

## Electrochemical and Spectroelectrochemical Studies of Bis(diketonate) Thorium(IV) and Uranium(IV) Porphyrins

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### Introduction

The synthesis, characterization and chemical properties of actinide and lanthanide metalloporphyrin complexes have been the subject of several recent reports [1–6]. A combination of the coordination properties of actinide metals [7] with the ligation properties of metalloporphyrins has resulted in the generation of several distinct sets of molecular structures. These include monomeric species, trimeric species and triple decker type species. The monomeric [2–4] complexes are represented by dichloro and bis(acetylacetonato) porphyrins of the form  $(P)MCl_2L_2$  and  $(P)M(acac)_2$  where L is the solvent molecule, acac is acetylacetonate, P is the dianion of a given porphyrin macrocycle and M is Th or U. Other structures include 'triple decker' complexes of the form  $(P)_3M_2$  [5], where M is one of 12 different metal ions and a trimeric complex of the form  $[(P)Th(OH)_2]_3$  [6]. In each case, crystallographic determinations [4–6] have been reported.

Although largely uncharacterized, the properties of actinide metalloporphyrins are of potential interest to workers in a number of fields. The monomeric complexes are known to form both oxo and bis  $\mu$ -oxo products upon reaction with molecular  $O_2$  and thus present a system for modelling the activation of molecular oxygen. The electrochemistry of monomeric actinide porphyrin complexes can also be compared with monomeric actinide phthalocyanine complexes which have only recently been reported [8]. Other actinide phthalocyanines are typified by the sandwich complexes  $(Pc)_2M$ , where M = Th [9], U [9], Np [10], and Pa [11, 12].

Electrochemical and spectroelectrochemical properties of the monomeric actinide phthalocyanine complexes  $(Pc)M(acac)_2$ , where M = Th or U [8] and a trimeric actinide metalloporphyrin  $[(P)Th(OH)_2]_3$

have recently been reported [6]. All electrode reactions of the porphyrin or phthalocyanine species were found to occur on the macrocyclic ligand and, for the case of trimeric  $[(P)Th(OH)_2]_3$ , up to six electrons could be either reversibly abstracted or added to the molecular unit at low temperature on the electrochemical time scale. A three electron oxidation step was also observed for this trimeric complex.

The electrochemical properties of  $[(P)Th(OH)_2]_3$  are unusual and may reflect properties of the trimeric unit, properties of the actinide metal or both. Hence, it was of interest to examine the electrochemical properties of representative monomeric actinide metalloporphyrins and to compare the electrochemical results for these complexes with those of trimeric  $[(P)Th(OH)_2]_3$ . This is done in the present paper which reports the electrochemical and spectroelectrochemical properties of  $(OEP)Th(acac)_2$  and  $(OEP)U(acac)_2$ , where OEP is the dianion of octaethylporphyrin. One reversible ring centered reduction is observed for both complexes. The first oxidation of  $(OEP)Th(acac)_2$  occurs at the porphyrin ring but  $(OEP)U(acac)_2$  appears to undergo an oxidation at the central metal. A complete, self-consistent electron transfer reaction scheme is presented and comparisons are made between the electrochemical data of  $[(OEP)Th(OH)_2]_3$  and the monomeric actinide phthalocyanine complexes  $(Pc)Th(acac)_2$  and  $(Pc)U(acac)_2$ .

### Experimental

#### Materials

Reagent grade benzonitrile (PhCN) was pre-dried with calcium carbonate and then vacuum distilled from  $P_2O_5$  for electrochemical analysis. HPLC grade dichloromethane ( $CH_2Cl_2$ ) was distilled from  $P_2O_5$ . Solvents were either distilled under an inert atmosphere or vacuum distilled (PhCN) just prior to use. Tetra-n-butylammonium perchlorate (TBAP) was

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purchased from Eastman Kodak Co., purified by two recrystallizations from ethyl alcohol, and stored in a vacuum oven at 40 °C. Unless otherwise noted, 0.1 M tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte in the electrochemical measurements.

### Instrumentation

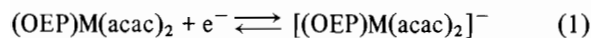
Cyclic voltammetric and polarographic measurements were obtained with either an IBM EC 225 voltammetric analyzer, or an EG&G Princeton Applied Research Model 174A/175 polarographic analyzer/universal programmer. This latter instrument was coupled with an EG&G Model 9001A X-Y recorder for potential scan rates less than 500 mV/s or a Tektronix 5111 storage oscilloscope for scan rates equal to or larger than 500 mV/s. UV-Vis spectra were recorded on an IBM 9430 spectrophotometer 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 Model 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 ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple was also used as an internal standard for potential measurements. Bulk controlled potential coulometry was carried out using an EG&G Princeton Applied Research Model 173 potentiostat/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

### Reduction of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub>

Cyclic voltammograms showing the reduction of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub> are presented in Fig. 1a and b. Both compounds are characterized by a single reversible one electron transfer (wave I) at the porphyrin  $\pi$  ring system and this reaction is given by eqn. (1) where M = Th or U.



The first reduction of (OEP)Th(acac)<sub>2</sub> occurs at  $E_{1/2} = -1.57$  V in PhCN while (OEP)U(acac)<sub>2</sub> is reduced at  $-1.56$  V in the same solvent, supporting electrolyte system (see Table 1). There is also a small

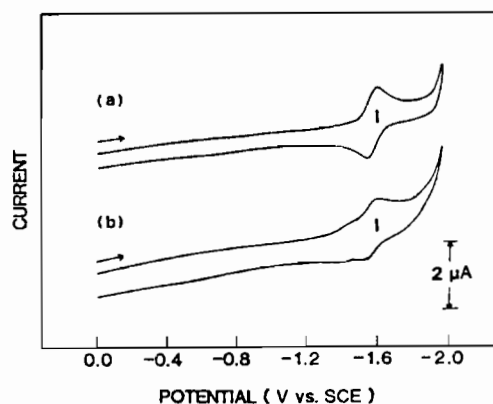


Fig. 1. Cyclic voltammograms illustrating the reduction of (a)  $1.0 \times 10^{-3}$  M (OEP)Th(acac)<sub>2</sub> and (b)  $1.2 \times 10^{-3}$  M (OEP)U(acac)<sub>2</sub> in PhCN, 0.1 M TBAP. Scan rate = 0.1 V/s.

TABLE 1. Oxidation and reduction potentials (V vs. SCE) of (OEP)M(acac)<sub>2</sub>, [(OEP)Th(OH)<sub>2</sub>]<sub>3</sub> and (Pc)M(acac)<sub>2</sub> in PhCN, 0.1 M TBAP

Complex	Oxidation processes			Reduction process
	II	III	IV	I
(OEP)Th(acac) <sub>2</sub>	0.76	1.15 <sup>a</sup>	1.23 <sup>b</sup>	-1.57
(OEP)U(acac) <sub>2</sub>	0.58	1.26 <sup>a</sup>		-1.56
[(OEP)Th(OH) <sub>2</sub> ] <sub>3</sub> <sup>c</sup>	0.62	1.00 <sup>a</sup>		-1.62
(Pc)Th(acac) <sub>2</sub> <sup>d</sup>	0.73			-0.85
(Pc)U(acac) <sub>2</sub> <sup>d</sup>	0.79			-0.83

<sup>a</sup> $E_{pc}$  at 0.1 V/s. <sup>b</sup> $E_{pc}$  at 0.1 V/s; oxidation was observed only after scanning past wave III. See text for further discussion. <sup>c</sup>Ref. 6. <sup>d</sup>Ref. 8.

reduction wave at  $E_p = -1.33$  V for (OEP)U(acac)<sub>2</sub>. This reaction is due to trace amounts of (OEP)H<sub>2</sub> as demonstrated by the increase in current for this process upon addition of the free base (OEP)H<sub>2</sub> to solution.

Each reduction of the two complexes is characterized by  $|E_{pa} - E_{pc}| = 60 \pm 5$  mV and a constant value of  $i_p/v^{1/2}$ . Reversible differential pulse voltammograms are also observed for both complexes. Another wave is observed at  $E_p = -1.98$  V in the differential pulse voltammogram of (OEP)Th(acac)<sub>2</sub> but this process is difficult to characterize due to its proximity to the solvent edge. It is most likely due to a second reduction at the porphyrin  $\pi$  ring system.

Controlled potential electrolysis of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub> lead to the type of spectral changes shown in Fig. 2a for (OEP)U(acac)<sub>2</sub> and clearly indicate ring centered reductions [13]. The electrochemical reduction of U<sup>IV</sup> to U<sup>III</sup> has been reported for other organometallic species [14-16], but this reaction does not appear to occur for the investigated U(IV) porphyrin complexes.

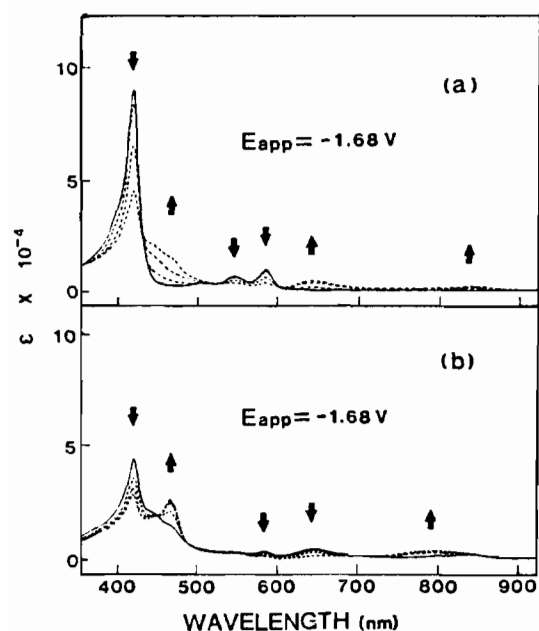


Fig. 2. Electronic absorption spectra obtained during controlled potential reduction of (OEP)U(acac)<sub>2</sub> at an  $E_{app} = -1.68$  V in PhCN, 0.2 M TBAP from (a) 0 to 5 min and (b) from 5 to 10 min.

Table 2 presents spectral data for the reduced octaethylporphyrin complexes. The spectral changes for reduction of (OEP)Th(acac)<sub>2</sub> or (OEP)U(acac)<sub>2</sub> at short electrolysis times were reversible and the original spectra could be regenerated by applying a controlled potential of 0.00 V. However, a reduction of (OEP)U(acac)<sub>2</sub> for longer than 5 min at  $-1.68$  V resulted in the UV-Vis spectral changes which are shown in Fig. 2b, and suggest the occurrence of a slow chemical reaction involving the monoanion of (OEP)U(acac)<sub>2</sub>. In contrast, the final spectral features

of reduced (OEP)Th(acac)<sub>2</sub> do not change from those of a porphyrin anion radical upon holding the potential for up to 8 min at  $-1.76$  V, thus indicating that the  $\pi$  anion radical of (OEP)Th(acac)<sub>2</sub> is more stable than that of (OEP)U(acac)<sub>2</sub>.

#### Oxidation of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub>

Cyclic voltammograms illustrating the oxidation of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub> are shown in Fig. 3a and b. The first oxidation of each complex (wave II, dotted line in Fig. 3) has  $|E_{pa} - E_{pc}| = 60 \pm 5$  mV and a constant value of  $i_p/v^{1/2}$ . This indicates diffusion controlled, one-electron transfer processes which are given by eqn. (2) where M = Th or U.



The potentials for these oxidations are listed in Table 1.

The second oxidation of (OEP)M(acac)<sub>2</sub> (wave III) is irreversible in that there is no return reduction peak coupled to this process. There is also no return peak coupled to the first oxidation when the potential sweep is scanned positive of peak III and this implies that the abstraction of a second electron from both complexes is followed by a fast chemical reaction. There is also an additional irreversible oxidation of (OEP)Th(acac)<sub>2</sub> which occurs at  $E_p = 1.23$  V (wave IV) when the potential is scanned more positively. This peak is due to a product of the chemical reaction and is seen in the voltammogram of Fig. 3a. The small peak at  $E_p = 0.90$  V in Fig. 3b results from oxidation of free (OEP)H<sub>2</sub> in solution.

The absolute peak potential separation between the first and the second oxidations of the complexes are 0.36 V for (OEP)Th(acac)<sub>2</sub> and 0.68 V for (OEP)U(acac)<sub>2</sub>. These values may be compared to an average separation of  $0.29 \pm 0.05$  V for a number of

TABLE 2. Absorption maxima (nm) and molar absorptivity ( $\epsilon$ ) for neutral, reduced and oxidized (OEP)M(acac)<sub>2</sub> in PhCN, 0.2 M TBAP

Complexes	Applied potential (V)	$\lambda_{max}$ (nm) ( $\epsilon \times 10^{-3}$ )				
(OEP)Th(acac) <sub>2</sub>	none	410(288)	538(17)	575(31)		
	-1.76	413(77)	435(53)	461(41)	633(13)	804(5)
	0.98 <sup>a</sup>	397(92)	407(104)	537(9)	574(13)	633(5)
	0.98 <sup>b</sup>	412(96)	903(7)			
	1.35	409(33)	526(10)			
(OEP)U(acac) <sub>2</sub>	none	414(82)	538(6)	577(9)		
	-1.68 <sup>a</sup>	416(41)	538(4)	577(3)	636(5)	825(2)
	-1.68 <sup>b</sup>	416(26)	461(24)	785(4)		
	0.70	407(47)	536(4)	577(5)		
	1.05 <sup>a</sup>	397(56)	533(3)	567(3)		
	1.05 <sup>b</sup>	392(25)				
	1.40	410(40)	512(9)	552(7)		

<sup>a</sup>Short period of time.

<sup>b</sup>Long period of time.

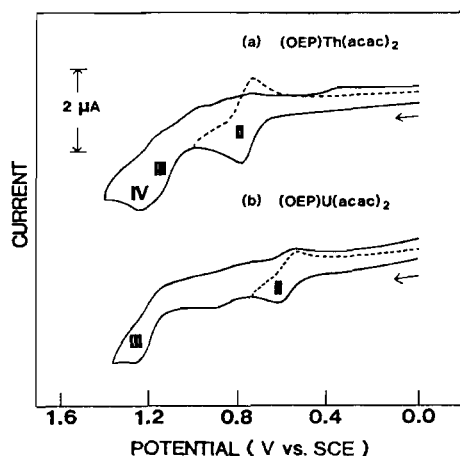


Fig. 3. Cyclic voltammograms illustrating the oxidation of (a)  $1.0 \times 10^{-3}$  M (OEP)Th(acac)<sub>2</sub> and (b)  $1.2 \times 10^{-3}$  M (OEP)U(acac)<sub>2</sub> in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

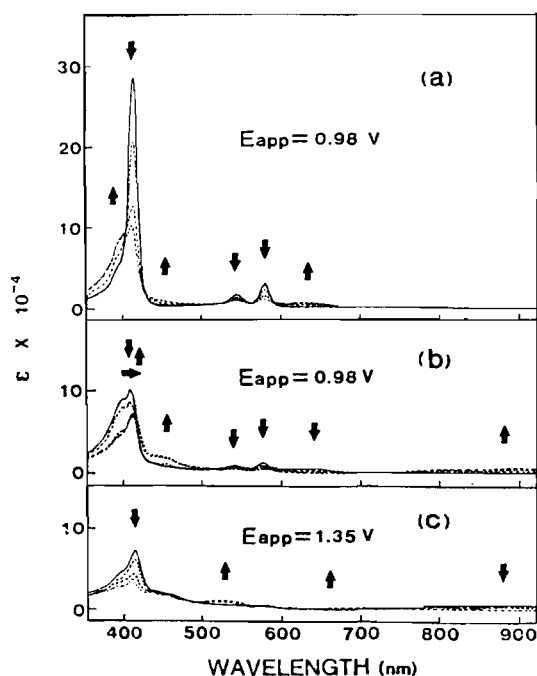


Fig. 4. Electronic absorption spectra obtained during controlled potential oxidation of (OEP)Th(acac)<sub>2</sub> in PhCN, 0.2 M TBAP at (a)  $E_{app} = 0.98$  V (0–2 min), (b)  $E_{app} = 0.98$  V (2–6 min) and (c)  $E_{app} = 1.35$  V.

other octaethylporphyrin complexes where both of the two oxidations are porphyrin ring centered [13]. Metal centered U<sup>IV</sup> to U<sup>V</sup> oxidations of uranocene have been reported in several non-aqueous solvents [17, 18] and the significantly larger potential difference between the two oxidations of (OEP)U(acac)<sub>2</sub> in PhCN suggests the possibility of a metal centered oxidation for the first process.

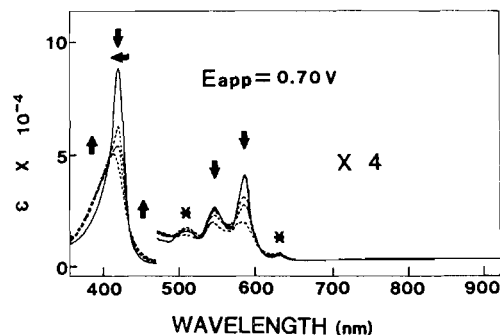


Fig. 5. Electronic absorption spectra obtained during controlled potential oxidation of (OEP)U(acac)<sub>2</sub> at a  $E_{app} = 0.70$  V in PhCN. \*Bands due to the presence of trace amounts of (OEP)(H)<sub>2</sub>.

Controlled potential oxidation of (OEP)Th(acac)<sub>2</sub> produces changes in the UV–Vis spectra which are characteristic of a porphyrin ring centered oxidation. These changes are shown in Fig. 4a and the spectral data for each oxidized complex is presented in Table 2.

The spectra of the electrooxidized species are not stable with time but change as shown in Fig. 4b when the potential is held at 0.98 V for longer time periods (6 min). Under these conditions, the original species is not regenerated upon bulk electrolysis at 0.00 V, and it is clear that the first oxidation is followed by a chemical reaction which is not reversible on the spectroelectrochemical time scale.

Figure 4c illustrates the UV–Vis spectral changes which result when the potential for oxidation of (OEP)Th(acac)<sub>2</sub> is set to 1.35 V. As seen in this Figure, most bands in the UV–Vis spectrum have decreased to background levels and this suggests a degradation of the porphyrin upon prolonged oxidation. However, the identities of the oxidation products are not known.

The resulting spectral changes after controlled potential oxidation of (OEP)U(acac)<sub>2</sub> are presented in Table 2. The spectral data is complicated and suggests formation of one or more intermediate products, which at this point have not been characterized. Changes in the UV–Vis spectra after oxidation of (OEP)U(acac)<sub>2</sub> at 0.70 V are shown in Fig. 5. The oxidation is not reversible on the spectroelectrochemical time scale since a rereduction at 0.00 V does not regenerate the original species. Consistent with the electrochemical data, trace amounts of (OEP)H<sub>2</sub> are indicated by the bands at 501 and 622 nm.

The Soret band and the two Q bands of (OEP)U(acac)<sub>2</sub> decrease in intensity and shift to the blue region upon oxidation at 0.70 V. However, no bands are observed between 650 and 900 nm and the spectral details normally observed for formation of a porphyrin based cation radical are absent [13]. This

also suggests that the oxidation is metal centered with formation of an intermediate U(V) complex.

The ring centered reductions of (Pc)Th(acac)<sub>2</sub> and (Pc)U(acac)<sub>2</sub> occur at -0.85 and -0.83 V while the ring centered oxidations of the same two complexes occur at 0.73 and 0.79 V, respectively. This suggests that ring centered electrode reactions of U and Th complexes with the same macrocycle will occur at almost identical potentials. Although the ring centered reductions of (OEP)Th(acac)<sub>2</sub> and (OEP)U(acac)<sub>2</sub> occur at -1.57 and -1.56 V respectively, a 0.18 V difference in  $E_{1/2}$  is found between the first oxidation of the two OEP complexes. This further suggests a different site of electron transfer in the first one electron oxidation of (OEP)U(acac)<sub>2</sub> and (OEP)Th(acac)<sub>2</sub>.

The abstraction of a second electron from both (Pc)M(acac)<sub>2</sub> [8] and (OEP)M(acac)<sub>2</sub> is followed by a chemical reaction which is rapid enough to monitor on the cyclic voltammetric time scale. This is in contrast to [(OEP)Th(OH)<sub>2</sub>]<sub>3</sub> which undergoes a reversible three electron oxidation and shows reversible voltammetric behavior [6]. This difference between the monomeric and trimeric compounds can be accounted for, in part, by the structural aspects of [(OEP)Th(OH)<sub>2</sub>]<sub>3</sub> which has three metalloporphyrin units bridged by six OH<sup>-</sup> groups. The half wave potential for the three-electron oxidation of [(OEP)Th(OH)<sub>2</sub>]<sub>3</sub> is 0.62 V while  $E_{1/2}$  for the one-electron oxidation of (OEP)Th(acac)<sub>2</sub> is 0.76 V in PhCN. However, the difference between the peak potentials for porphyrin cation radical and dication formation from [(OEP)Th(OH)<sub>2</sub>]<sub>3</sub> is 370 mV which is very close to the experimentally measured 360 mV for the same reactions of (OEP)Th(acac)<sub>2</sub>. This indicates that the structure of the porphyrin complex strongly influences the electron transfer process but only slightly affects the energy barrier between the two electron transfers. Hence, a clear relationship between molecular structure and the corresponding electrochemical properties is observed with this set of complexes.

## Acknowledgements

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