

## Redox Behavior of Cyclo[6]pyrrole in the Formation of a Uranyl Complex

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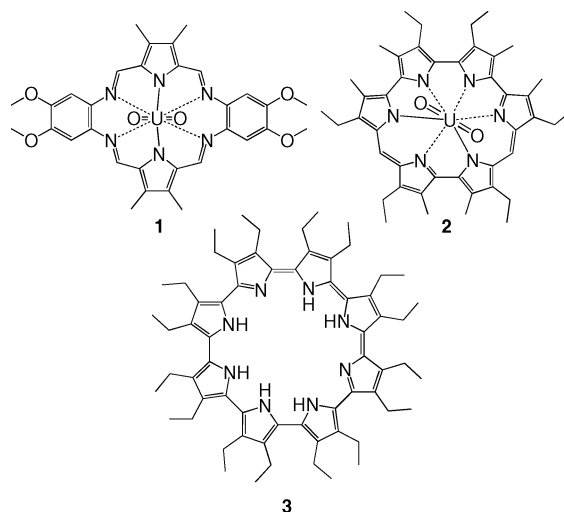
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A uranyl complex, the first metal complex to be formed from the cyclo[*n*]pyrrole series of expanded porphyrins, is formed when cyclo[6]pyrrole is treated with the uranyl cation under aerobic conditions. Spectroscopic, spectroelectrochemical, and electron spin resonance data of this species are consistent with the ligand in the complex being oxidized to an antiaromatic form.

In the current politically charged atmosphere of nuclear buildup and proliferation, the ability to detect and chemically remove radioactive byproducts of nuclear fission, especially the actinide cations uranyl ( $\text{UO}_2^{2+}$ ), neptunyl ( $\text{NpO}_2^{2+}$ ), and plutonyl ( $\text{PuO}_2^+$  or  $\text{PuO}_2^{2+}$ ), is a high priority for many governments. In response to this challenge, a number of groups have reported actinyl coordination complexes, with the majority of work focusing on the uranyl cation because of its low radioactivity and prevalence in nature.<sup>1</sup> In the context of these widespread efforts, work in the Sessler group has focused on the use of expanded porphyrins and related Schiff base pyrrolic macrocycles as actinide cation receptors; this has led to a demonstration that a number of these ligands are capable of coordinating readily with the uranyl, neptunyl, and plutonyl cations.<sup>2,3</sup> Moreover, it was found that the diverse redox chemistry of these macrocycles, as well as their

frequently distinct UV–visible properties, has made them attractive candidates as receptors and colorimetric “sensors” for the actinide cations. Some notable examples include alaskaphyrin<sup>4</sup> (**1**), which has been shown to self-assemble



around a uranyl cation template, and isoamethyrin (**2**), which displays a dramatic color change, from yellow to red, upon coordination of the actinide dioxocations.<sup>2</sup> In the latter case, the observed color change was rationalized as being due, at least in part, to the oxidation of the macrocycle from a formally antiaromatic framework containing a 24  $\pi$ -electron periphery to one containing 22  $\pi$ -electrons. Interestingly, however, both the starting antiaromatic species and the resulting aromatic complex proved stable under normal laboratory conditions, particularly in the absence of oxygen and light. This is consistent with the accepted notion that destabilization due to antiaromaticity decreases with increasing conjugation pathways,<sup>5</sup> as well as the finding that the difference between the first oxidation and reduction potentials of expanded porphyrins of fully conjugated expanded por-

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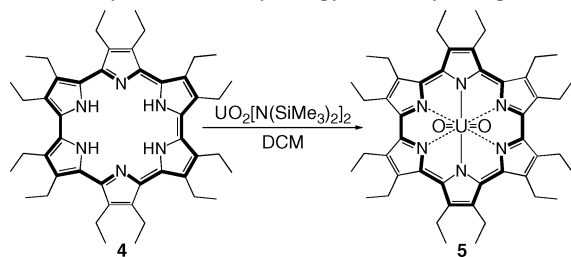
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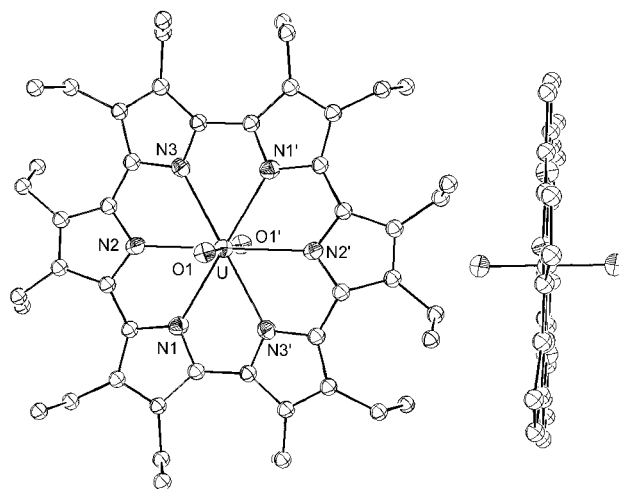
**Scheme 1.** Synthesis of the Cyclo[6]pyrrole Uranyl Complex **5**

phyrins is generally considerably lower than what is found for porphyrins.<sup>6,7</sup> In spite of this, reports in which aromatic expanded porphyrins are reduced or oxidized to produce a stable non- or antiaromatic species (the reverse of what was observed for isoamethyrin) are still surprisingly rare; typically, once made, the macrocycle retains its aromaticity or undergoes partial or complete decomposition if subjected to forcing conditions.<sup>8,9</sup> Exceptions to this trend have been made by Cavaleiro and co-workers, who isolated a meso-substituted hexaphyrin in both its aromatic and nonaromatic forms, and Mori and Osuka, who reported that an aromatic meso-substituted hexaphyrin may be reduced to an antiaromatic formation when stabilized as a bis-gold complex.<sup>10</sup> As an addition to this short list, we report here the finding that exposure of the free base form of cyclo[6]pyrrole (**4**) to  $\text{UO}_2[\text{N}(\text{SiMe}_3)_2]_2 \cdot 2\text{THF}$  produces the novel uranyl coordination complex of cyclo[6]pyrrole (**5**), which was observed to be a highly planar, antiaromatic, yet stable species.

Compound **4** was first produced as a side product in the synthesis of cyclo[8]pyrrole (**3**),<sup>11</sup> with its isolation and characterization under more optimized chloride-anion-templated conditions appearing in 2003.<sup>6</sup> The smaller size of the cavity of **4**, relative to that of **3**, as well as the presence of six, rather than eight, potential N donor atoms, led us to propose that it would prove more suitable for the complexation of the uranyl cation than its larger congener. Indeed, all efforts to produce a stable uranyl complex of **3** have so far proved unsuccessful. In contrast, the uranyl complex of **5** could be obtained by dissolving **4** in dry  $\text{CH}_2\text{Cl}_2$  under an inert atmosphere, treating it with 2 mol equiv of  $\text{UO}_2[\text{N}(\text{SiMe}_3)_2]_2$ , and stirring the resulting mixture first under argon for 12 h and then for another 12 h after exposing to air. After removal of the solvent and purification by column chromatography (alumina; 50–200  $\mu\text{m}$ ,  $\text{CH}_2\text{Cl}_2$  eluent), followed by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexanes, the uranyl complex **5** was isolated as a green solid (Scheme 1).

As might be expected, the UV–visible spectrum of the metal complex **5**, displaying bands at 387 nm ( $\epsilon = 31\,800\text{ dm}^3\text{ cm}^{-1}\text{ mol}^{-1}$ ), 439 (25 200), and 643 (25 700), is distinct from that of **4**, either as the free base or in the form of the bis(hydrochloride) salt ( $\text{H}_2\text{4}^{2+} \cdot 2\text{Cl}^-$ ) obtained during the initial synthesis. In fact, the extinction coefficients for the Soret band are over 4 times lower than those of this latter well-characterized species. On the other hand, the peak intensity of **5** is comparable to that of the “free base” form of **4**, although the Q-like band has shifted from 849 to 649 nm for **4** and **5**, respectively (cf. Supporting Information).

It is assumed that oxidation, occurring concurrently with metal insertion under the reaction conditions employed,

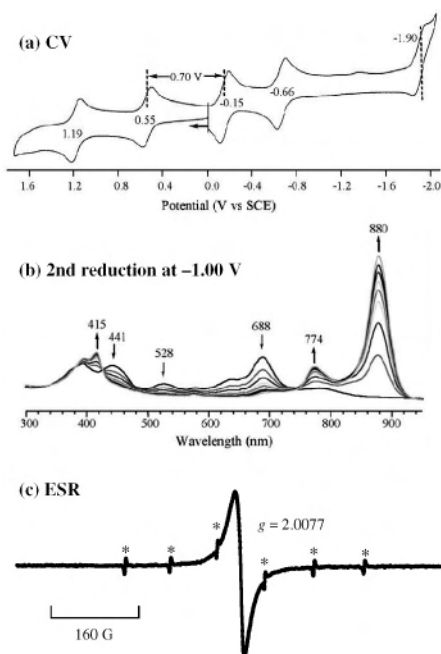


**Figure 1.** Front and side views of the uranyl complex **5**. All H atoms, two molecules of  $\text{CH}_2\text{Cl}_2$ , and the alkyl groups on the side view have been removed for clarity. Ellipsoids are scaled to the 50% probability level. Selected bond lengths ( $\text{\AA}$ ) and angles (deg): U–N(averaged) 2.535, U–O(averaged) 1.773; O–U–O 180.0°, O–U–N(averaged) 89.4°.

serves to convert the initial aromatic species, containing a 22  $\pi$ -electron periphery, to one that is formally a 20  $\pi$ -electron antiaromatic heteroannulene (cf. Scheme 1). Support for this unusual conversion came from an  $^1\text{H}$  NMR spectroscopic analysis carried out in  $\text{CD}_2\text{Cl}_2$ . It has been reported that  $\text{H}_2\text{4}^{2+} \cdot 2\text{Cl}^-$  displays one NH signal, at  $-2.12$  ppm, as well as well-resolved triplet and quartet signals that appear at 1.80 and 4.26 ppm, respectively.<sup>6</sup> However, in the case of **5**, the triplet and quartet signals, ascribed to the  $\text{CH}_2$  and  $\text{CH}_3$  protons, were found at  $-1.418$  and  $-1.120$  ppm, respectively. It is presumed that this dramatic upfield shift reflects a fundamental change in the ring current of the macrocycle from diatropic to paratropic. However, these signals, while still separate from each other, were no longer observed as a well-defined triplet or quartet but were broadened to single peaks. Cooling the  $\text{CD}_2\text{Cl}_2$  solution to  $-80^\circ\text{C}$  did not resolve these signals.<sup>12</sup>

Further confirmation of the proposed structure of **5** was obtained from a single-crystal X-ray diffraction analysis (Figure 1). Two crystallographically unique complexes were found in the asymmetric unit. However, in neither case was

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**Figure 2.** (a) Cyclic voltammogram and (b) thin-layer UV–visible spectral changes during controlled potential reductions of **5** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP at  $-1.00$  V vs SCE. (c) ESR spectrum for  $5^{\bullet-}$  produced by electron transfer from  $(\text{BNA})_2$  to **5** in  $\text{CH}_2\text{Cl}_2$  at 183 K. Asterisks denote a Mn marker.

any evidence of ancillary counterions seen, as would be consistent with the proposed oxidation of the macrocycle to the formally antiaromatic form shown in structure **5** of Scheme 1. Independent of which molecule in the lattice was considered, the system was found to be highly planar, with the deviation of the pyrrole rings ranging from  $1.8$  to  $6.4^\circ$  with respect to the mean macrocyclic plane. A comparison of these values to those reported previously for the bis-(trifluoroacetic acid) salt of **4** ( $\text{H}_2\text{4}^{2+} \cdot 2\text{TFA}^{2-}$ ), a structure wherein these angles were found to range between  $19$  and  $22.4^\circ$ , leads to the conclusion that incorporation of the uranyl cation leads to an *increase* in the planarity of the macrocycle. The uranyl cation, in a hexagonal-bipyramidal geometry, resides in the center of the macrocycle and the U–O bond lengths are similar to those seen for other  $\text{UO}_2^{2+}$  cations expanded porphyrin complexes.<sup>2,3</sup>

The electrochemical properties of complex **5** were investigated by cyclic voltammetry (CV) and spectroelectrochemistry in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). As can be seen by inspection of Figure 2a, two reversible one-electron oxidations and three reversible one-electron reductions are observed at  $E_{1/2} = 0.55, 1.19, -0.15, -0.66,$  and  $-1.90$  V. If it is presumed that the formation of the uranyl complex **5** occurs concurrent with an overall two-electron oxidation of **4**, the spectrum of **5** after a two-electron reduction should appear similar to that of **4**. When the region between  $700$  and  $900$  nm is considered, this is indeed the case as seen by inspection of Figure 2b, where the spectrum of doubly reduced **5** has an intense visible band at  $880$  nm and a lower intensity band at  $774$  nm. The shape of this spectrum is similar to that of  $\text{H}_2\text{4}^{2+} \cdot 2\text{Cl}^-$ , which has bands at  $792$  and  $704$  nm under the

same solution conditions,<sup>6</sup> with the main difference being a  $70$ – $88$  nm red shift in the case of **5**.

The energy difference between the first one-electron reduction and the first one-electron oxidation of  $0.70$  V is significantly smaller than the previously reported difference of  $1.30$  V observed in the case of **4**. Thus, the first reduction event may not be purely ligand based but rather involves partial reduction of the  $\text{U}^{\text{VI}}$  cation to the corresponding pentavalent state.

Spectroelectrochemical studies (reduction at a fixed potential of  $-0.40$  V vs saturated calomel electrode, SCE) reveal rather little change in the UV–visible spectrum, as would befit reduction processes that are not exclusively ligand-centered (cf. Supporting Information). Moreover, electron spin resonance (ESR) analyses of the one-electron-reduced species  $5^{\bullet-}$  produced by electron-transfer reduction by dimeric 1-benzyl-1,4-dihydronicotinamide  $[(\text{BNA})_2]$ <sup>13</sup> to **5** in  $\text{CH}_2\text{Cl}_2$  revealed a very broad signal with a  $g$  value of  $2.0077$  at 183 K (Figure 2c).<sup>14</sup> Such an unusually broad ESR signal with a significantly larger  $g$  value than the free-spin value ( $2.0023$ ) indicates that this is certainly not a purely ligand-centered radical anion but incorporate some contribution from a  $\text{U}^{\text{VO}_2^+}$  state.<sup>15</sup> While not a proof, the small HOMO–LUMO gap and the lack of appreciable UV–visible spectral changes produced after the first reduction are consistent with this conclusion. In any event, the addition of a second electron serves to produce an aromatic species analogous to **4**, as noted above. Under these conditions, charge-balance considerations lead us to propose that the coordinated uranyl cation is predominantly in its hexavalent state, as it is in **5**.

In summary, the first metal complex of the cyclo[ $n$ ]pyrrole series of expanded porphyrins is reported. Under normal conditions of synthesis, oxidation of the macrocycle occurs concurrently with metal insertion, with support for the oxidized nature of the isolated product coming from a combination of spectroscopic, structural, CV, and spectroelectrochemical analyses.

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**Supporting Information Available:** Experimental details and characterization data for the synthesis of compound **5** and UV–visible spectra, spectroelectrochemical data, and X-ray crystal structure data for **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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