

work of GORENSTEIN [6-8] who has shown that the ^{31}P -chemical shift of phosphate compounds is controlled by O-P-O bond angles. Thus, in base-on CH_3Cbl or $\text{CF}_3\text{CH}_2\text{Cbl}$ (Table) the conformation of the phosphodiester is apparently the same as that of all the base-off species and there is no difference in chemical shift between the base-on and base-off species. When coordination of the axial ligand is weaker (e.g., AdoCbl), lengthening of the axial Co-N bond causes a decrease in the RO-P-OR' bond angle and an upfield shift of the base-on ^{31}P -resonance. When the axial ligand coordination is tighter (e.g., CNCbl) the shortened axial Co-N bond causes an increase in the RO-P-OR' bond angle and a downfield shift in the base-on ^{31}P -resonance.

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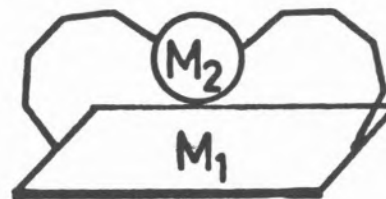
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SYNTHETIC PORPHYRINS CONTAINING ADJACENT, REDOX-ACTIVE SPECIES; MODELS OF BIOLOGICAL ELECTRON TRANSFER SITES

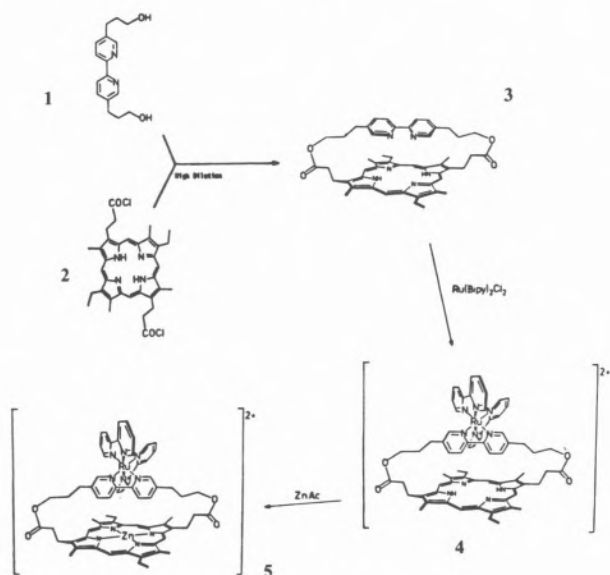
The remarkable diversity of function of hemes and chlorophylls in biochemistry is due, in large part, to changes in the surrounding protein environment. In systems which are involved in electron transport the nearby protein environment often includes other metal centers held in close proximity to the tetrapyrrole.

In an attempt to mimic some of the electron transport and photochemical charge separation properties of these centers we have prepared a series of model systems in which transition metals are covalently held a short distance from a metalloporphyrin.



The first binucleating ligand involves a 2,2'-bipyridine unit strapped across the face of a porphyrin. 5,5'-bis(3-hydroxypropyl)-2,2'-bipyridine (**1**) is prepared in six steps from β -picoline. Reaction of **1** with mesoporphyrin-II diacid chloride under high dilution conditions yields the bipyridine-bridged porphyrin **3** in good yield. Heterobinuclear complexes of **3** can be readily formed in a two step sequence. Refluxing **3** with $\text{Ru}(\text{bipy})_2\text{Cl}_2$ in

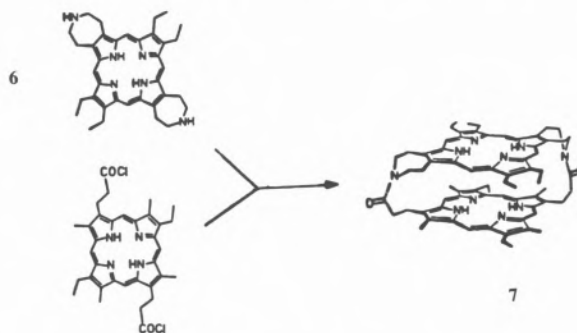
methanol gives the $\text{Ru}(\text{bipy})_3$ -porphyrin complex **4** with no insertion of ruthenium into the porphyrin. Treating **4** with zinc acetate affords heterobinuclear $\text{Ru}(\text{bipy})_3$ -zinc porphyrin (**5**).



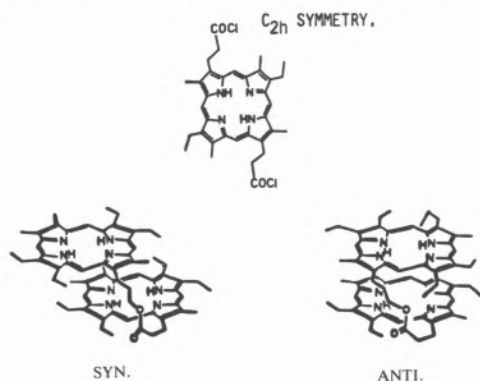
Electrochemical studies (cyclic voltammetry and differential pulse polarography) indicate that both metal centers are redox active. In addition, spectroscopic measurements indicate a strong interaction between the two chromophores. While the porphyrin luminescence is unperturbed, the emission from the lowest lying metal to ligand charge transfer band is quenched. The synthesis, physical properties and biological relevance of these novel binuclear complexes will be presented. Also the extension of this work to other transition metal complexes and to tri-, tetra- and polynuclear homologues will be discussed.

The second binucleating ligand relates to the multi-chlorophyll structures of photosynthetic reac-

tion centers and involves two or more covalently linked tetrapyrroles. In order to overcome the problems of diastereoisomerism that result when porphyrins of C_{2h} symmetry are cofacially linked (e.g. Fig. 2) we have synthesized diaminoporphyrin (**6**). This species has D_{2h} symmetry and when coupled to mesoporphyrin-II diacid chloride (**2**) provides a diastereomerically pure cofacial porphyrin dimer (**7**). The NMR spectrum of **7** shows the porphyrin NH proton signals at -8 ppm, equivalent to an inter-porphyrin distance of 4.5 \AA . The optical spectrum exhibits a blue-shif-



ted Soret peak (by 16 nm) characteristic of strong exciton coupling between the macrocycles. Various transition metal complexes of **7** have been prepared. They will be discussed in addition to the synthesis and properties of dimer **7**. The synthesis of cofacial porphyrin trimers using this strategy is under active investigation.





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METAL ION — AND VITAMIN B₆ — CATALYZED TRANSAMINATION AND DEPHOSPHONYLATION OF 2-AMINO-3-PHOSPHONOPROPIONIC ACID

Kinetic studies have been carried out for reactions of Schiff bases (SB) formed from pyridoxal 5'-phosphate (PLP) and 2-amino-3-phosphonopropionic acid (APP): 1:1:x Zn(II)-SB-PDA system where PDA is 2,6-pyridinedicarboxylic acid; 1:2 Ga(III)-SB system; and 1:2 Al(III)-SB system). Formation and disappearance of a ketimine intermediate and its complexes were followed by proton NMR and ³¹P NMR. The reaction occurs in two distinct sequential steps: transamination and dephosphorylation. The specific rate constants for individual species of the metal-free systems are: $k_{H_4SB} = 1.64 \times 10^{-4} \text{ s}^{-1}$, $k_{H_3SB} = 7.56 \times 10^{-5} \text{ s}^{-1}$, and $k_{H_2SB} = 2.34 \times 10^{-5} \text{ s}^{-1}$ for the transamination step. The values for k_{HSB} and k_{SB} are about zero. The corresponding dephosphorylation rate constants $k'_{H_4SB} = 4.27 \times 10^{-6} \text{ s}^{-1}$, $k'_{H_3SB} = 1.26 \times 10^{-6} \text{ s}^{-1}$ and $k'_{H_2SB} = 6.84 \times 10^{-7} \text{ s}^{-1}$ were determined for the dephosphorylation step. The values for k'_{HSB} and k'_{SB} are about zero. Transamination and dephosphorylation proceed more rapidly for the Ga(III) complexes than for those of Al(III) and Zn(II). The specific rate constants in the transamination step for the individual species of 1:2 Ga(III)-SB system are: $k_{Ga(H_3SB)_2} = 4.66 \times 10^{-4} \text{ s}^{-1}$, $k_{GaH_5(SB)_2} = 3.51 \times 10^{-4}$

s^{-1} ; $k_{Ga(H_2SB)_2} = 3.13 \times 10^{-4} \text{ s}^{-1}$ and $k_{Ga(SB)_2} = 3.12 \times 10^{-5} \text{ s}^{-1}$. The specific rate constants for the dephosphorylation step are: $k'_{GaH_5(SB)_2} = 5.2 \times 10^{-6} \text{ s}^{-1}$; $k'_{Ga(H_2SB)_2} = 5.20 \times 10^{-6} \text{ s}^{-1}$; $k'_{GaH_3(SB)_2} = 5.17 \times 10^{-6} \text{ s}^{-1}$; $k'_{Ga(HSB)_2} = 5.09 \times 10^{-6} \text{ s}^{-1}$; $k'_{GaH(SB)_2} = 2.53 \times 10^{-6} \text{ s}^{-1}$ and $k'_{Ga(SB)_2} = 4.92 \times 10^{-7} \text{ s}^{-1}$. The results show that the most active species are those in which the carboxylate group of the amino acid moiety of the SB ligand is coordinated to the metal ion and the phosphonate is not coordinated.

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