Organoactinide Chemistry: Polysilylated Actinidocenes of Thorium, Uranium, and Neptunium

Christos Apostolidis[a], Frank T. Edelmann[b,*], Basil Kanellakopulos[c,*], Ulrike Reißmann[d]

[a] European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76725 Karlsruhe, Germany
[b] Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany
[c] Institut für Technische Chemie/CPV, Forschungszentrum Karlsruhe, Technik und Umwelt, Postfach 3640, D-76021 Karlsruhe, Germany
[d] Institut für Anorganische Chemie der Universität Göttingen, Tammannstr. 4, D-37077 Göttingen

* Reprint requests to Prof. Dr. F. T. Edelmann or Prof. Dr. B. Kanellakopulos

Dedicated to Professor Heindirk tom Dieck on the occasion of his 60th birthday

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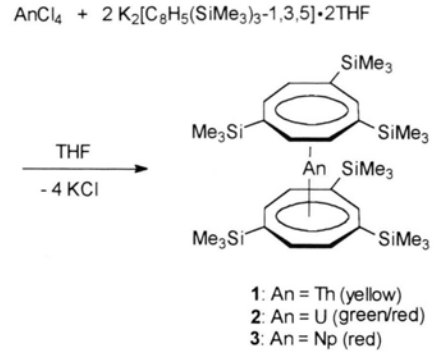
Actinidocenes, 1,3,5-Tris(trimethylsilyl)cyclooctatetraenyl Ligand, Thorium, Uranium, Neptunium

The preparation and characterization of three homologous actinidocenes of the composition $An[\eta^8\text{-}C_8H_5(SiMe_3)_3\text{-}1,3,5]_2$ (An = Th (**1**), U (**2**), 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 η^8-coordinated cyclooctatetraenyl ligands form an important and well-investigated class of organoactinide compounds [1,2]. Complexes of the type $An(\eta^8\text{-}C_8H_8)_2$ (An = actinide metal) are known for the first five elements of the actinide series (Th, Pa, U, Np, Pu) [2], and an anionic derivative, $K[Am(\eta^8\text{-}C_8H_8)_2]$, 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, $1,3,5\text{-}C_8H_5(SiMe_3)_3^{2-}$ [5].

Reactions of anhydrous actinide tetrachlorides [6] with two equivalents of $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\cdot 2THF$ [5] were carried out in THF solution at room temperature according to eq. (1).



(1)

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 hydrolyzed 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 $U(\eta^8\text{-}C_8H_8)_2$ [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 $Ce[\eta^8\text{-}C_8H_5(SiMe_3)_3\text{-}1,3,5]_2$ [5], thus confirming the isostructural nature of these sandwich complexes with η^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 U ($5f^2$, $^3H_4$), and tetravalent Np ($5f^3$, $^4I_{9/2}$) 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 ($\mu_{eff} = 2.828(\chi_{mol}\cdot T)^{1/2}$) of this compound is 1,15 (4,2 K), 2,20 (77,5 K), and 2,44 μ_B (193 K), resp. These values are somewhat

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lower than the corresponding ones for $U(\eta^8\text{-}C_8H_8)_2$ (1,55; 2,4; 2,63 μ_B) [7] and $U(\eta^8\text{-}C_8H_7SiMe_3)_2$ (1,80; 2,61; 2,78 μ_B) [8].

This study has shown that, as in the case of the lanthanide elements, the bulky 1,3,5-tris(trimethylsilyl)cyclooctatetraenyl ligand affords stable and highly soluble sandwich complexes of the early actinide 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 nitrogen using Schlenk line and dry-box techniques. THF and pentane were dried over sodium/benzophenone and freshly distilled under N_2 prior to use. Standard safety measurements were taken when handling ^{237}Np, using multiple levels of containment at all times. Work with air-sensitive Np compounds was done in a reverse-pressure glovebox. The starting materials $AnCl_4$ (An = Th, U, Np) [6] and $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\bullet 2THF$ [5] were prepared according to literature procedures.

General synthetic procedure: To a stirred solution of a given amount of $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\bullet 2THF$ in THF (30 ml) was added the solid actinide tetrachloride and stirring at room temperature 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 pentane until the supernatant became colorless (5–6 d). Crystallization at −20 °C afforded the pure crystalline materials.

Bis[η^8-1,3,5-tris(trimethylsilyl)cyclooctatetraenyl]thorium (**1**). The reaction of 116,3 mg (0,30 mmol) of $ThCl_4$ and 324,6 mg (0.30 mmol) of $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\bullet 2THF$ afforded 229 mg (79%) of bright yellow **1**.

$C_{34}H_{64}Si_6Th$ (873,43)
Calcd Th 26,57%,
Found Th 26,6%.

IR (KBr, 4000–380 cm^{-1}): ν = 2991 w, 2954 s, 2897 m, 1587 m, 1484 w, 1443 w, 1403 m, 1319 w, 1248 vs, 1059 vs, 1028 w, 988 m, 963 w, 929 m, 891 w, 863 sh, 834 vs br, 775 m, 749 s, 707 w, 689 m, 639 m, 542 w, 506 w, 449 w cm^{-1}; FIR (PE, 500–30 cm^{-1}) ν = 449 w, 367 m, 357 w, 337 w, 310 m, 291 s, 266 w, 252 w, 246/241 w, 226 vw, 168 w br, 101 vw cm^{-1}. MS/EI: *m/z* (% rel. int.) 873 [M, 100], 800 [M − $SiMe_3$, 15], 727 [M − $2SiMe_3$, 5], 578 [M − $4SiMe_3$, 4], 551 [$Th\{C_8H_5(SiMe_3)_3\}$, 16], 479 [$Th\{C_8H_5(SiMe_3)_2\}$, 4], 406 [$Th\{C_8H_5(SiMe_3)\}$, 1], 73 [$SiMe_3$, 11].

Bis[η^8-1,3,5-tris(trimethylsilyl)cyclooctatetraenyl]uranium (**2**). Treatment of 92,1 mg (0,24 mmol) of UCl_4 with 263,4 mg (0,24 mmol) of $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\bullet 2THF$ as described above yielded 179 mg (84%) of **2** as a dichroitic (green/red) crystalline solid.

$C_{34}H_{64}Si_6U$ (879,42)
Calcd U 27,07%,
Found U 27,1%.

IR (KBr, 4000–380 cm^{-1}): ν = 2990 w, 2955 s, 2897 m, 1587 m, 1485 w, 1444 w, 1403 m, 1318 w, 1248 vs, 1055 vs, 1028 w, 991 w, 961 w, 929 m, 891 w, 861 sh, 833 vs br, 779 m, 748 s, 707 w, 687 m, 639 m, 562 w, 540 w, 505 w, 455 w cm^{-1}; FIR (PE, 500–30 cm^{-1}) ν = 455 m, 375 w, 355 vw, 343 m, 332 w, 309 m, 290 s, 253 w sh, 246/241 w, 228 vw, 167 w br cm^{-1}. MS/EI: *m/z* (% rel. int.) 879 [M, 100], 806 [M − $SiMe_3$, 6], 733 [M − $2SiMe_3$, 2], 559 [$U\{C_8H_5(SiMe_3)_3\}$, 33], 485 [$U\{C_8H_5(SiMe_3)_2\}$, 3], 412 [$U\{C_8H_5(SiMe_3)\}$, 1], 73 [$SiMe_3$, 32]. ^1H NMR (C_6D_6, 27 °C): δ = -0.14 (m, 19 H, C_8H_5), -6.98 (s br, 36 H, $SiMe_3$), -8.87 (s, 18 H, $SiMe_3$) ppm.

Bis[η^8-1,3,5-tris(trimethylsilyl)cyclooctatetraenyl]neptunium (**3**). 233 mg (88%) of red crystalline **3** were obtained from the reaction of 127,0 mg (0,34 mmol) of $NpCl_4$ and 364,2 mg (0,34 mmol) $K_2[C_8H_5(SiMe_3)_3\text{-}1,3,5]\bullet 2THF$.

$C_{34}H_{64}NpSi_6$ (878,39)
Calcd Np 26,99%,
Found Np 27,0%.

IR (KBr, 4000–380 cm^{-1}): ν = 2955 s, 2897 m, 1587 m, 1492 w, 1443 w, 1403 m, 1319 w, 1248 vs, 1055 vs, 1028 w, 994 w, 962 w, 930 m, 891 w, 862 sh, 835 vs br, 778 m, 749 s, 707 w, 689 m, 638 m, 540 w, 507 w, 452 w cm^{-1}; FIR (PE, 500–30 cm^{-1}) ν = 452 m, 374 w, 355 m, 336 w, 310 m, 288 s, 266 m, 251 m, 246/241 m, 227 vw, 167 w br cm^{-1}.

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