2 (curve C) $D = 4 \times 10^{-10}$ cm^2/s. This corresponds, according to the Dahms–Ruff equation,[9,10] to the rate constant of the electron exchange of ca. 2×10^4 M^{-1} s^{-1}. The latter is two orders of magnitude smaller than a value obtained for a homogeneous solution.[11]

$$D = \frac{\pi}{4} k_{ex}\delta^2 C \qquad (1)$$

The results presented here are the first measurements of the lateral electron transport directly at the water/air interface under controlled surface pressure. It is easy to envision the relevance of these two-dimensional electrochemical experiments to the studies of the dynamics of lateral transport in organized monolayers and, in general, to the investigations of transport processes in biological membrane systems. Perhaps more importantly, the technique described here opens a possibility to investigate electron-transfer kinetics in well organized monolayer assemblies where the transfer of an electron involves molecules at known distances and in well defined and controllable orientations.

Acknowledgment. We gratefully acknowledge the National Science Foundation for supporting this research under Grant CHE-8504368.

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Actinide Bis(porphyrinate) π-Radical Cations and Dications, Including the X-ray Crystal Structure of $[(TPP)_2Th][SbCl_6]$

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Received November 19, 1987

The chemistry of actinide porphyrin complexes remains in large part undeveloped.[1-3] We report here the first synthesis, isolation, and detailed characterization of several actinide bis-porphyrin sandwich complexes, including the neutral, π-radical monocation, and π-radical dication complexes,[4] $[(TPP)_2M]^{n+}$, where M = Th(IV) or U(IV) and n= 0, 1, or 2. In addition, the X-ray crystal structures of both the neutral Th complex and its oxidized π-radical cation, $[(TPP)_2Th][SbCl_6]$, have been solved. These complexes are among the very first π-radical cations where close interaction between two porphyrins occurs. Moreover, these complexes belong to an unusual class of actinide complexes where redox processes can occur in near proximity to the f-element. In addition, the involvement of porphyrin π-radical cations is well established in a variety of biological processes, including the storage of oxidizing equivalents in the hydroperoxidases,[5] the oxidation of hydrocarbons by cytochrome P450,[6] and the generation of chemical potential in the photosynthetic reaction center.[7,8]

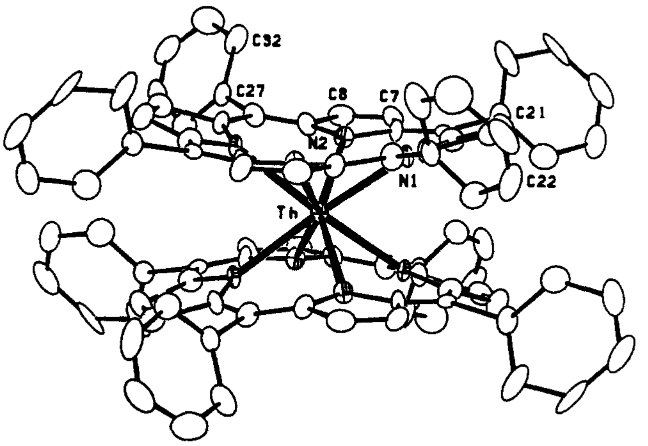

Figure 1. Molecular structure of the $[(TPP)_2Th]^+$ cation. The Th–N average bond distance is 2.52 (2) Å; the distance between mean porphyrin planes is 2.89 Å with a twist angle of 31°.

We have recently described the preparation of the "sandwich" compound $(TPP)_2U$ from $U(NEt_2)_4$ and H_2TPP in toluene[1] and find that the thorium analogue,[9] $(TPP)_2Th$, may be obtained in a similar manner from $Th(NEt_2)_4$.[10] Cyclic voltammetry experiments in $CHCl_3$ reveal that *both* $(TPP)_2M$ compounds undergo *two* chemically reversible oxidation processes near 580 and 990 mV versus SCE. The similarities of the cyclic voltammograms for the thorium and uranium complexes strongly suggest that both oxidations are porphyrin based.[11]

The oxidized $[(TPP)_2M]^+$ species may be prepared and isolated by treatment of $(TPP)_2M$ with phenoxathiinylium hexachloroantimonate,[12] $(C_{12}H_8SO)SbCl_6$, in CH_2Cl_2. Crystallization from CH_2Cl_2/toluene or CH_2Cl_2/pentane yields $[(TPP)_2Th][SbCl_6]$[13] and $[(TPP)_2U][SbCl_6]$[14] as blue-violet crystalline solids. The Soret bands of these compounds appear at 396 and 392 nm, respectively, and are shifted to higher energy with respect to the neutral precursors (402 and 404 nm). The π-radical cation nature of $[(TPP)_2M][SbCl_6]$ is supported by the presence of new bands in the IR spectra[15] of the oxidized species at 1297 and 1264 cm^{-1} for M = Th and at 1305, 1274, and 1266 cm^{-1} for M = U. The $[(TPP)_2M][SbCl_6]$ complexes are EPR active in frozen CH_2Cl_2 glasses at 77 K and exhibit signals at g = 1.9985 (line width 4.7 G) and g = 1.9975 (line width 5.9 G) for M = Th and U, respectively. In each case there is no observed anisotropy in the g-tensor under these experimental conditions.

$[(TPP)_2Th][SbCl_6]$ is NMR silent in CH_2Cl_2, but $[(TPP)_2U][SbCl_6]$ is not (although the lines are broadened), which

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(14) Anal. Calcd for $[(TPP)_2U][SbCl_6]\cdot 2C_7H_8\cdot 2CH_2Cl_2$: C, 58.0; H, 3.7; N, 5.2; U, 11.1; Sb, 5.7; Cl, 16.5. Found: C, 58.7; H, 3.6; N, 4.9; U, 10.9; Sb, 5.7; Cl, 17.1. ^{1}H NMR (CD_2Cl_2, –60 °C) δ 9.00 (d, J_{HH} = 6.2 Hz, o-H), 8.85 (s, fwhm = 18 Hz, m-H), 5.80 (t, J_{HH} = 7.0 Hz, p-H), 3.82 (s, fwhm = 27 Hz, m-H), 0.47 (s, fwhm = 30 Hz, o-H), –3.48 (s, fwhm = 29 Hz, pyrrole-H).

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suggests that there is some interaction between the unpaired electrons of the f^2 U(IV) center and the single unpaired electron of the porphyrin radical. $[(TPP)_2U][SbCl_6]$ in CH_2Cl_2 at −60 °C exhibits six broadened ^1H NMR signals;[14] the pattern is similar to that of the unoxidized starting precursor[1] $(TPP)_2U$ except that the pyrrole signal is shifted significantly upfield. In the diamagnetic limit (infinite temperature), the five phenyl proton signals of $[(TPP)_2U][SbCl_6]$ collapse to the normal δ 6 to 9 ppm region while the pyrrole signal extrapolates instead to δ −14 ppm. This behavior indicates that the porphyrin π-radical cation possesses high unpaired spin density near the pyrrole protons.

The $[(TPP)_2M][SbCl_6]$ complexes in CH_2Cl_2 exhibit very broad, intense ($\epsilon \sim 10^3$ cm^{-1} M^{-1}), featureless absorptions in the near-IR region at 1480 nm (fwhm 300 nm) and 1270 nm (fwhm 140 nm) for M = Th and U, respectively. These bands were first assigned in the analogous Ce(IV) complex to interporphyrin charge-transfer transitions;[11] recent resonance Raman data,[16] however, show that the electron hole is delocalized over both porphyrins, which implies that this interporphyrin transition involves little charge transfer. Of interest in this context is the near-infrared transition observed in the special pair of bacteriochlorophyll-b found in the bacterial reaction center protein of *Rhodopseudomonas viridis*.[7,8] The special pair radical cation dimer, $(BChl)_2^+$, has an interplanar spacing of ≈3 Å and a characteristic intramolecular transition at 1300 nm.[8] For comparison, $[(TPP)_2Th][SbCl_6]$ has an interplanar spacing of 2.89 Å (see below) and an absorption at 1480 nm. Similar comparisons have previously been made for the lanthanide bis(porphyrinate) cations.[11a,b]

$(TPP)_2Th$ and $[(TPP)_2Th][SbCl_6]$ have been structurally characterized by X-ray crystallography (Figure 1).[17] While the $(TPP)_2Th$ units in both the neutral species and the cation are generally similar, the Th–N bond distances, 2.55 (1) versus 2.52 (2) Å, and the displacement of the thorium atom from the mean N_4 plane of the porphyrinate core, 1.47 versus 1.45 Å, are slightly smaller in the cation. The structural parameters are similar to those of the half-sandwich complexes[1,2] $(TPP)UCl_2(thf)$ and $(OEP)Th(acac)_2$: the Th–N bond distances of the latter average 2.50 Å and the Th out-of-plane distance, Th–N_4, is 1.43 Å. The porphyrinate N_4 planes of $[(TPP)_2Th][SbCl_6]$ are 2.89 Å apart with a twist angle of ~30°, resulting in a distorted square antiprismatic geometry about thorium; this may be compared to the 2.75 Å interplanar spacing and a twist angle of 42° between the porphyrinate rings in the neutral species $(OEP)_2Ce$.[11,18] The difference in interplanar spacing between the Th and Ce complexes reflects the smaller ionic radius[19] of Ce^{IV} versus Th^{IV} and possibly the reduced steric demand of OEP versus TPP. Due to the high point symmetry of the crystallographic site (222), the two porphyrinate rings in $[(TPP)_2Th][SbCl_6]$ are crystallographically identical, and no variations of the C–C or C–N bond lengths are apparent. We note that the porphyrinate rings in $[(TPP)_2Th][SbCl_6]$ are close enough together to allow significant direct overlap of the two π-systems. Consistent with this, the NMR spectra suggest complete delocalization of the unpaired electron over both porphyrinate rings.

Preliminary spectroscopic characterization of the bis(porphyrin) dications $[(TPP)_2M][SbCl_6]_2$ (M = Th, U) has also been completed.[20] These compounds are prepared in the same fashion as the monocations but with the use of 2 equiv of $(C_{12}H_8SO)SbCl_6$. The complexes possess intense near-infrared bands at 1080 nm (M = Th) and 990 nm (M = U), and spectroscopic data are consistent with a bis[porphyrin π-radical cation] formulation. Further characterization of the magnetic coupling present in these bis(porphyrinato)metal systems is underway.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (Grant No. HL 25934) for their support. K.S.S. gratefully acknowledges an NIH Research Career Development Award. Both K.S.S. and G.S.G. are recipients of Sloan Foundation Research Fellowships. We particularly thank Dr. Scott Wilson, Charlotte Stern, and Connie Odle of the University of Illinois X-ray Crystallographic Laboratory for performing the structural analysis. We also thank Professor D. F. Bocian for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and complete bond distances and angles for $(TPP)_2Th$ and $[(TPP)_2Th][SbCl_6]$ (8 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(17) Crystal data for $(TPP)_2Th\cdot C_7H_8$ (T = 25 °C): space group $I2/a$, a = 15.377 (4) Å, b = 31.119 (6) Å, c = 15.378 (3) Å, β = 90.59 (2)°, V = 7358 (5) Å^3, Z = 4, R_F = 5.4%, R_{wF} = 6.9% on 333 variables and 3646 unique data with $I > 2.58\sigma(I)$. Crystal data for $[(TPP)_2Th][SbCl_6]\cdot 2C_7H_8\cdot CH_2Cl_2$ (T = 25 °C): space group $P4/nnc$, with a = 19.104 (3) Å, c = 26.335 (3) Å, V = 9612 (4) Å^3, Z = 4, R_F = 6.5%, R_{wF} = 10.6% on 248 variables and 1894 unique data with $I > 2.58\sigma(I)$. All non-hydrogen atoms except those of the solvate molecules were refined with independent anisotropic thermal parameters. The refinement of $[(TPP)_2Th][SbCl_6]$ was complicated by the presence of disordered solvate molecules; however, the structural parameters of the $[(TPP)_2Th]$ cation are well defined.

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Theory of Vibrational Circular Dichroism: *trans*-2,3-Dideuteriooxirane

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Received November 9, 1987

We have recently developed[1-3] and implemented[3-10] an a priori theory of vibrational rotational strengths and vibrational circular dichroism (VCD) spectra. To date, comparisons of this theory with experimental VCD spectra have been limited by the paucity

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