Communications

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

Sir:

There has been increasing interest in lanthanide porphyrin and phthalocyanine complexes1 as paramagnetic NMR shift reagents,2 electrochromic flat-panel displays,3 and potential luminescent probes of heme proteins.4 In contrast, the only actinide porphyrin5 complexes that have been described are Th(TpP)(aca)2,6 Th-(OEP)Cl2L2,7 and U(OEP)Cl2L2,7 while the only reported phthalocyanine complexes are Th(p~)5,8 U(PC)3,9 and the "superphthalocyanine" UO2(N4C4H4)5.10 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). In addition, we report the synthesis and full spectroscopic characterization of the "sandwich" compound U(TPP)2.

5,10,15,20-Tetraphenylporphyrin, H2TPP, was treated with 5 equiv of anhydrous UC14 and excess 2,6-lutidine in benzonitrile at 150°C, while argon was slowly passed over the solution to remove HCl. Heating was continued for 4 h until the Soret band of H2TPP near 418 nm had disappeared. Removal of the solvent under vacuum and extraction of the residue with a 1:1 mixture of CH2C12/CH3CN followed by concentration and cooling to -30°C gave large red crystals of a nonstoichiometric actinolitrite solvate, U(TPP)Cl2·xCH3CN. Solvate-free U(TPP)Cl211 is readily obtained by washing with pentane followed by exposure to vacuum.

U(TPP)Cl2 is only sparingly soluble in neat CH2C12 or neat CH3CN but readily dissolves in a 1:1 mixture of these two solvents; this behavior is probably due to the formation of an actinolitrite adduct that is insoluble in that medium but soluble in dichloromethane. The electronic spectrum of UC14·xCH2C12/CH3CN shows that rotation of the phenyl groups is slow on the time scale of the NMR experiments. Complete data on U(TPP)Cl2 is presented in Table 1.

Figure 1. Molecular structure of U(TPP)Cl2(thf) (near phylen 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-ClA = 2.624 (4), U-ClB = 2.642 (4), O-U = 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).

(11) Anal. Calcd for U(TPP)Cl2: C, 57.3; H, 3.06; N, 6.08; Cl, 7.69; U, 25.8. Found: C, 57.3; H, 3.21; N, 5.88; Cl, 7.74; U, 26.0. Mps: >250°C. 1H NMR spectrum at 25°C in CD3Cl2/C6D6 shows that rotation of the phenyl groups is slow on the time scale, since five different proton environments are observed.11 One of the ortho protons is shifted significantly upward.
to $\delta$ 0.52, evidently due to its proximity to the paramagnetic (Fe) uranium(IV) center.

Recrystallization of U(TPP)Cl$_2$ from tetrahydrofuran/1,2-dichloroethane/heptane gives X-ray-diffraction-quality crystals of the tetrahydrofuran adduct U(TPP)Cl$_2$(thf)$_2$. 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 (1) Å is comparable to the U–N(sp$^3$) contacts of 2.43 Å in U(pc)$_2$ and 2.45 Å in U(bpy)$_2$ but is significantly longer than typical U–N distances of 2.20–2.25 Å in uranium amido (NR$_2$)$_2$ complexes. 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. The most interesting features of the structure are that the molecular structure along with selected bond distances and angles is given in Figure 1.

We have synthesized other actinide porphyrins as complexes with the "sandwich" complex bis[5,10,15,20-tetraphenylporphinato]uranium(IV), U(NEt$_2$)$_2$, and 2 equiv of H$_2$TPP in toluene. After 12 h, the solution was evaporated to dryness and the residue chromatographed on basic alumina with CH$_2$Cl$_2$ as eluent. A purple band of H$_2$TPP 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)$_2$.

The electronic spectrum in CH$_2$Cl$_2$ 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 $^1$H NMR data are fully consistent with a square-antiprismatic geometry similar to that of U(pc)$_2$.

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)Cl$_2$ and Th(TPP)$_2$.

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Supplementary Material Available: Electronic spectra of U(TPP)Cl$_2$(thf) and U(TPP)$_2$, ORTEP view of U(TPP)Cl$_2$(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)Cl$_2$(thf) (5 pages). Ordering information is given on any current masthead page.


