Communications

Synthesis and Characterization of Actinide Mono- and Bis(porphyrin) Complexes

Sir:

There has been increasing interest in lanthanide porphyrin and phthalocyanine complexes as paramagnetic NMR shift reagents, electrochromic flat-panel displays, and potential luminescent probes of heme proteins. In contrast, the only actinide porphyrin complexes that have been described are Th(TpP)(aca)2, Th-(OEP)Cl2L2, and U(OEP)Cl2L2, while the only reported phthalocyanine complexes are Th(pc)2 and U(pc)2 and the "superphthalocyanine" UO2(N2C5H4)5. No structural data on actinide porphyrin complexes are available, and only the two uranium phthalocyanine derivatives have been crystallographically characterized. We now report the synthesis, characterization, and first X-ray crystal structure of an actinide porphyrin complex, U(TPP)Cl2(thf).

Figure 1. Molecular structure of U(TPP)Cl2(thf) (near phenyl ring omitted for clarity). Selected distances (Å) and angles (deg): U-N1 = 2.40 (1), U-N2 = 2.40 (1), U-N3 = 2.43 (1), U-N4 = 2.41 (1), U-Cl1A = 2.624 (4), U-ClB = 2.642 (4), U-O = 2.496 (9), N1-U-N2 = 73.1 (3), N2-U-N3 = 74.0 (3), N3-U-N4 = 72.7 (3), N4-U-N1 = 73.6 (3), N1-U-N3 = 115.2 (3), N2-U-N4 = 115.2 (3), C1A-U-C1B = 89.1 (1), C1A-U-O = 77.7 (2), C1B-U-O = 79.7 (2).

We have synthesized other actinide porphyrin complexes as well. The "sandwich" complex bis(5,10,15,20-tetraphenylporphyrinato)uranium(IV) may be prepared under nonacidic conditions by refluxing a solution of tetrakis(diethyiamido)uranium(IV), (U(NEt₂)₄), and 2 equiv of H₂TPP in toluene. After 12 h, the solution was evaporated to dryness and the residue chromatographed on basic alumina with CH₂Cl₂ as eluent. A purple band of H₂TPP was eluted first and discarded, and a brown second band was retained. This fraction was filtered and evaporated to dryness, and the residue was treated with chloroform/pentane to give dark purple microcrystals of (U(TPP)₂H₂O). Its electronic spectrum in CH₂Cl₂ shows a Soret band at 404 nm and less intense Q bands at 485, 550, and 620 nm (supplementary material). The fast atom bombardment mass spectrum shows a parent envelope at m/z = 1465, and the ¹H NMR data are fully consistent with a square-antiprismatic geometry similar to that of (U(NEt₂)₄)₉.

The uranium complexes reported here include the first structurally characterized actinide porphyrin. We are continuing to explore the reaction chemistry of these complexes and the synthesis of related actinide porphyrins such as the thorium analogues Th(TPP)Cl₂ and Th(TPP)₂.¹¹

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Supplementary Material Available: Electronic spectra of U(TPP)Cl₂(thf) and U(TPP)₂, ORTEP view of U(TPP)Cl₂(thf) perpendicular to the porphyrin plane with full numbering scheme, and tables of atomic coordinates and thermal parameters for the crystal structure of U(TPP)Cl₂(thf) (5 pages). Ordering information is given on any current masthead page.

12. (a) Del Piero, G.; Perego, G.; Zazzetta, A., "1,2-dichloroethane/heptane gives X-ray-diffraction-quality crystals of the tetrahydrofuran adduct U(TPP)Cl₂(thf)." A drawing of the molecular structure along with selected bond distances and angles is given in Figure 1. The coordination geometry about the uranium center is best described as a 4:3 piano stool with the porphyrin occupying the square base. The U-N distance of 2.41 Å is comparable to the U-N(sp²) contacts of 2.43 Å in (U(NEt₂)₄)₉ and 2.48 Å in U(bpy)₄, but is significantly longer than typical U-N distances of 2.20-2.25 Å in uranium amido (NR₂) complexes.¹³ The U-Cl and U-O contacts of 2.63 (1) and 2.50 (1) Å are similar to distances observed in other uranium(IV) complexes.¹⁴ The most interesting features of the structure are that the uranium atom is slightly "saucer-shaped", which may improve bonding between the nitrogen atoms and the uranium center. Such large displacements of the metal atom out of the ring plane and similar saucer- or domelike conformations of the macrocycle have been noted in the structure of U(PO₃)₅ and several lanthanide phthalocyanine¹⁵ and porphyrin¹⁶ complexes.


