Synthesis and Characterization of an Amethyrin-Uranyl Complex Displaying Aromatic Character

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This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (DOE) (grant DOE-FG02-01ER15186 to J.L.S.) and the Robert A. Welch Foundation (F-0018 to J.L.S.). The authors declare no competing financial interests.

Abstract: The reaction between amethyrin and non-aqueous uranyl silylamide ($UO_2[N(SiMe_3)_2]_2$) under anaerobic conditions afford a bench-stable uranyl complex. UV-Vis spectroscopy, cyclic voltammetry, as well as proton NMR spectroscopic analyses provide support for the conclusion that all six pyrrole subunits participate in coordination of the uranyl dication and that, upon complexation, the amethyrin-core undergoes a 2-electron oxidation to yield a formal 22 π-electron aromatic species.

Keywords: Amethyrin, Hexaphyrin, Expanded Porphyrin, Uranyl, Actinide

The hexaphyrin class of expanded porphyrins continues to play a key role in terms of exploring the determinants of aromaticity, as well as being central to understanding the coordination chemistry of larger porphyrinoid species [1]. Indeed, considerable effort has been devoted to the synthesis and study of classical amethyrin (**1**) [2-6], its structural isomers isoamethyrin (**2**) [7,8] and naphthoisoamethyrin [9], as well as hybrid dipyriamethyrin (**3**) [10], dithiaamethyrin [11,12], and dibenziamethyrin [12,13], among other hexaphyrin congeners [14-17] (Figure 1).

Previous studies on the coordination chemistry of amethyrin (**1**) have yielded a number of metal complexes with attendant exploration into the ligand redox chemistry [2-5]. These species in particular served to demonstrate the ability of expanded porphyrins to rearrange π-conjugation as well as deviate from planarity to allow for the formation of complexes with large cations and coordination of multiple metal ions (Figure 2). In the context of this prior work we explored whether amethyrin would stabilize a 1:1 complex with a high valent actinide cation. However, initial efforts to prepare such a complex failed to yield a well-characterized product, leading to the proposal that, if coordinated at all the actinyl cation (e.g., UO_2^{2+}, $NpO_2^{+/2+}$ or $PuO_2^{+/2+}$) would not be bound to all six nitrogen donor atoms. On the other hand, it was found that treatment of iso- or naphthoisoamethyrin [6-8] and cyclo[6]pyrrole [18] with UO_2^{2+}, and in some instances $NpO_2^{+/2+}$ and $PuO_2^{+/2+}$, furnished the corresponding actinyl coordination complex where all six nitrogen donor atoms were involved in metal cation complexation. An attendant redox switch accompanies metal complexation to yield aromatic and antiaromatic species in the case of isoamethyrin and cyclo[6]pyrrole, respectively. We thus sought to revisit the coordination chemistry of amethyrin and determine whether conditions could be found where insertion of the uranyl dication (UO_2^{2+}) could be accomplished and whether attendant changes in the electronic structure of the ligand would occur. Here, we report the synthesis and characterization of a bench-stable amethyrin-uranyl complex. In contrast to previously reported coordination modes for amethyrin [2,6], the resultant complex is characterized by hexadentate metal cation chelation with the ligand undergoing a 2-electron oxidation to yield a 22 π-electron aromatic amethyrin-core. Support for these conclusions came from proton NMR and UV-vis spectroscopic analyses, as well as cyclic voltammetry.

Treatment of the free base methyl-substituted amethyrin **4** with a non-aqueous uranyl precursor, namely uranyl silylamide [$UO_2(N(SiMe_3)_2$] [19], in anhydrous THF under anaerobic conditions yielded the corresponding uranyl

complex (**5**) as a dark red solid with green metallic luster in 83% yield, after removal of solvent and purification by flash chromatography over basic aluminum oxide (2% acetone in CH_2Cl_2, eluent) under normal laboratory conditions (Scheme 1). The product obtained in this way proved bench stable, with no evidence of degradation being observed over the course of several weeks.

Proton NMR spectroscopic studies of complex **5** revealed a downfield shift (ca. 4.17 ppm) in the signals ascribed to the *meso*-C*H* protons (i.e., from 5.73 ppm (**a**) to 9.90 ppm (**a'**); Figure 3). Downfield shifts were also observed in the peripheral methyl CH_3 protons from 1.85 (**b**), 1.83 (**c**), and 1.63 ppm (**d**) to 3.85 (**b'**), 3.62 (**c'**), and 3.42 ppm (**d'**). No signals attributed to the pyrrole N*H* protons were observed. Previous studies on related systems in which the uranyl was thought to be complexed without the attendant redox chemistry were characterized by only minute downfield shifts (ca. 0.5 ppm), which were rationalized in terms of loss in electron density arising from metal complexation [10, 20]. In analogy to what was seen upon uranyl cation complexation to iso- [6,7] and naphthoisoamethyrin [9], wherein a switch from a formally antiaromatic to aromatic species occurs, the significant downfield shifts observed in the context of complex **5** provide support for the presence of a diatropic ring current. The 2-electron oxidation needed to produce an aromatic form of **4** provides a ligand with two pyrrolic NH protons. Their removal provides a formal dianionic ligand capable of balancing the charge of the UO_2^{2+} cation. Considered in concert, the absence of N*H* protons, the dianionic nature of the oxidized ligand, and the observed chemical shift changes, serve to support the notion all six nitrogen atoms participate in coordination and that a redox switch to produce a stable uranyl complex with aromatic character occurs under the above metal insertion conditions.

As prepared, the freebase ligand **4** displays a UV-vis spectrum reminiscent of related hexaphyrin systems. Notably, a strong Soret-type band at 490 nm (ε = 28,400 M^{-1} cm^{-1}) and a smaller absorbance peak at 595 nm (ε = 3,900 $M^{-1}cm^{-1}$) are observed (Figure 4). Upon metalation, an easy-to-visualize color change from orange to red takes place. These visual changes are accompanied by a significant bathochromic shift in the Soret-like band to 520 nm, an increase in molar absorptivity (ε) to 89,200 M^{-1} cm^{-1}, as well as the appearance of a red-shifted Q-band at 826 nm (ε = 29,400 M^{-1} cm^{-1}) in the corresponding absorption spectrum (Figure 4). These changes mirror what are seen in other related systems that undergo a 2-electron oxidative switch to yield 22 π-electron aromatic forms [1,7,9].

Cyclic voltammetry studies of the free-base amethyrin **4** (1 mM) were performed in dry CH_2Cl_2 in the presence of 0.1 M [(*n*-Bu_4N)(PF_6)] in an inert glove box at room temperature. All potentials are referenced to the ferrocene/ ferrocenium (Fc/Fc^+) couple (Figure 5). Two quasi-reversible single electron oxidation waves are seen near 0 V *vs.* $Fc^{0/+}$ and are attributed to the oxidation of the 24 π-electron antiaromatic ligand to the corresponding 22 π-electron aromatic species; these features are seen at 0.0 V and 0.20 V at a scan rate of 0.1 V s^{-1}. A third quasi-reversible oxidation is also observed at 0.52 V and is tentatively assigned to additional oxidation of the amethyrin core to yield a putative 21 π-electron radical cation. Cyclic voltammetry studies on the uranyl complex **5** under similar conditions revealed two predominant higher potential reduction features at – 0.84 V and – 1.19 V and two oxidation events at 0.57 V and 0.80 V, respectively (Figure 5). The reduction features at – 0.84 V and – 1.19 V are ascribed to reduction of the ligand from a 22 π-electron aromatic form to a metalated 24 π-electron antiaromatic species electronically analogous to ligand **4** [9].

In conclusion, a bench-stable amethyrin-uranyl complex has been prepared and characterized by NMR and UV-Vis spectroscopy, as well as cyclic voltammetry. In analogy to what has been seen in the case of several related hexaphyrin congeners, ligand **4** supports the formation of a uranyl complex obtained in 83% yield by reaction with uranyl silylamide under anaerobic conditions. The present findings thus lead us to propose that, in contrast to earlier inferences, amethyrin can indeed serve as a hexadentate ligand for high valent actinyl cations and that, upon complexation of UO_2^{2+}, the as-prepared macrocycle undergoes a 2-electron oxidation to produce a 22 π-electron aromatic system.

Supporting Information.

Detailed experimental procedures, analytical data, and spectra.

Acknowledgements

JTB and HZ would like to thank the Kuhn Foundation for IE Kuhn graduate and undergraduate fellowships, respectively. GA would like to thank Fundacion Ramon Areces (Madrid, Spain) for a postdoctoral fellowship.

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Figure Captions

Figure 1. Representative hexaphyrin expanded porphyrins.

Figure 2. Potential coordination modes and π-conjugation (bolded) pathways of amethyrin.

Scheme 1. Synthesis of amethyrin-uranyl complex (**5**).

Figure 3. Partial ^{1}H NMR spectra of (top) uranyl complex **5** and (bottom) neutral macrocycle **4** in $CDCl_3$. Labels shown correspond to those of Scheme 1. An asterisk designates residual protic solvents.

Figure 4. UV-vis spectrum of ligand **4** (—) and uranyl complex **5** (- - -) recorded in CH_2Cl_2.

Figure 5. Cyclic voltammograms for ligand **4** and its uranyl complex **5** as measured in CH_2Cl_2. Further experimental details are provided in the supporting information.