

The Chemistry of Actinide Mono- and Bis-Porphyrin Complexes

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Transition metal porphyrin complexes have been studied extensively for several decades. In contrast, actinide porphyrin complexes have been only sparsely investigated. In 1975, Wong and Horrocks [1] reported that treatment of thorium tetra(acetylacetonate) with tetraphenylporphyrin (H_2TPP) gave $(TPP)Th(acac)_2$. Nine years later Guillard reported that treatment of MCl_4 ($M = Th, U$) with octaethylporphyrin (H_2OEP) yielded $(OEP)MCl_2L_2$ ($M = Th, U$) [2]. No other reports of actinide porphyrin complexes appeared before our work began in 1986.

We have prepared two types of actinide porphyrin complexes. The first type possess two porphyrin ligands per actinide metal center. The "sandwich" complex bis(5,10,15-20-tetraphenylporphyrinato)uranium(IV) may be prepared under nonacidic conditions by refluxing a solution of tetrakis(diethylamido)uranium(IV), $U(NEt_2)_4$, and 2 equiv of H_2TPP in toluene, followed by chromatography and crystallization from chloroform/pentane to give dark purple microcrystals [3]. The thorium analog may be prepared similarly from $Th(NEt_2)_4$. The $(TPP)_2M$ complexes exhibit an unusually blue shifted Soret band at 404 nm and 402 nm for $M = U$ and Th , respectively. $(TPP)_2Th$ has been crystallographically characterized. Two views of this complex are illustrated in Figure 1. The complex is a distorted antiprism and the $Th-N$ bond distance is 2.55Å; the thorium center is displaced 1.47Å from the porphyrin core. The $Th-N$ distance and $Th-N_{11}$ displacement are comparable to those observed for $(OEP)Th(acac)_2$ where $Th-N = 2.50Å$ and $Th-N_{11} = 1.43Å$ [4].

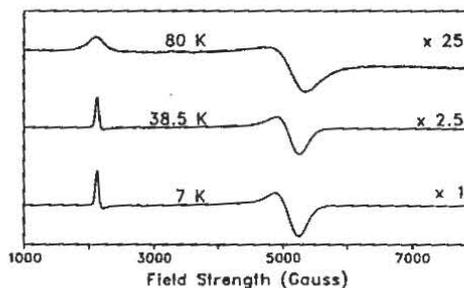
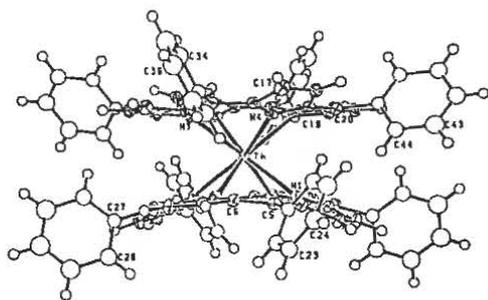
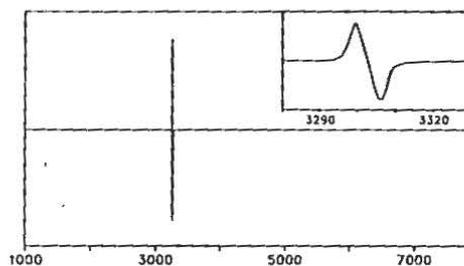
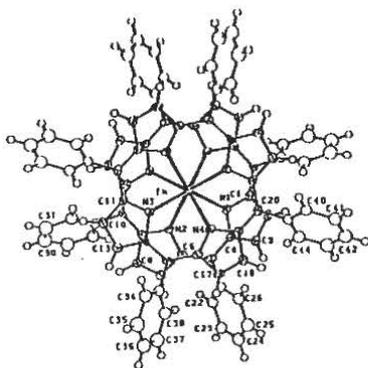
Cyclic voltammetry experiments in $CHCl_3$ reveal that both $(TPP)_2M$ compounds undergo two chemically reversible oxidation processes near 580 and 990mV versus SCE. The similarities of the cyclic voltammograms for the thorium and uranium complexes strongly suggest that both oxidations are porphyrin-based. The oxidized $[(TPP)_2M]^+$ species may be prepared and isolated by treatment of $(TPP)_2M$ with phenoxathiinium hexachloroantimonate, $(C_{12}H_8SO)SbCl_6$, in CH_2Cl_2 . Crystallization from CH_2Cl_2 /toluene or CH_2Cl_2 /pentane yields $[(TPP)_2Th][SbCl_6^-]$ and $[(TPP)_2U][SbCl_6^-]$ as blue-violet crystalline solids. The Soret bands of these compounds appear at 396 and 392 nm, respectively. $[(TPP)_2Th][SbCl_6^-]$ is NMR silent in CH_2Cl_2 , but $[(TPP)_2U][SbCl_6^-]$ is not (although the lines are broadened), which suggests that there is some interaction between the unpaired electrons of the $f^2 U^{IV}$ center and the single unpaired electron of the porphyrin radical. $[(TPP)_2U][SbCl_6^-]$ in CH_2Cl_2 at $-60^\circ C$ exhibits six broadened 1H NMR signals; the pattern is similar to that of the unoxidized precursor $(TPP)_2U$ except that the pyrrole signal is shifted significantly upfield. In the diamagnetic limit (infinite temperature), the five phenyl proton signals of $[(TPP)_2U][SbCl_6^-]$ collapse to the normal δ 6 to 9 ppm region while the pyrrole signal extrapolates instead to δ -14 ppm. This behavior indicates that the porphyrin π -radical cation possesses high unpaired spin density near the pyrrole protons. $[(TPP)_2Th^+][SbCl_6^-]$ is EPR active in the solid state at room temperature and exhibits a single sharp line at $g = 2.0029$ (line width 6.4 Gauss). The uranium analog, $[(TPP)_2U^+][SbCl_6^-]$ is not EPR active at room temperature but does exhibit an EPR spectrum below 80 K. The 7 K EPR spectrum of $[(TPP)_2U^+][SbCl_6^-]$ is clearly that of an axial complex with $g_{||} = 3.175$ and $g_{\perp} = 1.343$; $A_{g_{iso}} = 1.832$. The calculated isotropic g value is 1.95 (Figure 2). Preliminary SQUID magnetic susceptibility measurements on $[(TPP)_2Th^+][SbCl_6^-]$ show that the value of μ_{eff} above 200 K is $2.6 \mu_B$; between 200 K and 70 K the value of μ_{eff} decreases to a lower limit of $1.88 \mu_B$ and is constant below 70 K.

This behavior suggests that above 70 K, excited spin states with metal character are thermally populated. For the uranium complex, $\mu_{\text{eff}} = 5.2\mu_B$ above 200 K; between 200 K and 70 K, μ_{eff} decreases to a limiting value of $2.2\mu_B$. This behavior may indicate that the spin state changes from $S = 3/2$ to $S = 1/2$ on cooling. The ground state may be a metal-centered $S = 1/2$ state that results from antiferromagnetic coupling of the porphyrin to the uranium center. Both ferromagnetic and antiferromagnetic coupling of porphyrin radicals to paramagnetic metal centers are known [7].

The $[(\text{TPP})_2\text{M}][\text{SbCl}_6^-]$ complexes in CH_2Cl_2 exhibit very broad, intense ($\epsilon \cdot 10^3 \text{ cm}^{-1}\text{M}^{-1}$), featureless absorptions in the near-IR region at 1480 nm (fwhm 300 nm) and 1270 nm (fwhm 140 nm) for $\text{M} = \text{Th}$ and U , respectively. These bands were first assigned in the analogous Ce^{IV} complex to interporphyrin charge-transfer transitions [5]; however, recent resonance Raman data [6] show that the electron hole is delocalized over both porphyrins, and that this interporphyrin transition involves little charge transfer.

$[(\text{TPP})_2\text{Th}^+][\text{SbCl}_6^-]$ has been structurally characterized and is generally similar to $(\text{TPP})_2\text{Th}$ described above. The Th-N distance in the cation of 2.52 Å is 0.03 Å shorter than in the neutral complex; similarly, the Th-N₄ displacement of 1.45 Å is 0.02 Å shorter in the cation. The electronic structure of the $(\text{TPP})_2\text{M}$ complexes appears to be most correctly described by Bocian et al., who have proposed that the porphyrin π systems overlap when placed in close proximity. In the case of two porphyrins coordinated to one metal, the interaction is strong and results in new composite molecular orbitals that have contributions from both porphyrin ligands and the metal center [6]. Krishnan has proposed that a similar interaction occurs when K^+ salts are added to metal complexes of tetra(benzo-15-crown) porphyrin.

The dicationic complexes $[(\text{TPP})_2\text{M}^{2+}][\text{SbCl}_6^-]_2$ ($\text{M} = \text{Th}, \text{U}$) are prepared in the same fashion as the monocations but with the use of 2 equiv of $(\text{C}_{12}\text{H}_8\text{SO})\text{SbCl}_6$. The complexes possess intense near-infrared bands at 1080 nm ($\text{M} = \text{Th}$) and 990 nm ($\text{M} = \text{U}$). The dicationic thorium complex is apparently diamagnetic as judged by ^1H NMR spectroscopy. Others have proposed that a "super bond" can be formed between porphyrin π -radical cations by stacking in a dimeric arrangement [8].



The second type of actinide porphyrins complexes contain only one porphyrin per metal. The X-ray crystal structure of $(\text{TPP})\text{UCl}_2(\text{thf})$ has been determined, and this is the first uranium porphyrin complex that has been crystallographically characterized. The structure of $(\text{TPP})\text{UCl}_2 \cdot \text{thf}$ is similar to that of $(\text{OEP})\text{Th}(\text{acac})_2$. The U-N₄ displacement is 1.29Å, and the U-N bond distance of 2.41Å is comparable to the Th-N distance of 2.50Å in $(\text{OEP})\text{Th}(\text{acac})_2$. Treatment of $(\text{TPP})\text{UCl}_2$ with potassium 2,6-dichlorophenoxide results in $(\text{TPP})\text{U}(\text{OC}_6\text{H}_3\text{Cl}_2)_2$. The reactivity of this complex toward Lewis bases and dioxygen has been studied.

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