Communications to the Editor

Preparation and Characterization of the First Organoactinide Polysulfide ($(\eta^5\text{-}C_5Me_5)_2ThS_5$). A Unique Example of the Twist-Boat Conformation of the MS_5 Ring

Debra A. Wrobleski, Don T. Cromer, J. V. Ortiz,[1a]
Thomas B. Rauchfuss,[1b,c] Robert R. Ryan,* and
Alfred P. Sattelberger

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

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Polysulfide chelates (S_x^{2-}) are an emerging class of inorganic ligands whose reactions are of interest to transition-metal and main-group specialists alike. Stable derivatives have been synthesized for most of the d-block elements, and a wide range of MS_x ring sizes (x = 2–7, 9) and bonding modes have been established via X-ray crystallography.[2] The reaction chemistry of these transition-metal derivatives is frequently complex,[3] but there are a number of useful synthetic applications such as the high-yield preparations of cyclo-S_6 and -S_7 from Cp_2TiS_5 ($Cp = \eta^5\text{-}C_5H_5$) and S_xCl_2 (x = 1, 2).[4] To date, polysulfido chelates have not been introduced into the coordination spheres of f elements, but this is an obvious extension for the area and an opportunity to study the effects of the larger ionic radii and higher Lewis acidities of f elements on MS_x ring sizes, conformations, and reactivity patterns. We report here the synthesis, properties, and structure of the first actinide polysulfido complex, bis(pentamethylcyclopentadienyl)thorium pentasulfide, and provide some theoretical insight on the nature of the Th(IV)–S_5^{2-} interactions.

Treatment of $Cp^*_2ThCl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[5] with an equimolar quantity of Li_2S_5, generated in situ by reaction of sulfur with lithium triethylborohydride in THF,[6] gave yellow crystalline $Cp^*_2ThS_5$,[7] **1**, in ca. 75% isolated yield. The 200-MHz proton NMR spectrum of **1**, in toluene-d_8, is temperature-independent over the range 25 to −90 °C and shows a single, sharp methyl resonance at δ 2.03 in contrast to nonequivalence of Cp rings[8] observed for Cp_2TiS_5 in which the MS_5 ring is in the chair conformation.[9] At 25 °C, the proton NMR spectrum of $(\eta^5\text{-}C_5Me_4Et)_2ThS_5$[10] shows two sharp Cp_5Me_4Et *ring* methyl resonances. Upon cooling, these resonances broaden and, at ca. −50 °C, four sharp *ring* methyl singlets are resolved. The two C_5Me_4Et ring ethyl resonances[10] are sharp multiplets at 25 °C; as the temperature is lowered, the CH_2CH_3 quartet and CH_2CH_3 triplet broaden significantly but do not split. This behavior, coupled with the NMR data obtained for **1**, is consistent with a fluxional twist-boat ThS_5 ring conformation (eq 1). The barrier to interconverting conformers was calculated to be 57.4 (5) kJ mol^{-1}, on the basis of the observed coalescence temperature of **2** and the frequency separations in the low-temperature limiting spectrum.[11]

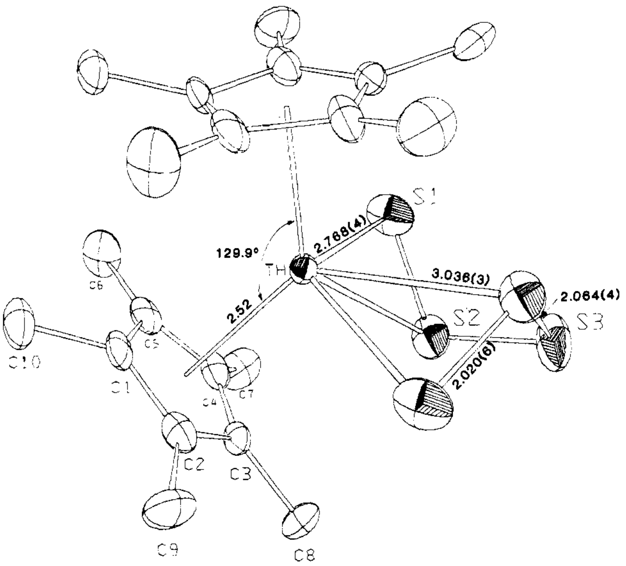
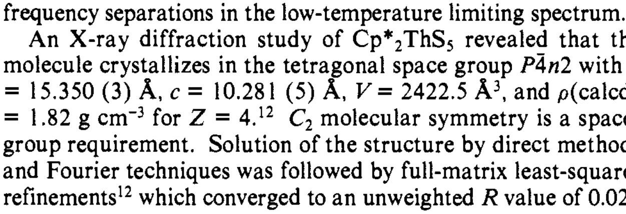


Figure 1. ORTEPII drawing of the $Cp^*_2ThS_5$ molecule. Distances in angstroms, angles in degrees. Hydrogen atoms have been omitted for clarity (30% thermal ellipsoids). Angles: Th–S_1–S_2 = 76.9 (2)°, Th–S_2–S_1 = 62.7 (2)°, S_2–Th–S_2' = 63.6 (1)°, S_1–Th–S_1' = 113.3 (1)°, S_1–S_2–S_3 = 108.2 (3)°.



(1)

An X-ray diffraction study of $Cp^*_2ThS_5$ revealed that the molecule crystallizes in the tetragonal space group $P\bar{4}n2$ with a = 15.350 (3) Å, c = 10.281 (5) Å, V = 2422.5 Å^3, and ρ(calcd) = 1.82 g cm^{-3} for Z = 4.[12] C_2 molecular symmetry is a space-group requirement. Solution of the structure by direct methods and Fourier techniques was followed by full-matrix least-squares refinements[12] which converged to an unweighted R value of 0.028 (Figure 1).

The molecular structure of **1** confirms the presence of a twist-boat ThS_5 ring. This ring stereochemistry is unprecedented among MS_5-containing transition-metal complexes, all of which exhibit MS_5 chair conformations.[2] The latter group includes Cp_2TiS_5[9] and its Zr and Hf analogues.[6] Only the terminal sulfurs of the S_5^{2-} chelates are coordinated to M in these systems, and the chair conformations mimic that found in cyclo-S_6.[4] The change in ring conformation from the nd^0 transition-metal complexes to

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(1) (a) Department of Chemistry, University of New Mexico, Albuquerque, NM 87131. (b) School of Chemical Sciences, University of Illinois, Urbana, IL 61801. (c) Fellow of the Alfred P. Sloan Foundation (1983–1985); Camille and Henry Dreyfus Teacher-Scholar (1983–1988).

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(7) Anal. Calcd for $C_{20}H_{30}S_5Th$: C, 36.24; H, 4.56; S, 24.20; Th, 35.02. Found: C, 36.33; H, 4.62; S, 23.88; Th, 35.17. ^1H NMR (200.1 MHz, toluene-d_8): 2.032 (s, Cp*).

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(10) Cp''_2ThS_5 ($Cp'' = C_5Me_4Et$) was prepared from Cp''_2ThCl_2 in the same manner as for $Cp^*_2ThS_5$. Cp''_2ThCl_2 was prepared from the Cp″MgCl·THF using the method of Marks et al.[5] Cp''_2ThCl_2: ^1H NMR (200.1 MHz, toluene-d_8, 25 °C) δ 2.47 (q, CH_2CH_3, ^3J(H–H) = 7 Hz), 1.96 (s, CH_3), 1.91 (s, CH_3), 0.77 (t, CH_2CH_3, ^3J(H–H) = 7 Hz). Cp''_2ThS_5: ^1H NMR (200.1 MHz, toluene-d_8, 25 °C) δ 2.58 (q, CH_2CH_3, ^3J(H–H) = 8 Hz), 2.08 (s, CH_3), 2.01 (s, CH_3), 0.82 (t, CH_2CH_3, ^3J(H–H) = 8 Hz).

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(12) Crystal data are presented as supplementary material.

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1 is presumably a consequence of coordination of four ring sulfur atoms, i.e., S1, S1′, S2, and S2′, to thorium (vide infra). The Th–S1 and Th–S2 distances are 2.768 (4) and 3.036 (3) Å, respectively. These values bracket the average Th–S bond lengths in Th(S$_2$PMe$_2$)$_4$[13] (2.90 Å), Th(S$_2$CNEt$_2$)$_4$[14] (2.87 Å), Th$_2$S$_3$[15] (2.90 Å), and ThS$_2$[16] (2.95 Å). The Th–S2 bond may be thought of as a dative bond while the Th–S1 bond is best described as ionic. The difference in Th–S bond lengths of 0.268 Å is comparable to the difference of 0.284 Å observed for the phosphine and phosphide systems, Th(CH$_2$Ph)$_4$(dmpe)[17] (where dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) and Cp*$_2$Th(PPh$_2$)$_2$,[18] thereby supporting coordination of S2 to thorium. Donor bonding from S2 and S2′ to the Lewis acidic Th(IV) center manifests itself in two other ring metrical parameters. The S1–Th–S1′ angle of 113.3 (1)° is 14–20° larger than X–Th–X angles previously reported in Cp*$_2$ThX$_2$ complexes,[18,19] and the Th–S1–S2 angle at 76.9 (2)° is the smallest M–S–S angle (by 30°) observed in an MS$_5$ ring.[2,9] The S–S distances, on the other hand, are comparable to those found in Cp$_2$TiS$_5$.[9] The methyl-substituted (C$_5$Me$_{5-x}$H$_x$)$_2$M complexes are invariably found as staggered rotamers,[2] which would also tend to stabilize the twist-boat conformation for the ThS$_5$ ring due to nesting of the methyl groups. Other metrical parameters associated with **1**, e.g., the Th–Cp* distance and Cp*–Th–Cp* angle, are unexceptional.

Thorium–sulfur bonding in **1** has been investigated by using extended Hückel molecular orbital calculations[20] performed on the model compound (C$_5$H$_5$)$_2$ThS$_5$. These calculations show a variety of bonding interactions between the Cp$_2$Th and S$_5$ fragments. Bonding between the two highest occupied molecular orbitals of S$_5^{2-}$ and Cp$_2$Th^{2+} virtual orbitals composed of 6d, 7s, and 7p produces the largest overlap populations between fragments. The HOMO of S$_5^{2-}$ is antisymmetric with respect to the C_2 axis while the level just beneath it in energy is symmetric. All five sulfur atoms contribute to these orbitals, but the β sulfurs have more electron density (about 0.95 electrons) than the α sulfurs (0.70) or the γ sulfur (0.35). Symmetry-adapted combinations of the p orbitals on the β sulfurs in these two orbitals point toward the plane that contains Th and the Cp centroids. The C_{2v} Cp$_2$Th^{2+} fragment has an empty b$_1$ orbital, a hybrid of xz and x metal character, that stabilizes the S$_5^{2-}$ HOMO. Another metal fragment empty orbital has a_1 symmetry, being a mixture of z^2 and x^2–y^2; this orbital stabilizes the second HOMO of S$_5^{2-}$. Both of these interactions give rise to more Th bonding to the β sulfur than to the α sulfur, but the aggregate of many other interfragment mixings (too small and numerous to discuss here) produces an overall Th–α-sulfur overlap population that exceeds the overall Th–β-sulfur overlap population.

In summary, the unusual twist-boat ThS$_5$ ring conformation in **1** is likely a consequence of donor–acceptor bonding between the β-sulfur atoms of the S$_5^{2-}$ chelate and the electron-deficient thorium(IV) center. An extension of polysulfide chemistry to other actinide ions, as well as an examination of the effect of MS$_5$ ring conformation on ring reactivity, are projects currently underway in this laboratory.

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Supplementary Material Available: Crystal data and tables of final atomic positional and thermal parameters, and observed and calculated structure factors for complex **1** (8 pages). Ordering information is given on any current masthead page.

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Photoinduced C–C Bond Cleavage via Electron-Transfer Reactions: Visible-Light-Mediated Scission of Tertiary Amines

Lester Y. C. Lee, Xiaohong Ci, Charles Giannotti,[1] and
David G. Whitten*

Department of Chemistry, University of Rochester
Rochester, New York 14627
CNRS-Institut de Chimie des Substances Naturelles
F91190 Gif-sur-Yvette, France

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Electron-transfer quenching of potential excited acceptors including such diverse molecules as ketones, metal complexes, hydrocarbons, and dyes is a well-documented reaction.[2–10] Frequently used donors in these reactions include various tertiary amines such as triethylamine.[10–15] Depending upon the amine, the most often observed fates for the photochemically produced radical cation in solution are back electron transfer or deprotonation; deprotonation at the α-carbon of tertiary amines produces a neutral but rather strongly reducing free radical which, after electron loss, gives an iminium ion which can often be hydrolyzed to give a secondary amine and a carbonyl compound.[10,12,14–16] The deprotonation of tertiary amine radical cations involves reaction of carbon acids, which might be anticipated to be relatively slow; however, laser flash spectroscopic investigations indicate this process can occur extremely fast, on the scale of picoseconds.[14,17–19] An alternative fate of reactive amine radical cations could be cleavage of a carbon–carbon σ bond α to the nitrogen; this reaction

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