

Figure 3. Rates of reaction of  $\text{Cl}_2^-$  with several di- and trivalent metal ions vs. oxidation potential: (O, □) published values; (X) this work.

$\Delta G^\circ$  function is approaching a maximum. The results could also be used to suggest that the mechanism for the oxidation might involve an atom-transfer mechanism. These considerations will be explored in the contemplated studies with the dioxo cations of Pu and Am.

The trivalent cations provide a series of simple aquo species that are used to explore the reactivity patterns of  $\text{Cl}_2^-$ . The present results, along with those previously reported for the oxidations of U(III)<sup>4</sup> and Ti(III),<sup>13</sup> are plotted in Figure 3 vs. the formal reduction potentials. The linear free energy correlation not only is valuable for the systemization but can also be used with con-

fidence for predictive purposes.

There are a number of additional important aspects to be considered.

(1) The values reported for the rates of oxidation of the divalent (5d) transition elements by  $\text{Cl}_2^-$  are correlated by the same linear  $E^\circ$  function as the trivalent cations. This observation can be used to imply that any electrostatic interactions do not have a significant influence on the dynamics of oxidation of these cations by  $\text{Cl}_2^-$ .

(2) A linear relation between  $\log k$  and  $\Delta G^\circ$  is generally assumed as a necessary condition for an outer-sphere electron-transfer mechanism to be a valid description of a series of reactions with a common reagent. However, since  $\text{Cr}^{2+} + \text{Cl}_2^- \rightarrow \text{Cr}^{3+} + 2\text{Cl}^-$  proceeds equally via inner- and outer-sphere mechanisms while  $\text{V}^{2+} + \text{Cl}_2^- \rightarrow \text{V}^{3+} + 2\text{Cl}^-$  proceeds by an outer-sphere diffusion-controlled mechanism,<sup>17</sup> it is evident that the observed linearity is not also a sufficient condition.

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 (18) (a) Cohen, D.; Sullivan, J. C.; Hindman, J. C. *J. Am. Chem. Soc.* **1955**, 77, 4964. (b) The rates of the isotopic exchange reactions between Np(VI) and Np(V) were measured as a function of chloride concentration at 0.0, 4.78, and 9.84 °C. At an ionic strength of 3.0, the values at 1 M  $\text{Cl}^-$  were extrapolated to 25 °C. From the measured ionic strength dependencies, the 25 °C value was corrected to unit ionic strength.

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## First Example of 1:1 Actinide-Phthalocyanine Complexes: Synthesis, Electrochemical, and Spectral Characterization of Bis(diketonato)thorium(IV) and -uranium(IV) Phthalocyaninates

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The synthesis of  $(\text{Pc})\text{Th}(\text{acac})_2$  and  $(\text{Pc})\text{U}(\text{acac})_2$ , where Pc is the dianion of phthalocyanine and acac is the anion of 2,4-pentanedione, is reported. These are the first examples of 1:1 actinide-phthalocyanine complexes. NMR data suggest that the metal is out of the plane of the porphyrin ring and that the two acac ligands are in a cis geometry about the metal. Electrochemical, spectroelectrochemical, and ESR studies on these complexes were performed and demonstrate that both  $(\text{Pc})\text{U}(\text{acac})_2$  and  $(\text{Pc})\text{Th}(\text{acac})_2$  can undergo two ring reductions and two ring oxidations.

### Introduction

Lanthanide or actinide metalation reactions with phthalocyanines typically result in formation of the bis(phthalocyanine) complexes  $(\text{Pc})\text{M}(\text{PcH})$  or  $(\text{Pc})\text{M}(\text{Pc})$ , where Pc is the dianion of phthalocyanine and M is a lanthanide or actinide metal in the +3 or +4 oxidation state and is located at the top of an antiprism. Lanthanide bis(phthalocyanine) complexes are typified by Nd(III), Pr(III), Er(III), and La(III) complexes, which were first described<sup>2</sup> in 1965, followed by numerous detailed studies of their physicochemical, spectroscopic, and photoconductive properties.<sup>3-25</sup> The

actinide bis(phthalocyanine) complexes are typified by  $(\text{Pc})_2\text{Np}$ ,<sup>26</sup>  $(\text{Pc})_2\text{Th}$ ,  $(\text{Pc})_2\text{U}$ ,<sup>27</sup> and a proactinium complex<sup>28</sup> whose sandwich

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structure was later demonstrated.<sup>29</sup>

The properties and the possible applications of these "semimetal" phthalocyanines have also been investigated.<sup>5,6,8,12,30-42</sup> For example, the plutonium analogues are capable of directly transforming fission energy to electrical energy,<sup>39</sup> and the americium complex can be used as an isotopic separation reagent.<sup>40</sup>

Numerous research groups have attempted to synthesize monometallic phthalocyanines with actinide metals. A uranyl "super phthalocyanine", (SPc)UO<sub>2</sub>, has been reported<sup>44,45</sup> as have bis- (rare-earth metal) monophthalocyanine tetrakis( $\beta$ -diacetonate) complexes with actinide metals.<sup>42,46</sup> However to date, an actinide-phthalocyanine complex has not been described in which the actinide is coordinated to only one macrocycle. In this present work, we present a synthetic method that gives such a product. These monophthalocyanine complexes with uranium and thorium were synthesized from dilithium phthalocyaninate, (Pc)Li<sub>2</sub>, and uranium acetylacetonate, U(acac)<sub>4</sub>. <sup>1</sup>H NMR and IR data for the resulting (Pc)U(acac)<sub>2</sub> and (Pc)Th(acac)<sub>2</sub> are presented, and the electrochemical behavior of these two complexes is described.

## Experimental Section

**Materials.** Reagent grade benzonitrile (PhCN) was predried with calcium carbonate and then vacuum distilled from P<sub>2</sub>O<sub>5</sub> for electrochemical analysis. HPLC grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from P<sub>2</sub>O<sub>5</sub>. Reagent grade tetrahydrofuran (THF) was distilled first from CaH<sub>2</sub> and then from sodium and benzophenone. Solvents were either distilled under an inert atmosphere or vacuum distilled (PhCN) just prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Eastman Kodak Co., purified by two recrystallizations from ethyl alcohol, and stored in a vacuum oven at 40 °C. Unless otherwise noted, 0.2 M tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte in the electrochemical and spectroelectrochemical measurements.

For synthesis, benzonitrile was distilled, refluxed over CaH<sub>2</sub> for 24 h, distilled again under argon, and stored under argon over CaH<sub>2</sub>. Commercial chloroform containing ethanol (95/5) was boiled over CaCl<sub>2</sub> for 24 h prior to distillation under argon.

**Syntheses.** Syntheses and handling of the phthalocyanines and the uranium or thorium tetrachloride were performed under an argon atmosphere. All common solvents were thoroughly dried in an appropriate manner and were distilled under argon prior to use. Schlenk techniques were used for all operations.

Uranium tetrachloride was synthesized by following a method similar to that described by Hermann and Suttle.<sup>47</sup> Thorium tetrachloride was kindly supplied by M. Guillaumont from IPN Orsay and was prepared by heating thorium metal under a chlorine atmosphere. The isolated compound contained small particles of carbon but was used without further purification. These two metal tetrachlorides are quite hygroscopic and were handled under argon. In addition, the two metals are both toxic and radioactive and hence were handled with appropriate precautions.

**Dilithium Phthalocyaninate, (Pc)Li<sub>2</sub>.** A 60-g (0.47-mol) sample of phthalonitrile was added to 4 g (0.57 mol) of Li in amyl alcohol (300 mL). The mixture was refluxed with stirring for 30 min as the solution turned from green to blue. The reaction mixture was then cooled, diluted with benzene (1 L), and maintained at 0 °C. The resulting blue precipitate was filtered, dried, and Soxhlet extracted with acetone (250 mL). The solution was then concentrated to 80 mL by evaporation and left for 24 h at 0 °C. Twenty-seven grams of dark blue crystals were recovered and were kept under a dry atmosphere.

**Tetrakis(2,4-pentanedionato)uranium(IV), U(acac)<sub>4</sub>.** This complex was prepared by reaction of UCl<sub>4</sub> with the sodium salt of 2,4-pentanedione in THF by the following procedure: A solution of 2.2 g (5.8 mmol) of UCl<sub>4</sub> and 2.9 g (24 mmol) of sodium acetylacetonate in THF (50 mL) were refluxed for 1 h. The solution was evaporated, extracted with toluene (50 mL), filtered through Celite, concentrated, and crystallized at -20 °C. The reaction gave 1.5 g of brown-green needles (42% yield).

**Tetrakis(2,4-pentanedionato)thorium(IV), Th(acac)<sub>4</sub>.** The procedure was similar to that described above for U(acac)<sub>4</sub> and gave lemon yellow crystals with a yield of 42%.

**Bis(2,4-pentanedionato)(phthalocyaninato)thorium(IV), (Pc)Th(acac)<sub>2</sub>.** A THF solution (40 mL) containing 1.28 g (2.2 mmol) of Th(acac)<sub>4</sub> was added to 1.16 g (2.21 mmol) of (Pc)Li<sub>2</sub> in THF (50 mL). The reaction mixture was evaporated to dryness and Soxhlet extracted with toluene (50 mL). After concentration to 20 mL, the solution was cooled to -20 °C. Workup yielded 0.65 g of dark blue crystals (31%), and elemental analysis indicated one solvent molecule per molecule of compound. Anal. Calcd for (Pc)Th(acac)<sub>2</sub>·toluene, C<sub>49</sub>H<sub>38</sub>N<sub>8</sub>O<sub>4</sub>Th: C, 56.86; H, 3.67; N, 10.83; Th, 22.43. Found: C, 56.57; H, 3.54; N, 10.74; Th, 24.27.

**Bis(2,4-pentanedionato)(phthalocyaninato)uranium(IV), (Pc)U(acac)<sub>2</sub>.** The procedure described for the thorium analogue was carried out with U(acac)<sub>4</sub>. Workup gave dark blue crystals of (Pc)U(acac)<sub>2</sub> with a yield of 45%. Analysis also indicated that the product crystallized with one solvent molecule per molecule of compound. Anal. Calcd for (Pc)U(acac)<sub>2</sub>·toluene, C<sub>49</sub>H<sub>38</sub>N<sub>8</sub>O<sub>4</sub>U: C, 56.53; H, 3.65; N, 10.63; U, 22.88. Found: C, 56.62; H, 3.73; N, 10.76; U, 22.69.

**Instrumentation.** Elemental analyses were performed by the Service de Microanalyse du CNRS. <sup>1</sup>H NMR spectra were recorded on a Bruker WM 400 of the Cerema (Centre de Resonance Magnetique of the University of Dijon) and were measured from solutions of 5 mg of complex in CDCl<sub>3</sub> with tetramethylsilane as internal reference. Infrared spectra were obtained on a Perkin-Elmer 580B apparatus. Samples were prepared as 1% dispersions in CsI pellets. All electrochemical measurements with the exception of spectroelectrochemistry, were performed by Schlenk techniques. Cyclic voltammetric and polarographic measurements were obtained with either an IBM EC 225 voltammetric analyzer or an EG&G Princeton Applied Research Model 174A/175 polarographic analyzer/potentiostat. This latter instrument was coupled with an EG&G Model 9002A X-Y recorder for potential scan rates less than 500 mV/s or a Tektronix 5111 storage oscilloscope for scan rates equal to or larger than 500 mV/s. UV-visible spectra were recorded on an IBM 9430 spectrometer or a Tracor Northern 1710 holographic optical spectrometer/multichannel analyzer. ESR measurements were performed with ESR cells modified for use with a Schlenk line. ESR spectra were recorded on an IBM ED-100 electron spin resonance system.

Platinum working and counter electrodes were used for all electrochemical measurements. In the case of the thin-layer spectroelectrochemical cell, a platinum minigrad electrode was used. A saturated calomel electrode (SCE) that was separated from the bulk of the solution by a fritted-glass disk junction was used as the reference electrode. The

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**Table I.**  $^1\text{H}$  NMR Data for Metallophthalocyanines and the acac Ligands of  $(\text{Pc})\text{M}(\text{acac})_2$  and  $(\text{P})\text{M}(\text{acac})_2$ 

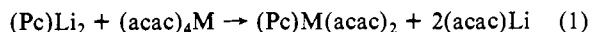
complex	acac ligand	
	$\text{C}_6\text{H}_4^a$	$\text{CH}^b$ $\text{CH}_3^c$
$(\text{Pc})\text{Li}^d$	9.38, 8.04	
$(\text{Pc})\text{Zn}$	9.50, 7.96	
$(\text{Pc})\text{Th}(\text{acac})_2$	9.61, 8.29	4.45 1.50
$(\text{Pc})\text{U}(\text{acac})_2$	6.73, 5.86	13.04 -7.91
$(\text{SPc})\text{NO}_2$	9.06, 7.68	
$(\text{OEP})\text{Th}(\text{acac})_2^{e,f}$		4.22 1.37
$(\text{TPP})\text{Th}(\text{acac})_2^{e,f}$		4.27 1.24
$(\text{OEP})\text{U}(\text{acac})_2^{e,f}$		9.87 -7.42
$(\text{TPP})\text{U}(\text{acac})_2^{e,f}$		13.64 -5.65

<sup>a</sup> Multiplet, 8 H. <sup>b</sup> Singlet, 2 H. <sup>c</sup> Singlet, 6 H. <sup>d</sup> Spectrum taken in  $(\text{CD}_3)_2\text{CO}$ . <sup>e</sup> Only resonances for protons of the acac axial ligands are presented. <sup>f</sup> Reference 48.

ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple was also used as an internal standard for potential measurements. Bulk controlled-potential coulometry was carried out by using an EG&G Princeton Applied Research Model 173 potentiostat/Model 179 coulometer system, coupled with an EG&G Model RE 0074 time-based X-Y recorder. Thin-layer spectroelectrochemical measurements were made with an IBM EC 225 voltammetric analyzer coupled with a Tracor Northern 1710 spectrometer/multichannel analyzer.

### Results and Discussion

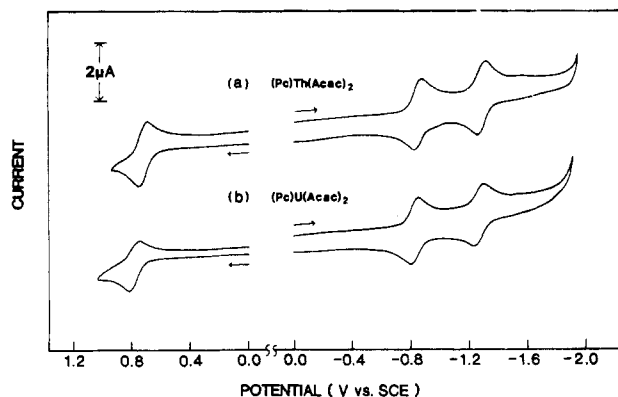
The syntheses of thorium and uranium bis(phthalocyanines) require 20 equiv of phthalonitrile/1 equiv of metal salt at temperatures close to 260 °C.<sup>27</sup> Attempts to prepare monophthalocyanine analogues using the recently described<sup>48</sup> procedure for synthesis of dichlorouranium(IV) and-thorium(IV) monoporphyrins from  $\text{UCl}_4$  or  $\text{ThCl}_4$  and the free base porphyrins were not successful. The reaction of dilithium phthalocyaninate with actinide tetrachloride also failed to produce the expected monophthalocyanines but a reaction of the same dilithium phthalocyaninate with  $\text{U}(\text{acac})_4$  or  $\text{Th}(\text{acac})_4$  easily led to  $(\text{Pc})\text{M}(\text{acac})_2$  as shown in eq 1.



The above reaction was monitored by UV-visible spectroscopy. In contrast to reactions involving the  $(\text{Pc})_2\text{M}$  complexes, all of the starting materials disappeared after refluxing for 2-3 h in THF. The isolated monophthalocyanines were quite soluble in THF and somewhat soluble in toluene or chlorinated solvents. Recrystallization of  $(\text{Pc})\text{M}(\text{acac})_2$  in toluene led to air-stable dark blue crystals. Lithium acetylacetonate is formed as a side product in the reaction, and this makes purification of the monophthalocyanine complexes difficult. Consequently the yield of the reaction was never greater than 40%.

The two monophthalocyanine derivatives were characterized on the basis of elemental analyses and spectroscopic measurements. Analytical data provided evidence for the proposed compound as well as for the presence of toluene as a solvent molecule of crystallization. Crystallization of toluene was also confirmed by the  $^1\text{H}$  NMR data and is not surprising, since it is well-known that such large macrocycles often crystallize with solvent molecules.

$^1\text{H}$  NMR spectral data of the monophthalocyanine complexes in  $\text{CDCl}_3$  at 25 °C are summarized in Table I. Comparative NMR data for uranyl superphthalocyanine<sup>44</sup> and other well-characterized phthalocyanines are also given in Table I. The resonance positions of  $(\text{Pc})\text{Th}(\text{acac})_2$  and the morphology of the AA'BB' multiplet of the phenyl protons are similar to those of other metallophthalocyanines (8.29 and 9.61 ppm). Spectral patterns of the isoindoline protons are similar for the paramagnetic complex  $(\text{Pc})\text{U}(\text{acac})_2$ , but are shifted to higher fields by approximately 3 ppm. A similar shielding has already been reported for the phenyl protons of  $(\text{TPP})\text{U}(\text{acac})_2$  relative to those of  $(\text{TPP})\text{Th}(\text{acac})_2$ <sup>48</sup> (see Table I).



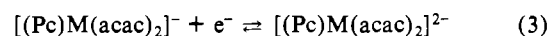
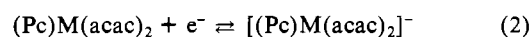
**Figure 1.** Cyclic voltammogram of (a)  $9.2 \times 10^{-4}$  M  $(\text{Pc})\text{Th}(\text{acac})_2$  and (b)  $1 \times 10^{-3}$  M  $(\text{Pc})\text{U}(\text{acac})_2$  in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

NMR resonances of the  $(\text{Pc})\text{Th}(\text{acac})_2$  and  $(\text{Pc})\text{U}(\text{acac})_2$  acac ligands suggest that the structures of these two complexes are similar to those of  $(\text{P})\text{Th}(\text{acac})_2$  and  $(\text{P})\text{U}(\text{acac})_2$  where P = OEP and TPP. Crystallographic data show that the Th and U of  $(\text{P})\text{Th}(\text{acac})_2$  and  $(\text{P})\text{U}(\text{acac})_2$  are octacoordinated with the two acac ligands on the same side of the macrocycle<sup>48</sup> (a cis coordination), and resonances for the acetylacetonate ligands of the phthalocyanine and porphyrin complexes are observed in the same region.

The methine and methyl protons of  $(\text{Pc})\text{Th}(\text{acac})_2$  appear at 4.45 and 1.50 ppm, respectively. Similar resonances are observed at 4.22–4.27 and 1.37–1.24 ppm for the corresponding proton groups of  $(\text{OEP})\text{Th}(\text{acac})_2$  and  $(\text{TPP})\text{Th}(\text{acac})_2$ .<sup>48</sup> Acetylacetonate ligand signals of the paramagnetic  $(\text{Pc})\text{U}(\text{acac})_2$  complex are located at 13.04 ppm for the methine protons and at -7.91 ppm for the methylene protons. This is very close to signals observed for the  $(\text{OEP})\text{U}(\text{acac})_2$  and  $(\text{TPP})\text{U}(\text{acac})_2$  porphyrin complexes (see Table I). Thus the NMR data suggest a similar structure for the  $(\text{Pc})\text{M}(\text{acac})_2$  complexes and the  $(\text{OEP})\text{U}(\text{acac})_2$  derivative whose exact structure has been established by X-ray crystallography.<sup>48</sup> Specifically, the similarity of the NMR data suggests that the two phthalocyanine complexes are cis coordinated by two acetylacetonate ligands and have the metal atom out of the macrocycle plane.

Infrared spectra of the  $(\text{Pc})\text{M}(\text{acac})_2$  derivatives exhibit vibrational bands typical of acetylacetonate complexes. These types of metal derivatives have been extensively studied by IR spectroscopy, and on the basis of previous results,<sup>49</sup> the bands near 1570 and 1540  $\text{cm}^{-1}$  can be assigned to the  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}=\text{C}}$  frequencies, respectively. IR ( $\text{cm}^{-1}$ ): for  $(\text{Pc})\text{Th}(\text{acac})_2$ ,  $\nu_{\text{C}=\text{O}} = 1553$ ,  $\nu_{\text{C}=\text{C}} = 1522$ ; for  $(\text{Pc})\text{U}(\text{acac})_2$ ,  $\nu_{\text{C}=\text{O}} = 1555$ ,  $\nu_{\text{C}=\text{O}} = 1526$ . An absorption due to the metal-oxygen vibration is located close to 400  $\text{cm}^{-1}$  for both complexes. The presence of this absorption peak in the low-frequency region also agrees with a cis coordination geometry for the two acetylacetonate ligands.

**Reduction of  $(\text{Pc})\text{M}(\text{acac})_2$  Where M = Th and U.** Two reversible ring reductions are observed for  $(\text{Pc})\text{Th}(\text{acac})_2$  and  $(\text{Pc})\text{U}(\text{acac})_2$ . These reductions are shown in parts a and b of Figure 1 and are given by eq 2 and 3 where M = Th and U.



The reduced species are stable on both the electrochemical and spectrochemical time scales. Cyclic voltammetry indicates two diffusion-controlled, one-electron reductions. These occur at  $E_{1/2} = -0.85$  and  $-1.29$  V for  $(\text{Pc})\text{Th}(\text{acac})_2$  in PhCN containing 0.1 M TBAP and at  $E_{1/2} = -0.83$  and  $-1.28$  V for  $(\text{Pc})\text{U}(\text{acac})_2$  in the same solvent/supporting electrolyte system. A peak separation  $|E_{pa} - E_{pc}| = 60 \pm 5$  mV and a constant value of  $i_p/v^{1/2}$  are

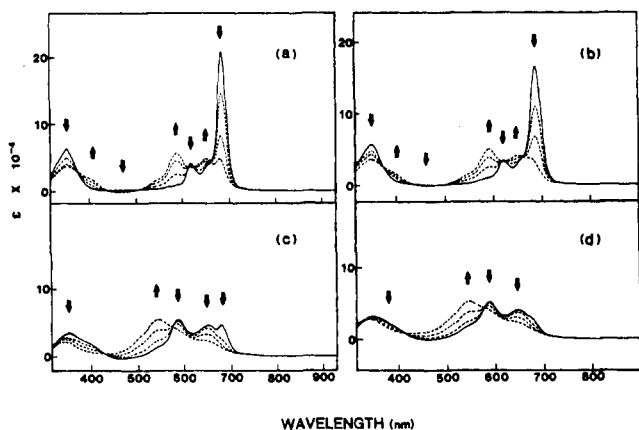
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**Table II.** Spectral Data for Neutral, Oxidized, and Reduced (Pc)M(acac)<sub>2</sub> Complexes in PhCN Containing 0.2 M TBAP

compd	$\lambda$ , nm ( $10^{-4}\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )				
(Pc)Th(acac) <sub>2</sub>	353 (6.3)	617 (4.0)	684 (20.7)		
(Pc)U(acac) <sub>2</sub>	351 (5.7)	620 (3.4)	689 (16.6)		
[(Pc)Th(acac) <sub>2</sub> ] <sup>-</sup>	352 (3.5)	587 (5.3)	617 (3.2)	651 (4.6)	679 (4.1)
[(Pc)U(acac) <sub>2</sub> ] <sup>-</sup>	352 (3.5)	591 (5.0)	620 (3.2)	652 (4.1)	677 (3.7)
[(Pc)Th(acac) <sub>2</sub> ] <sup>2-</sup>	351 (2.2)	544 (5.6)	649 (2.2)		
[(Pc)U(acac) <sub>2</sub> ] <sup>2-</sup>	349 (2.9)	549 (5.3)	646 (2.3)		
[(Pc)Th(acac) <sub>2</sub> ] <sup>+a</sup>	351 (3.1)	516 (0.9)	617 (1.3)	684 (6.3)	845 (0.7)
[(Pc)Th(acac) <sub>2</sub> ] <sup>+b</sup>	358 (1.9)	511 (0.4)	685 (0.8)	846 (0.3)	
[(Pc)U(acac) <sub>2</sub> ] <sup>+a</sup>	350 (3.8)	537 (0.8)	624 (1.7)	691 (6.1)	729 (1.7)
[(Pc)U(acac) <sub>2</sub> ] <sup>+b</sup>	348 (2.1)	694 (1.5)			852 (0.5)

<sup>a</sup>Spectrum on short time scales. <sup>b</sup>Final spectrum on long time scales.



**Figure 2.** Electronic absorption spectra monitored during the first reduction of (a) (Pc)Th(acac)<sub>2</sub> and (b) (Pc)U(acac)<sub>2</sub> and during the second reduction of (c) (Pc)Th(acac)<sub>2</sub> and (d) (Pc)U(acac)<sub>2</sub> in PhCN containing 0.2 M TBAP.

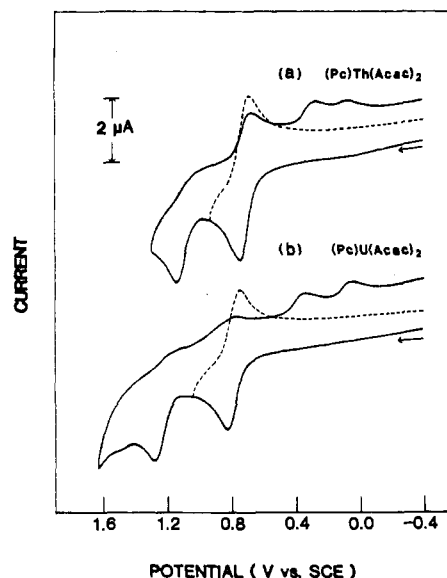
obtained for both reduction waves. Coulometry for the first reduction of (Pc)U(acac)<sub>2</sub> also agrees with a one-electron transfer. Finally, the differential-pulse voltammograms of both complexes indicate two reversible waves, with no sign of compound decomposition.

The spectra of neutral and reduced (Pc)Th(acac)<sub>2</sub> and (Pc)U(acac)<sub>2</sub> are nearly identical. Parts a and b of Figure 2 show the UV-visible spectra obtained during controlled-potential reduction of (Pc)Th(acac)<sub>2</sub> and (Pc)U(acac)<sub>2</sub> at -1.10 and -1.00 V, respectively, while parts c and d of Figure 2 show changes in the spectra during controlled-potential reduction at -1.50 V. Table II lists spectral details for all of the complexes in PhCN containing 0.2 M TBAP.

Changes in the spectral absorption bands can be associated with the stepwise addition of two electrons to the phthalocyanine ring. These reductions are reversible on the spectroelectrochemical time scale. For example, reoxidation of [(Pc)Th(acac)<sub>2</sub>]<sup>2-</sup> at -1.00 V generates the spectrum of [(Pc)Th(acac)<sub>2</sub>]<sup>-</sup>, while reoxidation at 0.00 V generates the initial (Pc)Th(acac)<sub>2</sub> spectra.

ESR measurements were carried out on frozen electrolyzed solutions of (Pc)U(acac)<sub>2</sub>. A free-radical signal is observed when the solution is bulk electrolyzed at -1.05 V. This signal is characterized by a *g* value of 2.00 and a signal width of 5 G. When the controlled-reduction potential was switched from -1.05 to -1.50 V, the ESR signal disappeared. These data agree with data from electronic absorption spectra, which indicate that the first and second reductions are ring centered, thus suggesting generation of a phthalocyanine anion radical and dianion.

**Oxidation of (Pc)M(acac)<sub>2</sub> Where M = Th and U.** Cyclic voltammograms for the first oxidation of (Pc)Th(acac)<sub>2</sub> and (Pc)U(acac)<sub>2</sub> in PhCN are shown in Figure 1. These oxidations are reversible, one-electron, diffusion-controlled processes that are characterized by  $|E_{pa} - E_{pc}| = 60 \pm 5$  mV and a constant value of  $i_p/v^{1/2}$ . Potentials for both oxidation and reduction of (Pc)M(acac)<sub>2</sub> are shifted positively upon going from M = Th to M = U. The potentials for oxidation of (Pc)Th(acac)<sub>2</sub> and (Pc)U-



**Figure 3.** Cyclic voltammogram of (a)  $9.2 \times 10^{-4}$  M (Pc)Th(acac)<sub>2</sub> and (b)  $1 \times 10^{-3}$  M (Pc)U(acac)<sub>2</sub> in PhCN containing 0.1 M TBAP. Scan rate = 0.5 V/s.

(acac)<sub>2</sub> are 0.73 and 0.79 V, respectively while potentials for reduction of the same two compounds are -0.85 and -0.83 V.

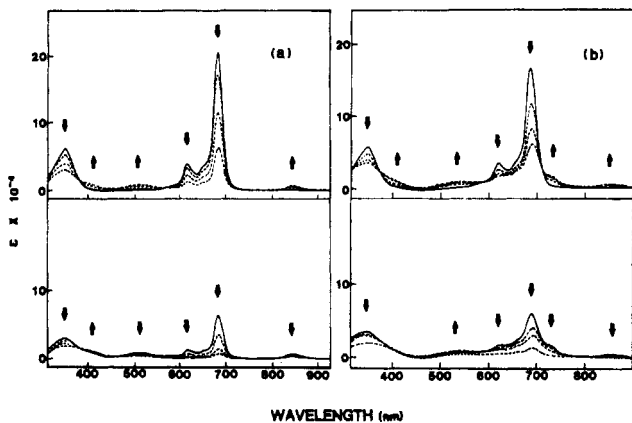
The potential difference between the first oxidation and the first reduction of the two (Pc)M(acac)<sub>2</sub> complexes is 1.58 V for M = Th and 1.62 V for M = U. These values may be compared to an average separation of 1.56 V between the HOMO and the LUMO of other metal-phthalocyanine complexes<sup>50,51</sup> when both the oxidation and the reduction occur at the conjugated  $\pi$ -ring system.

The two oxidation peaks of (Pc)M(acac)<sub>2</sub> are separated by 0.39 V for M = Th and 0.47 V for M = U as shown in Figure 3. These potential separations are less than the 0.61-V difference in  $E_{1/2}$  between the two oxidations of (Pc)Mg<sup>II</sup> in DMF but they are comparable to the 0.315-V separation in stepwise oxidation potentials of (Pc)Ba<sup>II</sup>.<sup>50</sup> These latter reactions occur at the phthalocyanine conjugated ring system.

After further oxidation of electrochemically generated [(Pc)M(acac)<sub>2</sub>]<sup>+</sup>, two new irreversible rereduction waves appear as illustrated by the cyclic voltammograms in Figure 3. The new reduction peaks are not present on initial sweeps that terminate after the first oxidation process and thus are generated from decomposition of the oxidized phthalocyanine complex after the second electron abstraction. The nature of the species generated during the second oxidation is not known. However, the currents for the new reduction peaks are enhanced upon the addition of free acetylacetonate ligand to the solution, suggesting that these

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**Figure 4.** Electronic absorption spectra monitored during the first oxidation of (a) (Pc)Th(acac)<sub>2</sub> and (b) (Pc)U(acac)<sub>2</sub> in PhCN containing 0.2 M TBAP.

peaks may be related to reduction of the electrooxidized ligand.

Parts a and b of Figure 4 illustrate initial changes that occur in the electronic absorption spectra of (Pc)Th(acac)<sub>2</sub> and (Pc)U(acac)<sub>2</sub> upon controlled-potential oxidation in a thin-layer cell. Table II lists the wavelengths and molar absorptivities associated with these spectra. The initial spectra indicate an oxidation at the conjugated ring structure. However, upon rereduction at 0.00 V, the original spectra are not regenerated, thus indicating that the first oxidation is not reversible on a time scale of 5–8 min.

When (Pc)Th(acac)<sub>2</sub> is oxidized at 0.95 V for periods longer than 8 min, continual changes occur in the UV–visible spectra. Under these conditions all of the bands show a general decrease in intensity as the spectral detail disappears. This is illustrated

by the spectra in Figure 4a. Also, after controlled-potential oxidation at 0.95 V the second oxidation peak on the voltammogram is greatly reduced in current, further demonstrating the presence of an irreversible chemical reaction. Finally, when the potential is set to +1.30 V, all of the absorption bands decrease in intensity, nearly to base line levels. The same result is observed for (Pc)U(acac)<sub>2</sub> and must be due to a demetalation or degradation of the phthalocyanine conjugated ring system.

An empirical formula, based on a limited data set, has been used to predict the first reduction and first oxidation potentials for (Pc)M(L)<sub>n</sub> complexes containing the metal ion in the plane of the phthalocyanine ring.<sup>50,51</sup> This formula is based on the size and charge of the metal ion in (Pc)M(L)<sub>n</sub>. With this formula, the first oxidation of (Pc)U(acac)<sub>2</sub> is calculated to be 0.84 V and the first reduction to be –0.73 V. The first oxidation of (Pc)Th(acac)<sub>2</sub> is calculated to be 0.82 V and the first reduction to be –0.74 V. These calculated values are not in good agreement with the experimental values and suggest that the Th and U metals in (Pc)M(acac)<sub>2</sub> are not in the plane of the phthalocyanine ring or that a reduction or oxidation occurs at the metal center. This latter possibility is eliminated on the basis of ESR and spectroelectrochemical data.

In conclusion, the synthesis of (Pc)U(acac)<sub>2</sub> and (Pc)Th(acac)<sub>2</sub> provides a relatively easy route to 1:1 actinide–phthalocyanine complexes. The <sup>1</sup>H NMR data suggest a cis configuration of the acac ligands and a metal atom out of the plane of the phthalocyanine ring. The electrochemical data indicate ring-centered reactions and also support a structure with the metal out of the phthalocyanine ring.

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## Phosphate-Mediated Electron Transfer during the Reduction of Cobalt(III) Complexes by Titanium(III)

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The kinetics of electron-transfer reactions between hexa-aquatitanium(III) and cobalt(III) complexes containing monodentate or bidentate ortho-, pyro-, or triphosphate were investigated at 25.0 °C in 1.0 M LiCl–HCl. The reactions are first order with respect to each of the reactants. The dependence of the rate upon the concentration of hydrogen ion indicates that at least one oxygen atom of the phosphate group must be deprotonated in order for the electron-transfer reaction to occur and that TiOH<sup>2+</sup> is the active reductant. The calculated rate constants for the reduction reactions of TiOH<sup>2+</sup> are within the range (0.5–10) × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> when a value of K<sub>a</sub> = 2.3 × 10<sup>-3</sup> M is used. An inner-sphere mechanism is proposed in which substitution on titanium(III) is the rate-limiting step followed by rapid electron transfer within the transient dinuclear intermediate. The efficiency of phosphate ligands in mediating electron transfer from titanium(III) to cobalt(III) is compared with that of other bridging ligands reported in the literature.

### Introduction

The acceleration of the hydrolysis reactions of coordinated polyphosphates and nucleotides by certain complexes of platinum(II) and cobalt(III) has been reported previously from this and other laboratories.<sup>2,3</sup> On the basis of stoichiometric data, phosphorus-31 NMR data, and the dependence of the rate of hydrolysis upon the concentration of hydrogen ion, it has been

suggested that coordinated hydroxide ion catalyzes the hydrolysis within a phosphate-bridged dinuclear intermediate. In these systems maximal acceleration of the rate was observed at neutral or basic pH.<sup>3</sup> In our continuing effort to understand the role of metal ions in phosphate hydrolysis reactions, we have begun to explore the possibility of using metal ions that might accelerate phosphate hydrolysis<sup>4</sup> at lower pH. Hexa-aquatitanium(III), having a pK<sub>a</sub> value in the range 1.9–2.7 dependent on the supporting electrolyte,<sup>5</sup> would be a likely candidate to catalyze phosphate hydrolysis of cobalt(III) polyphosphate complexes if

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