# D021 HYDROGEN-BONDING TO M-$O_2$ AND M=O IN PORPHYRIN MODELS EQUIPPED WITH AN INTRAMOLECULAR CARBOXYL GROUP.

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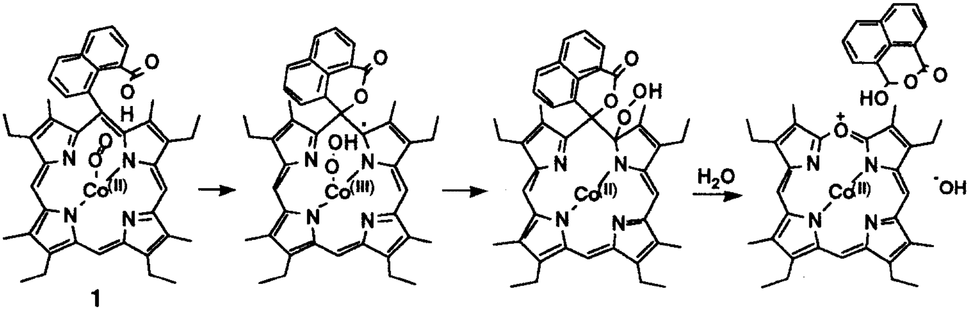
Reduction and activation of dioxygen in hemoproteins generally involve proton transfers during O-O bond cleavage in the catalytic cycle. Porphyrin models equipped with intramolecular proton donors are useful in probing the reactivity of dioxyheme as well as other heme-substrate complexes. Previously, Co(II)porphyrin naphthoic acid **1** was shown to have a very high $O_2$ affinity constant [1], but the close proximity of -COOH to the porphyrin methine carbon facilitates an unusual ring degradation yielding an oxaporphyrin.



**1**

To prevent this verdoheme-like formation, a porphyrin Kemp acid has been synthesized in which a carboxyl group overhangs above the heme binding site and imposes its proton on any mono- or diatomic heme substrates. The free base porphyrin proves to be an excellent ditopic ligand for water (FIG 1); NMR measurements in $CDCl_3$ gave $K = 67.5\ M^{-1}$. The crystal structure of Zn(II)-MeOH complex reveals the interaction between the methanolic proton and the carboxyl group (FIG. 2). The Co(II) complex exhibits a $O_2$ affinity as high as **1** ($P_{1/2}$ = 0.03 torr in DMF at -45°C). Significantly, it is stable in $CH_2Cl_2$ and electrochemically mediates the 4-electron reduction of $O_2$ when coated on graphite electrodes. Using the porphyrin Kemp acid, H-bonding effects on ferryl and metal-oxo species as probed by IR and resonance Raman spectroscopy provide a benchmark of the frequency shift expected. For example, vanadyl VO has a vibrational frequency of 978 $cm^{-1}$ in the presence of H-bonding versus 992 $cm^{-1}$ without it. The characterization of H-bonded Fe=O is important for understanding the reaction intermediates in the catalytic cycle of cytochrome *c* oxidase.

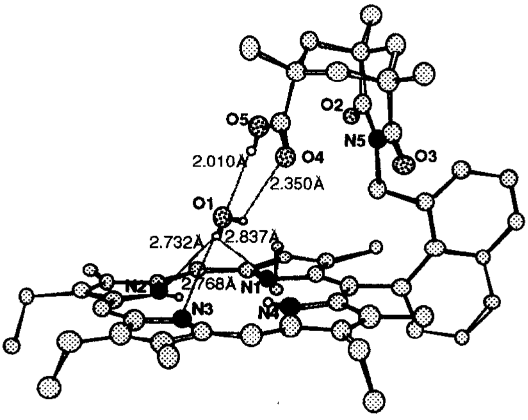


**FIGURE 1. Crystal structure of free base porphyrin.**

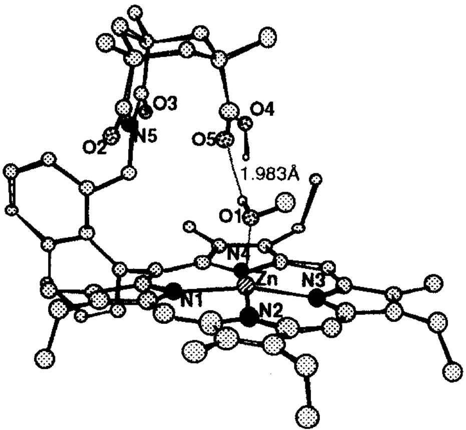


**FIGURE 2. Crystal structure of Zn-MeOH complex.**

1. C. K. Chang and H. Kondylis, *J. Chem. Soc. Chem. Commun.*, 316 (1986).