afforded purple crystals of FeBr($\alpha,\alpha,\alpha,\alpha$-TpivPP), **3**[17a] (80%, λ_{max} 510 nm, C$_6$H$_6$). Reduction of the Fe(III) complex, **3** ([Cr(acac)$_2$]$_2$),[15a] yielded purple-black crystals of the Fe(II) complex, Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP),[18a] **4** ($\lambda_{max}$ 540 nm, μ = 5.0 BM at 25°). Strong field ligands react with **4** affording crystalline, diamagnetic complexes (**5**), FeL$_2$($\alpha,\alpha,\alpha,\alpha$-TpivPP), L = 4-*tert*-butylimidazole,[18a] piperidine,[18a] and 1-methylimidazole[18a] (1-Me(imid)). Only with the bulkier sulfonamide picket fence complex, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl)porphyrin ($\alpha,\alpha,\alpha,\alpha$-H$_2$TtosPP), does five coordination prevail. For example, we have prepared the high-spin complex Fe-

atropisomer. Heating a toluene solution of the remaining unwanted atropisomers to reflux for 20 min effects equilibration to the statistical mixture of atropisomers allowing the system to be "milked" for an overall high yield of the $\alpha,\alpha,\alpha,\alpha$-atropisomer. Once pivalamide formation has been achieved the barrier to phenyl ring rotation is sufficiently high that only after 16 hr of heating under reflux in THF could any interconversion be detected. Complete equilibration to the statistical mixture of H$_2$TpivPP requires several hours in boiling xylene.

(4-*t*-Bu(imid)($\alpha,\alpha,\alpha,\alpha$-TtosPP) [$\mu$ = 4.88 BM at 25°], a better model for deoxymyoglobin,[15] but find that treatment of this complex with oxygen results in immediate irreversible oxidation. We believe that the acidic sulfonamide protons located adjacent to the vacant coordination site may be responsible for the protonation of coordinated dioxygen giving rise to a hydroperoxide and providing a ready pathway to oxidation. However, this problem is apparently overcome with the less acidic pivalamide. Also, despite the isolation of six-coordinate complexes with Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP) we suspect that the binding constant of an imidazole on the "picket fence" side of the porphyrin is less than that on the "open" side, thus promoting five coordination (Scheme I).

Scheme I. Probable Equilibria Involved in the Oxygenation and Deoxygenation of Fe(1-Me(imid))$_2$($\alpha,\alpha,\alpha,\alpha$-TpivPP)
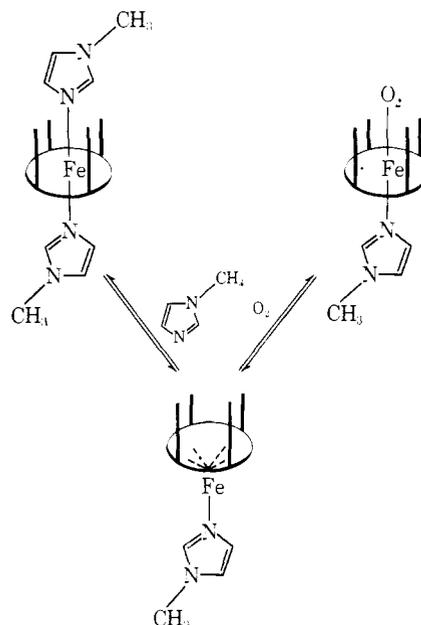
A benzene solution of **5** (L = 1-Me(imid)) prepared under nitrogen in the presence of a small excess of the axial base was exposed to oxygen (1 atm) at room temperature. Dropwise heptane addition actuated crystallization of a new complex, **6**, quite different from **5** which could be reisolated from an identical solution not exposed to oxygen. We formulate these purple-red crystals of **6** as the dioxygen complex Fe(O$_2$)-(1-Me(imid))($\alpha,\alpha,\alpha,\alpha$-TpivPP)0.75C$_6H_6$[18a] (benzene solvate confirmed by glc). Recrystallization of **6** from benzene containing excess 1-Me(imid) under nitrogen returned a quantitative yield of **5**, indicating complete reversibility.

Rapid gas evolution is observed when **6** is dissolved in pyridine, and a series of manometric experiments revealed 0.97 ($\pm$0.05) mol of gas is liberated per mole of complex (definitive analysis of O$_2$ by glc[18c]). Manometric oxygen uptake by 10^{-2} M benzene solutions of **5** at room temperature with an oxygen pressure of 1 atm indicate approximately 70% adduct formation, a figure clearly related to the equilibria depicted in Scheme I. The reversibility of oxygen uptake was conveniently followed by visible spectral changes of approximately 10^{-4} M benzene solutions (Figure 1), at 25°. Notably, when a small excess of 1-Me(imid) is present (to inhibit oxygen coordination to the "open"
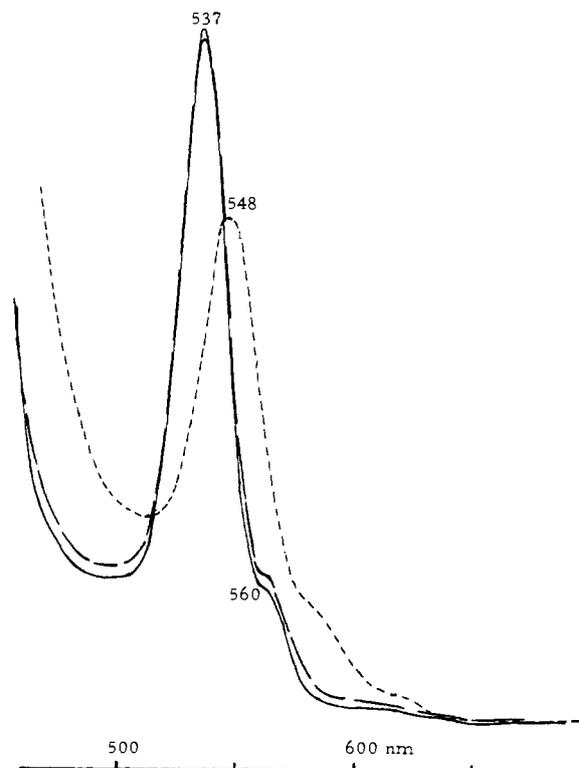
Figure 1. Visible spectrum of 3×10^{-5} M Fe(1-Me(imid))₂-(α,α,α,α-TpivPP) with 10^{-4} M 1-Me(imid) in benzene: (———) under nitrogen, (..........) under oxygen (1 atm), (— — —) under nitrogen after two oxygenation–deoxygenation cycles.

side of the porphyrin) several cycles of oxygenation and deoxygenation can be achieved before any irreversible oxidation can be detected. In solutions of **5** without any excess ligand present gradual oxidation ensues. However, despite the gradual superposition of the spectrum of the oxidized product, [Fe(α,α,α,α-Tpiv-PP)]₂O,[18a] several cycles of reversible oxygenation can be demonstrated. Total irreversible oxidation requires >12 hr at 25°! Similar spectral observations indicating reversible oxygen uptake have been made with a variety of axial bases L (L = imidazole, N-trityl-imidazole, 4-*tert*-butylimidazole) but in none of these cases has a solid oxygen adduct been isolated. We believe this is simply related to solubility; the least soluble six-coordinate species is always preferentially precipitated.

As expected for a six-coordinate ferrous complex and as is found in oxyhemoglobin,[20] **6** is diamagnetic. Its Mössbauer spectrum like that of oxyhemoglobin[21] indicates a strong temperature dependence in its quadrupole splitting (for **6** at 194°K, δ = 0.24 mm/sec, ΔE_Q = 1.4 mm/sec; at 77°K, δ = 0.26 mm/sec, ΔE_Q = 1.8 mm/sec; δ values relative to iron metal). We have unsuccessfully searched the ir and Raman spectra of **6** for an absorption ascribable to coordinated oxygen, despite comparison with a sample prepared with ¹⁸O₂ (90% enrichment). This was unexpected in view of the strong ir absorptions observed for both angular-bound (σ) oxygen in Co(II) complexes[22] and

(20) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci. U. S.*, **22**, 210 (1936).
(21) G. Lang and W. Marshall, *Proc. Phys. Soc., London*, **87**, 3 (1966).
(22) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970).

sideways-bound (π) oxygen in d⁸ complexes.[23] The ir absorption may, however, be weak and totally obscured by an abundance of strong porphyrin bands in the 900–1500 cm⁻¹ region. A total X-ray crystallographic analysis is in progress which should shed light on the controversy[24] regarding the geometry of iron-bound dioxygen.

(23) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973); V. J. Choy and C. J. O'Conner, *Coord. Chem. Rev.*, **9**, 145 (1972/1973).
(24) L. Pauling, *Nature (London)*, **203**, 182 (1964).

James P. Collman,* Robert R. Gagne, Thomas R. Halbert Jean-Claude Marchon, Christopher A. Reed
Department of Chemistry, Stanford University
Stanford, California 94305
Received August 30, 1973

The Aluminotitanium Hydrides [(C₅H₅)Ti]₂(H)(H₂AlEt₂)(C₁₀H₈) and [(C₅H₄)TiHAlEt₂]₂(C₁₀H₈)

Sir:

Recently, we characterized a triethylaluminum derivative of (C₅H₅)₂TiX₂ (X = Ph, Cl, Cl/2) as [(C₅H₅)-(C₅H₄)TiHAlEt₂]₂ (**1**), with titanium atoms bridged by (h^1:h^5-C₅H₄) ligands.[1,2] Wailes and Weigold described a triethylaluminum derivative of [(C₅H₅)(C₅H₄)-TiH]₂ ("titanocene" [3–5]), (C₁₀H₉TiAlEt₂)₂, of uncertain structure.[6] We now report a new triethylaluminum derivative of "titanocene," [(C₅H₅)Ti]₂(H)(H₂AlEt₂)-(C₁₀H₈) (**2**), its structure, and the structure of the Wailes and Weigold compound, [(C₅H₄)TiHAlEt₂]₂(C₁₀H₈) (**3**). We find the titanium atoms in **2** (Figure 1) bridged by C₁₀H₈ (h^5-C₅H₄–h^5-C₅H₄), H, and H₂AlEt₂ ligands, a structure strikingly different from that of **1**. In contrast, the titanium atoms in **3** (Figure 2) are bridged by both (h^1:h^5-C₅H₄) and C₁₀H₈ (h^5-C₅H₄–h^5-C₅H₄) ligands, a structure combining the characteristics of **1** and **2**. Our identification of C₁₀H₈ in **2** provides the first confirmation of a transition-metal-assisted synthesis of the fulvalenide ligand, although such a ligand was incorporated in one of the Brintzinger and Bercaw structure proposals for "titanocene." [4]

Compounds **2** and **3** are obtained by the following reactions. Reaction **3** was reported by Wailes and

(1) F. N. Tebbe and L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 227 (1973).
(2) Compound **1** was previously assigned the formula [(C₅H₅)₂Ti-AlEt₂]₂, based on heavy-atom X-ray data: P. Corradini and A. Sirigu, *Inorg. Chem.*, **6**, 601 (1967).
(3) "Titanocene" is a biscyclopentadienyltitanium complex of uncertain structure. It was formulated as [(C₅H₅)(C₅H₄)TiH]₂ by Brintzinger and Bercaw.[4] We prepared "titanocene" after the method of Watt, *et al.*,[5] and purified it by crystallization from hot toluene. The ir of the green solid matched that reported by Brintzinger and Bercaw.[4] Crystals were not suitable for X-ray studies.
(4) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).
(5) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *ibid.*, **88**, 1138 (1966).
(6) P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, **24**, 713 (1970).