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# Synthesis, Structural Characterization, and Properties of the Organothorium Alkylthiolate Complex $[(CH_3)_5C_5]_2Th(SCH_2CH_2CH_3)_2$

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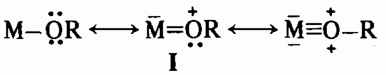
## Abstract

This contribution reports the synthesis and characterization of the organothorium alkylthiolate complex $[(CH_3)_5C_5]_2Th(SCH_2CH_2CH_3)_2$. This compound crystallizes in the monoclinic space group *C2/c* (#15) with four molecules in a cell of dimensions $a = 19.066(2)$, $b = 11.603(1)$, $c = 16.379(2)$ Å, and $\beta = 130.08(1)°$. Least-squares refinement led to a value for the conventional $R$ index (on $F_o$) of 0.040 for 132 variables and 2030 observations having $F_o^2 \geqslant 3\sigma(F_o^2)$. The molecular structure consists of an unexceptional 'bent sandwich' $[(CH_3)_5C_5]_2Th$ fragment coordinated to two n-propylthiolate ligands. The Th–S bond distance is 2.718(3) Å; the S–C(α) distance, 1.78(2) Å; the Th–S–C(α) angle, 108.3(5)°; and the S–Th–S′ angle, 102.5(2)°. Contrasts are drawn with the structures of analogous actinide alkoxides.

## Introduction

Alkoxide functionalities play important roles in organoactinide chemistry [1] both as reactivity-modulating ancillary ligands and as end-products in a variety of transformations (e.g., CO activation processes) [1, 2]. Thermochemical data indicate that actinide–alkoxide bonds are very strong ($D$(Th–OR) ≈ 120 kcal mol$^{-1}$) [1, 3] while structural [4] (short An–OR distances, obtuse An–O–C(α) angles) and theoretical [5] results argue that ligand-to-metal $\pi$ donation (e.g., **I**) represents an important component of the bonding. In contrast, few actinide alkylthiolates have been reported [6]** and none has been structurally characterized. We report here the synthesis and characterization, including a single crystal diffraction study, of the thorium bis(alkylthiolate), $Cp'_2Th[S(n\text{-}Pr)]_2$, $Cp' = \eta^5\text{-}(CH_3)_5C_5$ [7].



$$\mathrm{M}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\mathrm{R} \longleftrightarrow \bar{\mathrm{M}}=\underset{\cdot\cdot}{\overset{+}{\mathrm{O}}}\mathrm{R} \longleftrightarrow \underline{\bar{\mathrm{M}}}\equiv\underset{+}{\overset{+}{\mathrm{O}}}-\mathrm{R}$$

**I**

## Experimental

### *Materials and Methods*

All organoactinide compounds are exceedingly air- and moisture-sensitive, and hence were handled in Schlenk-type glassware interfaced to a high vacuum line, or on a Schlenk line, or in a $N_2$-filled glove box. Solvents were predried and distilled from Na/K/benzophenone. The gases Ar, $H_2$, CO and $N_2$ were purified by passage through a supported MnO oxygen removal column and a Davison 4 Å molecular sieve column. The complex $Cp'_2ThMe_2$ was prepared by the literature procedure [2c].

### *Synthesis of $Cp'_2Th[S(n\text{-}Pr)]_2$*

A 30 ml flask was charged with 0.40 g (0.75 mmol) of $Cp'_2ThMe_2$. Next, 15 ml of toluene was condensed into the flask, and then a ten-fold excess of HS(n-Pr) (Aldrich, predried over $CaCl_2$, then over freshly activated 4 Å molecular sieves) was condensed in. The reaction mixture was stirred at −78 °C for 0.5 h, then at room temperature for 2.5 h. The volatiles were next removed in vacuo, 20 ml of pentane was condensed into the flask, and the resulting solution was filtered. The residual solids were washed once with 3 ml pentane and the volume of the filtrate was reduced to *ca.* 10 ml. Slow cooling and cold filtration (−78 °C) afforded a white crystalline solid. Yield: 53%. $^1$H NMR ($C_6D_6$): $\delta$ 3.13 (t, 4H), 2.12 (s, 30H), 1.78 (quart., 4H), 1.06 (t, 6H). *Anal.* Calc. for $C_{26}H_{44}S_2Th$: C, 47.84; H, 6.79; S, 9.82. Found: C, 47.83; H, 6.89; S, 9.84%.

### *X-ray Crystallographic Study of $Cp'_2Th[S(n\text{-}Pr)]_2$*

The compound $Cp'_2Th[S(n\text{-}Pr)]_2$ crystallizes from pentane as colorless broken polyhedra in a C-centered monoclinic cell with dimensions $a = 19.066(2)$, $b = 11.603(1)$, $c = 16.379(2)$ Å, $\beta = 130.08(1)°$, and $Z = 4$ at 225 K ($D_{calc} = 1.564$ g cm$^{-3}$). The extinctions are consistent with the space groups *Cc* (#9) and *C2/c* (#15); in the latter case the molecule must be located on a two-fold rotation axis. Data in a quadrant of reciprocal space (3167 unique reflections having $2\theta \leqslant 55°$) were measured at 225 K on an Enraf-Nonius CAD4 diffractometer using Mo Kα

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**In ref. 6c the synthesis of several actinide alkylthiolates has been reported.

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radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. An empirical correction was made for absorption [crystal size: $0.40 \times 0.40 \times 0.25$ mm; $\mu = 57.20$ cm$^{-1}$; factors (on **I**): 0.53–1.00] and for decomposition (−2.3% over 4 days).

Th–Th and Th–S vectors were located readily in an origin-removed, sharpened Patterson function, and were most simply interpreted in terms of the centrosymmetric space group *C*2/*c*. The C atoms were subsequently located, with some difficulty, in difference Fourier maps. The $(CH_3)_5C_5$ ring is well-defined (see Fig. 1 and the tables of bond lengths and angles), but the entirety of the propyl group is not. The anisotropic displacement parameters for C(12) and C(13) are very large and their bond lengths and angles are not physically reasonable. We conclude that this group is disordered, probably by an approximate 180° rotation about an axis passing through C(11) and a point near the midpoint of the C(12)–C(13) vector. The electron-density in this region has the general form of a slab; the only clear maxima in the distribution correspond to the positions refined for atoms C(12) and C(13). At some temperature below *ca.* 220 K, the crystal undergoes a destructive phase transition in which the C-centering is lost and the volume of the unit cell is doubled. Below the phase transition the propyl groups are probably ordered.

The structure was refined (Enraf-Nonius Structure Determination Package [8]; neutral-atom scattering factors [9]; no contribution from H atoms; full-matrix least-squares) to agreement factors $R$ and $R_w$ on $F_o$ of 0.040 and 0.044 for 132 variables and the 2030 observations having $F_o^2 \geqslant 3\sigma(F_o^2)$. The error in an observation of unit weight is 1.49. The largest features of the final difference Fourier map have heights 0.82 and −1.20 e Å$^{-3}$. The two largest peaks are associated with the Th atom, and the next five are in the region of the propyl group. The deepest trough is near the Th, the C(1) and the C(2) atoms, and the next two deepest are in the vicinity of the ring center.

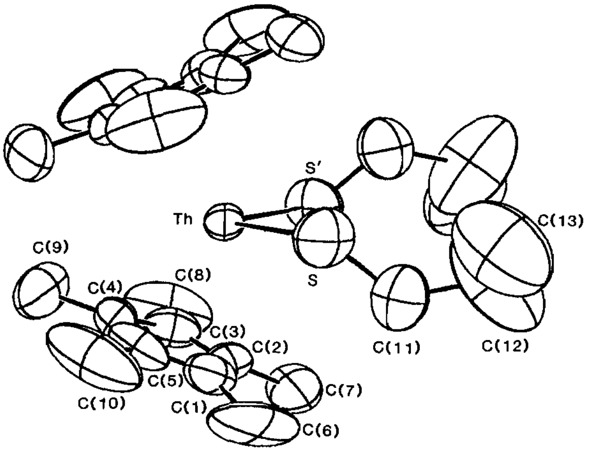

Fig. 1. Perspective drawing of the molecular structure of $Th[(CH_3)_5C_5]_2[SCH_2CH_2CH_3]_2$. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement, and the hydrogen atoms have been omitted for the sake of clarity.

## Results and Discussion

### *Synthesis and Reactivity*

The thorium alkylthiolate $Cp'_2Th[S(n\text{-}Pr)]_2$ can be cleanly prepared in high yield via the route of eqn. (1). It was characterized by standard spectroscopic

$$Cp'_2ThMe_2 + 2n\text{-}PrSH \xrightarrow{\text{toluene}} Cp'_2Th[S(n\text{-}Pr)]_2 + 2CH_4 \qquad (1)$$

and analytical methodology. Interestingly, attempted NMR-scale reactions of $Cp'_2Th[S(n\text{-}Pr)]_2$ with CO or $H_2$ in toluene-$d_8$ showed no change at temperatures as high as 100 °C for periods of several weeks. Reaction with t-butanol rapidly and cleanly yielded the known [3b] alkoxide complex (eqn. (2))

$$Cp'_2Th[S(n\text{-}Pr)]_2 + 2t\text{-}BuOH \longrightarrow Cp'_2Th[O(t\text{-}Bu)]_2 + 2n\text{-}PrSH \qquad (2)$$

### *Molecular Structure of $Cp'_2Th[S(n\text{-}Pr)]_2$*

Single crystals of $Cp'_2Th[S(n\text{-}Pr)]_2$ suitable for X-ray diffraction were grown by slow cooling of pentane solutions. The structural analysis reveals discrete, mononuclear molecules having the familiar pseudo-tetrahedral 'bent sandwich' coordination geometry [1] (Fig. 1) and located on a crystallographic two-fold axis. Final positional parameters are listed in Table I, while bond lengths and bond angles are given in Tables II and III, respectively. As can be seen from these data, the metrical parameters associated with the $Cp'_2Th$ fragment are unexceptional. Thus, the Cg–Th–Cg (Cg = ring center-of-gravity) angle of 134.9°, the average Th–C(ring) distance of 2.799(8) Å, and the Th–Cg distance of 2.535 Å are in good agreement with results for other $Cp'_2ThX_2$ complexes [1, 10].

In regard to the $Th(SCH_2CH_2CH_3)_2$ fragment, the accuracy of the metrical parameters associated with the $\beta$ and $\gamma$ carbon atoms is limited by disorder. This is evident from the magnitudes of the thermal parameters and the C(12)–C(13) distance (see 'Experimental' for details). However, the $Th(SC_\alpha)_2$ portion of the molecule should be described with reasonable accuracy. The present Th–S bond distance of 2.718(3) Å is somewhat shorter than the corresponding distances of 2.768(4) in $Cp'_2ThS_5$ [11], 2.930(4), 2.878(4) Å in $Th(S_2PMe_2)_4$ [12], and 2.85(1), 2.87(1) Å in $Th(S_2CNEt_2)_4$ [13]. Subtracting an sp$^3$ carbon covalent

TABLE I. Positional Parameters and Equivalent $B$ Values for the Atoms of $Th[(CH_3)_5C_5]_2[SCH_2CH_2CH_3]_2$[a]

| Atom | $x$ | $y$ | $z$ | $B_{equ}$ (Å$^2$) |
|---|---|---|---|---|
| Th | 0.000 | 0.02033(4) | 0.250 | 3.843(8) |
| S | 0.0039(2) | −0.1263(3) | 0.3823(2) | 8.68(9) |
| C(1) | 0.1829(5) | 0.046(1) | 0.3393(6) | 6.8(3) |
| C(2) | 0.1896(5) | 0.018(1) | 0.4290(7) | 6.5(3) |
| C(3) | 0.1547(5) | 0.107(1) | 0.4458(5) | 6.0(3) |
| C(4) | 0.1281(5) | 0.1951(9) | 0.3737(7) | 6.5(3) |
| C(5) | 0.1456(5) | 0.154(1) | 0.3054(6) | 6.5(3) |
| C(6) | 0.2254(6) | −0.017(2) | 0.2986(9) | 18.3(5) |
| C(7) | 0.2354(9) | −0.089(1) | 0.496(2) | 15.5(7) |
| C(8) | 0.1526(7) | 0.116(2) | 0.5394(7) | 12.9(6) |
| C(9) | 0.0998(9) | 0.313(1) | 0.387(1) | 16.5(8) |
| C(10) | 0.1366(8) | 0.216(2) | 0.2146(9) | 14.6(5) |
| C(11) | −0.0737(9) | −0.241(2) | 0.305(1) | 11.3(5) |
| C(12) | −0.052(1) | −0.388(3) | 0.332(1) | 18.8(9) |
| C(13) | 0.000(1) | −0.380(3) | 0.428(1) | 20(1) |

[a]The equivalent displacement parameter is defined as (4/3)Tr(β·G), where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

TABLE II. Bond Lengths (Å) in $Th[(CH_3)_5C_5]_2[SCH_2CH_2CH_3]_2$[a]

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| Th | S | 2.718(3) | C(2) | C(3) | 1.36(1) |
| Th | C(1) | 2.797(8) | C(2) | C(7) | 1.50(2) |
| Th | C(2) | 2.831(7) | C(3) | C(4) | 1.38(1) |
| Th | C(3) | 2.798(7) | C(3) | C(8) | 1.56(1) |
| Th | C(4) | 2.795(8) | C(4) | C(5) | 1.44(1) |
| Th | C(5) | 2.776(8) | C(4) | C(9) | 1.53(2) |
| Th | Cg | 2.535 | C(5) | C(1) | 1.38(2) |
| S | C(11) | 1.78(2) | C(5) | C(10) | 1.56(1) |
| C(1) | C(2) | 1.43(1) | C(11) | C(12) | 1.75(3) |
| C(1) | C(6) | 1.53(1) | C(12) | C(13) | 1.20(3) |

[a]Numbers in parentheses are estimated standard deviations in the least significant digits. Cg is the centroid of the ring composed of atoms C(1) through C(5).

TABLE III. Selected Bond Angles (deg) in $Th[(CH_3)_5C_5]_2[SCH_2CH_2CH_3]_2$[a]

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|
| S | Th | S′ | 102.5(2) | C(2) | C(3) | C(4) | 110.4(8) |
| S | Th | Cg | 100.2 | C(2) | C(3) | C(8) | 126(1) |
| S | Th | Cg′ | 107.6 | C(4) | C(3) | C(8) | 124(1) |
| Cg | Th | Cg′ | 134.9 | C(3) | C(4) | C(5) | 106.4(8) |
| Th | S | C(11) | 108.3(5) | C(3) | C(4) | C(9) | 120(1) |
| C(2) | C(1) | C(5) | 107.7(9) | C(5) | C(4) | C(9) | 133(1) |
| C(2) | C(1) | C(6) | 128(1) | C(1) | C(5) | C(4) | 107.8(8) |
| C(5) | C(1) | C(6) | 124(1) | C(1) | C(5) | C(10) | 121(1) |
| C(1) | C(2) | C(3) | 107.6(9) | C(4) | C(5) | C(10) | 131(1) |
| C(1) | C(2) | C(7) | 125(1) | S | C(11) | C(12) | 127(2) |
| C(3) | C(2) | C(7) | 128(1) | C(11) | C(12) | C(13) | 97(3) |

[a]Numbers in parentheses are estimated standard deviations in the least significant digits. Cg is the centroid of the ring composed of atoms C(1) through C(5). The S′ atom and Cg′ are related to the S atom and Cg by the two-fold axis that passes through the molecule.

radius [14] of 0.77 Å from a normal Th–C(sp$^3$) distance taken to be *ca.* 2.50 Å (as found in typical Cp$'_2$ThR$_2$ complexes [10, 15]*) yields a thorium 'covalent radius' of *ca.* 1.73 Å. Addition of a two-coordinate sulfur covalent radius [14] of 1.04 Å to this value yields a calculated Th–S distance of *ca.* 2.77 Å, which appears to be slightly greater than the experimental distance (2.718(3) Å). In contrast, a similar calculation of a Th–OR distance yields *ca.* 2.39 Å**, which can be compared to experimental distances of 2.129(8) Å in Cp$'_2$Th(Cl)OC(R)=CNR$'$ (R = neopentyl, R$'$ = 1-2,6-Me$_2$C$_6$H$_3$) [10c] and 2.10 Å (corrected for U(IV) → Th(IV) [16]) in [Cp$'_2$U-(OCH$_3$)]$_2$PH [4a]†. Thus, for simple alkoxide ligands, the contraction (*cf.*, **I**) from what might be anticipated for a simple Th–O sigma bond is on the order of *ca.* 0.27 Å – considerably more drastic than for the above thiolate. The present S–C(11) distance of 1.78(2) Å is typical of alkyl thiols [14].

The S–Th–S$'$ angle in Cp$'_2$Th[S(n-Pr)]$_2$ is 102.5(2)°, which compares favorably with analogous parameters in other Cp$'_2$ThX$_2$ complexes [10]. The Th–S–C($\alpha$) angle in the present case is 108.3(5)°. The closest available comparisons are early transition metal d$^0$ arylthiolate complexes such as [Cp$_2$Zr-(SPh)]$_2$O [17] and Cp$_2$Ti(SPh)$_2$ [17b], where the metal–S–C(phenyl) angles are 105.9(2)° and 113.6°, 115.4°, respectively. In contrast, actinide–O–C angles in terminally bound alkoxide ligands usually approach 180°†† [4]. For example, these angles in the aforementioned Cp$'_2$Th(Cl)OC(R)=CNR$'$ and [Cp$'_2$U(OCH$_3$)]$_2$PH complexes are 178.7(6)° and 178(1)°, respectively.

At present, the most straight-forward interpretation of the Cp$'_2$Th[S(n-Pr)]$_2$ structural results is that actinide-thiolate bonding involves less ligand-to-metal $\pi$ donation than does actinide–alkoxide bonding (**I**). Further information on this issue awaits thermochemical measurements of metal–ligand bond energies and theoretical studies.

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*Complexes with highly distorted Th–C($\alpha$)–C($\beta$) angles are not considered.

**Similar results are obtained using C(alkyl)–S = 1.817(5) Å and C(alkyl)–O = 1.426(5) Å [14b].

†In cases of chelating, conjugated oxygenate ligands, analogous Th–O distances are usually closer to 2.25 Å [10c]; terminal U(IV)–O(alkyl distances in the 2.12–2.14 Å range are typical of homoleptic alkoxides [4b–d].

††Considerably more acute angles are observed in late transition metal alkoxides and aryloxides [18a–b].

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