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Communications

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

Sir:

There has been increasing interest in lanthanide porphyrin and phthalocyanine complexes[1] as paramagnetic NMR shift reagents,[2] electrochromic flat-panel displays,[3] and potential luminescent probes of heme proteins.[4] In contrast, the only actinide porphyrin[5] complexes that have been described are $Th(TPP)(acac)_2$,[6] $Th(OEP)Cl_2L_2$,[7] and $U(OEP)Cl_2L_2$,[7] while the only reported phthalocyanine[5] complexes are $Th(pc)_2$,[8] $U(pc)_2$,[9] and the "superphthalocyanine" $UO_2(N_2C_8H_4)_5$.[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, $U(TPP)Cl_2(thf)$. In addition, we report the synthesis and full spectroscopic characterization of the "sandwich" compound $U(TPP)_2$.

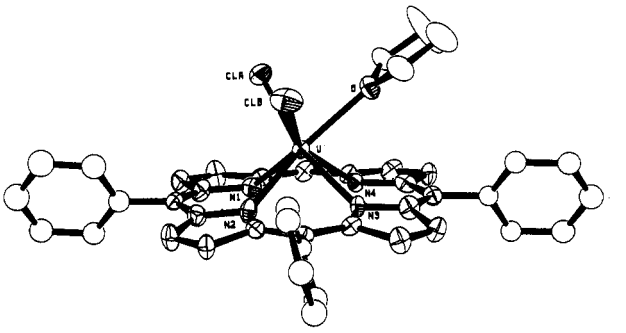

Figure 1. Molecular structure of $U(TPP)Cl_2(thf)$ (rear phenyl ring omitted for clarity). Selected distances (Å) and angles (deg): U–N1 = 2.40 (1), U–N2 = 2.40 (1), U–N3 = 2.43 (1), U–N4 = 2.41 (1), U–C1A = 2.624 (4), U–C1B = 2.642 (4), U–O = 2.496 (9); N1–U–N2 = 73.1 (3), N2–U–N3 = 74.0 (3), N3–U–N4 = 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).

5,10,15,20-Tetraphenylporphyrin, H_2TPP, was treated with 5 equiv of anhydrous UCl_4 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 H_2TPP near 418 nm had disappeared. Removal of the solvent under vacuum and extraction of the residue with a 1:1 mixture of CH_2Cl_2/CH_3CN followed by concentration and cooling to −30 °C gave large red crystals of a nonstoichiometric acetonitrile solvate, $U(TPP)Cl_2 \cdot xCH_3CN$. Solvate-free $U(TPP)Cl_2$[11] is readily obtained by washing with pentane followed by exposure to vacuum.

$U(TPP)Cl_2$ is only sparingly soluble in neat CH_2Cl_2 or neat CH_3CN but readily dissolves in a 1:1 mixture of these two solvents; this behavior is probably due to the formation of an acetonitrile adduct that is insoluble in that medium but soluble in dichloromethane. The electronic spectrum of $U(TPP)Cl_2$ in CH_2Cl_2 shows a Soret band at 427 nm and two less intense Q bands at 553 and 590 nm (supplementary material). The field-desorption mass spectrum shows a strong parent envelope at m/z = 920 for $U(TPP)Cl_2$. A 300-MHz ^1H NMR spectrum at 25 °C in CD_2Cl_2/CD_3CN shows that rotation of the phenyl groups is slow on this time scale, since five different proton environments are observed.[11] One of the ortho protons is shifted significantly upfield

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(5) Abbreviations used: TPP = 5,10,15,20-tetraphenylporphyrinato, OEP = octaethylporphyrinato, pc = phthalocyaninato, acac = 2,4-pentanedionato, thf = tetrahydrofuran.

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(11) Anal. Calcd for $U(TPP)Cl_2$: 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. Mp: >250 °C. ^1H NMR (CD_3CN/CD_2Cl_2, 25 °C): δ 8.29 (s, fwhm = 21 Hz, *o*-H), 7.67 (s, fwhm = 16 Hz, pyrrole H), 7.16 (s, fwhm = 21 Hz, *m*-H), 6.41 (t, J_{HH} = 7.2 Hz, *p*-H), 5.51 (s, fwhm = 23 Hz, *m*-H), 0.52 (s, fwhm = 27 Hz, *o*-H).

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to δ 0.52, evidently due to its proximity to the paramagnetic (f^2) 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 $U(TPP)Cl_2(thf)$.[12] A drawing of the molecular structure[13] 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^2) contacts of 2.43 Å in $U(pc)_2$[9] and 2.48 Å in $U(bpy)_4$[14] but is significantly longer than typical U–N distances of 2.20–2.25 Å in uranium amido (NR_2) complexes.[15] 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.[16] The most interesting features of the structure are that the uranium atom is 1.29 Å out of the porphyrin N_4 plane and the porphyrin ring itself 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 $U(pc)_2$[9] and several lanthanide phthalocyanine[17] and porphyrin[18] complexes.

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(diethylamido)uranium(IV), $U(NEt_2)_4$,[19] and 2 equiv of H_2TPP in toluene. After 12 h, the solution was evaporated to dryness and the residue chromatographed on basic alumina with CH_2Cl_2 as eluent. A purple band of H_2TPP 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 $U(TPP)_2$.[20] Its electronic spectrum in CH_2Cl_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 ^1H NMR data are fully consistent with a square-antiprismatic geometry similar to that of $U(pc)_2$.[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 $Th(TPP)Cl_2$ and $Th(TPP)_2$.[21]

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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.

(12) Anal. Calcd for $U(TPP)Cl_2(thf)\cdot{}^1/_2C_2H_4Cl_2$: C, 56.4; H, 3.67; N, 5.37; Cl, 10.2; U, 22.8. Found: C, 56.7; H, 3.69; N, 5.30; Cl, 10.2; U, 23.1. Mp: >250 °C. ^1H NMR (C_4D_8O, 25 °C): δ 8.55 (s, fwhm = 45 Hz, *o*-H), 7.31 (s, fwhm = 5 Hz, pyrrole H), 7.23 (s, fwhm = 45 Hz, *m*-H), 6.34 (t, J_{HH} = 7.2 Hz, *p*-H), 5.42 (s, fwhm = 48 Hz, *m*-H), 3.80 (s, $C_2H_4Cl_2$), 0.28 (s, fwhm = 48 Hz, *o*-H). The amount of 1,2-dichloroethane by integration was $^1/_2$ equiv/equiv of $U(TPP)Cl_2(thf)$.

(13) Red crystals of $U(TPP)Cl_2(thf)$ are triclinic, space group $P\bar{1}$, with a = 12.785 (4) Å, b = 14.211 (5) Å, c = 12.422 (4) Å, α = 93.85 (3)°, β = 115.69 (2)°, γ = 88.06 (3)°, V = 2029 (1) Å^3, Z = 2, d_{calcd} = 1.627 g/cm^3, and μ_{calcd} = 39.64 cm^{-1}. X-ray diffraction data were collected at 25 °C on a 0.1 × 0.1 × 0.3 mm crystal for 5683 independent reflections having $2\theta < 46°$ and for $\pm h,\pm k,+l$, on a Syntex $P2_1$ automated four-circle diffractometer using graphite-crystal-monochromated Mo Kα radiation, λ = 0.71069 Å, and $\omega/2\theta$ scans. The centric space group was confirmed by successful refinement of the proposed model. The nonunique data were averaged, and the data were corrected for Lorentz, polarization, anomalous dispersion, crystal decay (<4%), and absorption effects; for the last, the maximum and minimum transmission factors were 0.817 and 0.680. The structure was solved by Patterson methods followed by difference Fourier syntheses. All heavy atoms were independently refined with anisotropic thermal parameters except the carbon atoms of the phenyl substituents, which were independently refined isotropically. The final residuals for 386 variables refined against the 3874 data for which $I > 2.58\sigma(I)$ were R_F = 5.5% and R_{wF} = 5.5%. In the final cycle, hydrogen atoms were placed in calculated positions and included in the structure factor calculations and a common isotropic thermal parameter was refined for the group. The four largest peaks in the final difference map had electron densities of 1.1–2.2 e/Å^3 and were symmetrically disposed in pairs around the uranium center at chemically unreasonable sites, suggesting that these peaks result from inaccuracies in the scattering factors for uranium. There was no evidence in the final electron density difference map of a 1,2-dichloroethane molecule of solvation that was clearly present in the bulk sample as shown by microanalytical and ^1H NMR data. Therefore, the crystal from which data were collected differed from the bulk sample in that no solvate molecules were included in the crystal lattice.

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