Organoaactinide Chemistry: Poly-silylated Actinidocenes of Thorium, Uranium, and Neptunium

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Dedicated to Professor Heindrik von Dieck on the occasion of his 60th birthday

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Actinidocenes, 1,3,5-Tris(trimethylsilyl)cyclooctatetraenyl Ligand, Thorium, Uranium, Neptunium

The preparation and characterization of three homologous actinidocenes of the composition \( \text{An}^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5} \text{H}_2 \) (\( \text{An} = \text{Th} \)) (1), \( \text{U} \)) (2), \( \text{Np} \)) (3) is reported. Due to the presence of six trimethylsilyl groups these sandwich complexes are quite volatile and soluble in non-polar organic solvents.

Sandwich complexes containing \( \eta^8 \)-coordinated cyclooctatetraenyl ligands form an important and well-investigated class of organoactinide compounds [1,2]. Complexes of the type \( \text{An}^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5} \text{H}_2 \) \( \text{An} = \text{actinide metal} \) are known for the first five elements of the actinide series (Th, Pa, U, Np, Pu) [2], and an anionic derivative, \( \text{K}[\text{Am}^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5}] \), has been reported even for americium [3]. In previous studies it has been shown that the solubility of these sandwich complexes in non-polar organic solvents can be significantly improved by employing substituted cyclooctatetraenyl ligands [4]. We report here the preparation and characterization of a series of polysilylated derivatives containing the recently discovered 1,3,5-tris(trimethylsilyl)-cyclooctatetraenyl ligand, \( \text{L} = \text{C}_8\text{H}_5(\text{SiMe}_3)_3 \) [5].

Reactions of anhydrous actinide tetrachlorides [6] with two equivalents of \( \text{K}[\text{C}_8\text{H}_5(\text{SiMe}_3)_3]^+ \) \( \text{L} = \text{C}_8\text{H}_5(\text{SiMe}_3)_3 \) \( \text{L} = \text{C}_8\text{H}_5(\text{SiMe}_3)_3 \) \( \text{L} = \text{C}_8\text{H}_5(\text{SiMe}_3)_3 \) \( \text{L} = \text{C}_8\text{H}_5(\text{SiMe}_3)_3 \) were carried out in THF solution at room temperature according to eq. (1).

\[
\text{AnCl}_4 + 2 \text{K}[\text{C}_8\text{H}_5(\text{SiMe}_3)_3]^+ \rightarrow \text{An}^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5} \text{H}_2 \text{THF}
\]

\[
\begin{array}{c}
\text{THF} \\
+ 4 \text{KCl}
\end{array}
\]

Subsequent extraction with dry pentane afforded the analytically pure polysilylated actinidocenes 1-3 in high yields. All three compounds are soluble in non-polar organic solvents such as pentane, hexane, or toluene. They are easily hydrolized but are thermally highly stable and can be sublimed without decomposition at ca. 250–270 °C/10⁻³ torr. This significant volatility can be traced back to the presence of six trimethylsilyl substituents in the molecules. The effective shielding of the central metal ion also results in an increased oxidative stability. In sharp contrast to the pyrophoric parent uranocene \( \text{U}(\eta^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5})_2 \) [2] the polysilylated uranium complex 2 appears to be stable in dry air for several minutes. The new compounds were characterized by their spectroscopic and analytical data. In the mass spectra of 1 and 2 the molecular ion is observed with 100% relative intensity. The IR spectra of all three complexes are almost superimposable with those of the neutral cerocene derivative \( \text{Ce}(\eta^8(\text{C}_8\text{H}_5(\text{SiMe}_3)_3)^{13,5})_2 \) [5], thus confirming the isostructural nature of these sandwich complexes with \( \eta^8 \)-coordinated cyclooctatetraenyl rings. Electron absorption spectra of the uranium (2) and neptunium (3) compounds, taken in KBr matrix (2500 to 300 nm), show the characteristic absorption band of tetravalent \( \text{U} \) (5f², 3H₄), and tetravalent \( \text{Np} \) (5f³, 4L₃2) ions. The temperature-dependent paramagnetism of the uranium derivative 2 was measured in the temperature range from 4.2 K to 300 K. The effective magnetic moment (\( \mu_{eff} = 2.828(\mu_{\text{B}} \text{mol}^{-1} \cdot \text{T}^{-1})^{1/2} \)) of this compound is 1.15 (4.2 K), 2.20 (77.5 K), and 2.44 \( \mu_B \) (193 K), resp. These values are somewhat lower than those expected for a spin-free f-f-configuration.
lower than the corresponding ones for U(η⁸-
C₈H₈)₂ (1.55; 2.4; 2.63 μμB) [7] and U(η⁸-
C₈H₈SiMe₃)₂ (1.80; 2.61; 2.78 μμB) [8].

This study has shown that, as in the case of the lanthanide elements, the bulky 1,3,5-tris(trimethyl-
silyl)cyclooctatetraenyl ligand affords stable and
highly soluble sandwich complexes of the early acti-
nide elements. It appears to be a suitable ligand
for the preparation of homologous compounds
with other elements of the actinide series, because
it imparts to the resulting sandwich complexes
useful properties such as significant volatility and
a certain degree of air-stability.

Experimental Part

All preparations were carried out under nitro-
gen using Schlenk line and dry-box techniques.
THF and pentane were dried over sodium/benzo-
phenone using Schlenk line and dry-box techniques.

Standard safety measures were taken

when handling THF and pentane were dried over sodium/benzo-

phenone and freshly distilled under N₂

w ere prepared according to literature procedures.

The starting materials AnCl₃ (An = Th, Np) [6] and K₂[C₈H₈(SiMe₃)₃-1,3,5] • 2THF [5]
were prepared according to literature procedures.

General synthetic procedure: To a stirred solu-
tion of a given amount of K₂[C₈H₈(SiMe₃)₃-
1,3,5] • 2THF in THF (30 ml) was added the solid
actinide tetrachloride and stirring at room tem-
perature was continued for 48 h. After removal of the
solvent in vacuo the dry residue was transferred
to a G4 filter frit and continuously extracted with

a certain degree of air-stability.

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