

Transition Metal Bis(porphyrin) Complexes

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Metal bis(porphyrin) complexes $M(\text{porph})_2$ ($M = \text{Ce}, \text{U}, \text{and Th}$) have received much attention in recent years [1,2] due to their electronic and structural similarities to the Special Pair (SP) in photosynthetic bacteria [3]. The π - π interactions present in these sandwich complexes result in electronic properties very different from analogous mono(porphyrin) complexes. For example, these complexes are much easier to oxidize than monomeric analogs. In addition, when oxidized, they show an absorption in the near-IR not seen in mono(porphyrin) cations, but analogous to that observed in SP^+ . The energies of these features depend on the porphyrin-porphyrin separation, and thus can be varied to a certain extent by choice of metal. The work presented here will cover the chemistry of *transition metal* bis(porphyrin) complexes and modulation of their electronic properties. In addition, work will be presented on a series of uranium porphyrins with interesting electronic properties.

We have prepared bis(porphyrin) complexes of zirconium and hafnium by the reaction of the appropriate metal amide with the free-base porphyrin. These complexes have the shortest interplanar separations of any bis(porphyrin) complex to date. The first oxidation potential of $\text{Zr}(\text{OEP})_2$ is -37 mV vs. Ag/AgCl ; this is nearly 1 V easier to oxidize than $\text{Zr}(\text{OEP})(\text{OAc})_2$ [4]. A molecular orbital diagram is shown in Figure 1 which takes into account the overlap of subunit orbitals, and therefore readily explains the cathodic shift of the oxidation potentials vs. mono(porphyrin) complexes since the HOMO is now antibonding. The appearance of a near-IR absorption in the bis(porphyrin) cations and its blue-shift with decreasing interplanar separation is also rationalized by this diagram [5,6].

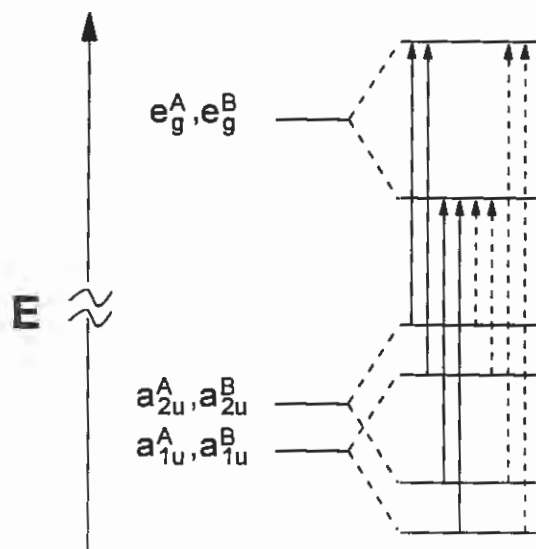


Figure 1

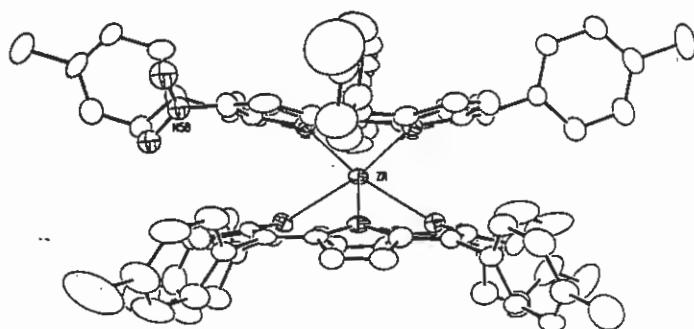


Figure 2

In order to gain some insight into the electronic structures of the bis(porphyrin) complexes, both electron-donating and -withdrawing groups have been substituted at the porphyrin β -pyrrole sites. The crystal structure of $\text{Zr}(\text{TTP})(2\text{-nitro-TTP})$ is shown in Figure 2. The nitro group does not greatly change the structure of the molecule relative to the parent complex; the separation between mean porphyrin planes is 3.24 Å.

Substitution does alter the redox potentials of the compounds. $\text{Zr}(\text{TTP})(2\text{-nitro-TTP})$ is 130 mV harder to oxidize than $\text{Zr}(\text{TTP})_2$ and 340 mV easier to reduce. In contrast, the amino derivative $\text{Zr}(\text{TTP})(2\text{-amino-TTP})$ is 110 mV easier to oxidize than $\text{Zr}(\text{TTP})$ and only 24 mV harder to reduce. The different effect of nitro and amino substituents on the reduction potentials can be accounted for in terms of π -resonance and inductive effects. Chloro-substituted sandwich complexes display a linear relationship between the number of chlorine atoms and the oxidation potentials.

The strong π - π interactions present in the sandwich complexes give rise to new visible bands which have been proposed to involve excited states with charge-resonance character ($\text{A}^+\text{B}^- + \text{A}^-\text{B}^+$, where A and B are the two porphyrin rings) [6]. These bands red-shift upon attaching either electron-donating or -withdrawing groups on the porphyrin periphery. The shift observed upon substitution supports the assignment of the Q' state as having CR character. If the substituted porphyrin is labelled A, the nitro group will stabilize the A^-B^+ microstate and the amino group will stabilize the A^+B^- microstate. In either case, a red-shift is predicted.

Uranium mono(porphyrin) complexes have also been investigated. Very little is known about the chemistry of uranium porphyrins; the only complexes known contain tetravalent uranium and electronically 'innocent' axial ligands such as chloride or alkoxides [7]. We have succeeded in synthesizing complexes such as $(\text{TTP})\text{U}(\text{diox})_2$, where diox is a member of the catechol \leftrightarrow semiquinone \leftrightarrow quinone redox series. The crystal structure of $(\text{TTP})\text{U}(\text{Cl}_4\text{-diox})_2$ is shown in Figure 3. The diox C-O bond lengths, diagnostic of the redox states of the ligands, suggest that one dioxolene ligand is bound as a catecholate and one as a semiquinone. Spectroscopic evidence supports this formulation. This makes the uranium pentavalent, the first example of U^{V} in porphyrin chemistry. In addition, uranium porphyrin peroxo complexes have been synthesized by the action of O_2 on $(\text{TTP})\text{U}^{\text{IV}}(\text{Cl}_4\text{-cat})$. The IR spectrum of $(\text{TTP})\text{U}(\text{Cl}_4\text{-cat})(\text{O}_2)$ shows absorptions at 908 and 679 cm^{-1} , typical of peroxo compounds [8]. Interestingly, this complex decomposes to $(\text{TPP})\text{U}^{\text{V}}(\text{Cl}_4\text{-cat})(\text{Cl}_4\text{-sq})$ in solution. A probable pathway is shown in Figure 4.

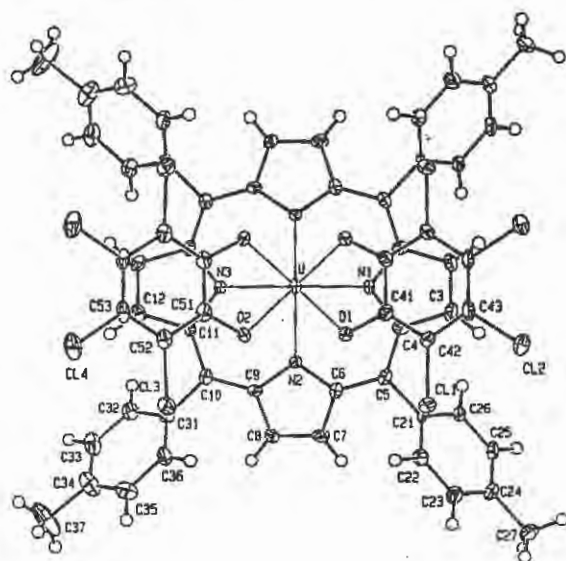


Figure 3

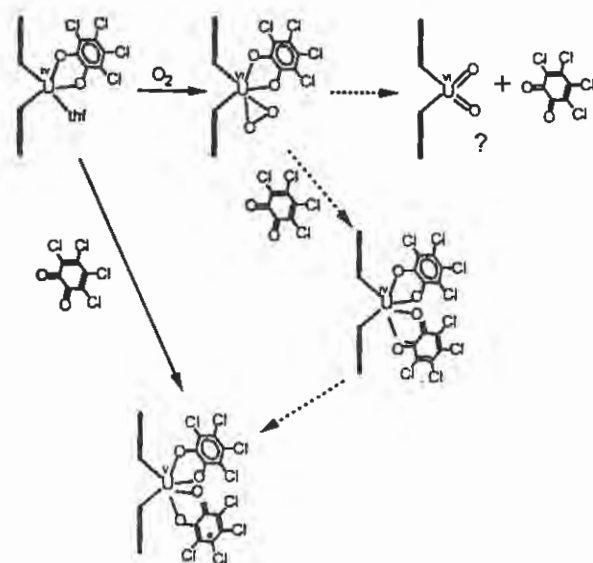


Figure 4

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