# Synthesis of Mixed-Ring Organoactinide Complexes. 2. $(C_8H_8)(C_5Me_5)U(THF)$ and Its 4,4′-Dimethyl-2,2′-bipyridine Derivative

Ann R. Schake,[†,‡] Larry R. Avens,[‡] Carol J. Burns,[*,†] David L. Clark,[†]
Alfred P. Sattelberger,[†] and Wayne H. Smith[‡]

*Isotope and Nuclear Chemistry Division (INC) and Nuclear Materials Technology Division (NMT), Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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*Summary: The (pentamethylcyclopentadienyl)uranium(III) complex $(C_5Me_5)UI_2(THF)_3$ reacts with $K_2C_8H_8$ in THF to form the mixed-ring uranium(III) complex $(C_8H_8)(C_5Me_5)U(THF)$ (1). Treatment of 1 with 4,4′-dimethyl-2,2′-bipyridine ($Me_2bpy$) gives the 10-coordinate complex $(C_8H_8)(C_5Me_5)U(Me_2bpy)$ (2). The syntheses of 1 and 2 and the X-ray structure of 2 are described herein.*

Transition-metal[1] and lanthanide[2] mixed cyclopentadienyl–cyclooctatetraenyl complexes were reported in the late 1960s and mid-1970s, respectively. However, to date, there have been no reports of the incorporation of this combination of ring systems on a uranium(III) metal center and, until recently,[3] this combination of ring systems had not been used on *any* actinide metal center. Our interest in this ligand combination stems from its unique ability to offer multiple coordination sites and, hence, multiple sites of reactivity at a neutral, electrophilic metal center in a pseudo-bent-metallocene coordination sphere. Here we report our preliminary results on the synthesis and characterization of the first mixed-ring uranium(III) complex.

Treatment of the monocyclopentadienyl complex $Cp^*UI_2(THF)_3$[4] ($Cp^* = C_5Me_5^-$) with $K_2COT$ ($COT = C_8H_8^{2-}$) in THF forms the mixed-ring complex $(COT)(Cp^*)U(THF)$ (1) (eq 1).[5] Complex 1 is isolated as a brown microcrystalline powder from hexane/THF (5:1) solution

$$(Cp^*)UI_2(THF)_3 + K_2COT \xrightarrow{THF} \underset{1}{(COT)(Cp^*)U(THF)} + 2KI \quad (1)$$

in ca. 75% yield. The assignment of complex 1 as the THF adduct is supported by $^1$H NMR,[5] IR,[6] and elemental analysis.[5]

Treatment of 1 with 4,4′-dimethyl-2,2′-bipyridine ($Me_2bpy$) in toluene at 25 °C followed by removal of solvent and recrystallization from THF/$Et_2O$ at −40 °C yields dark green crystals of the bipyridine adduct $(COT)(Cp^*)U(Me_2bpy)$ (2) in 70% yield[7] (eq 2).

$$(COT)(Cp^*)U(THF) + Me_2bpy \xrightarrow{tol} \underset{2}{(COT)(Cp^*)U(Me_2bpy)} \quad (2)$$

The structure of 2 was determined from X-ray diffraction data collected at −70 °C.[8] An ORTEP diagram of 2 is presented in Figure 1. The U–Cp* and U–COT distances compare well with those found in other uranium(III) complexes. The average $U–C_{Cp^*}$ distance of 2.752 Å is within the range of U–C distances observed in mono-,[4] bis-,[9] and tris(cyclopentadienyl)[10] complexes of uranium(III) (2.780, 2.76–2.79, and 2.668–2.703 Å, respectively). The $U–C_{COT}$ distances (average 2.703 Å) compare well with the only other structurally characterized $U^{III}$–COT complex reported, $[K(diglyme)][U(Me\text{-}COT)_2]$,[11a] where the average U–C distance to the COT ring opposite the K counterion is 2.707 Å. This U–C distance in 2 is

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[†] Isotope and Nuclear Chemistry Division.

[‡] Nuclear Materials Technology Division.

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(5) To a stirred THF solution (ca. 40 mL) of $(C_5Me_5)UI_2(THF)_3$ (2.00 g, 2.37 mmol) is added dropwise a 10-mL THF solution of $K_2COT$ (0.43 g, 2.37 mmol). After addition of ca. 5 mL of the $K_2COT$ solution the blue-green of $(C_5Me_5)UI_2(THF)_3$ changes to brown. After it is stirred for 1 h at room temperature, the brown solution is filtered through Celite and the solvent removed from the filtrate in vacuo. The resulting brown powder is extracted with a hexane/THF mixture (5:1), and 15–20 mg of uranocene (ca. 15%) is removed by filtration. After storage of the filtrate at −40 °C for 24 h, 1 g of (COT)(Cp*)U(THF) is isolated by filtration as a brown, crystalline powder in 75–80% yield. $^1$H NMR in $C_6D_6$ (ppm, 25 °C, 250 MHz): $\delta$ −6.0 (s, THF; $\Delta\nu_{1/2} = 33$ Hz), −13.4 (s, $C_5Me_5$; $\Delta\nu_{1/2} = 79$ Hz), −29.4 (s, THF; $\Delta\nu_{1/2} = 97$ Hz), −52.3 (s, $C_8H_8$; $\Delta\nu_{1/2} = 138$ Hz). Anal. Calcd for $C_{22}H_{31}OU$: C, 48.09; H, 5.69. Found: C, 47.29; H, 5.60.

(6) (a) Bands in the IR spectrum of 1 at 1016, 900, and 854 cm$^{-1}$ are assigned to bound THF.[6b–d] (b) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (c) Lewis, J.; Miller, J. R.; Richards, R. L.; Thompson, A. *J. Chem. Soc.* **1965**, 5850. (d) Clark, R. J. H.; Lewis, J.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379.

(7) $^1$H NMR for complex 2 in $d_8$-THF (ppm, 25 °C, 250 MHz): $\delta$ 101.5 (s, 6H, $CH_3$; $\Delta\nu_{1/2} = 109$ Hz), 3.05 (s, 2H, bpy; $\Delta\nu_{1/2} = 63$ Hz), −11.5 (s, 2H, bpy; $\Delta\nu_{1/2} = 63$ Hz), −16.2 (s, 15H, $C_5Me_5$; $\Delta\nu_{1/2} = 131$ Hz), −53.4 (s, 8H, $C_8H_8$; $\Delta\nu_{1/2} = 65$ Hz), −105.8 (s, 2H, bpy; $\Delta\nu_{1/2} = 44$ Hz). Anal. Calcd for $C_{30}H_{35}N_2U$: C, 54.46; H, 5.33; N, 4.23. Found: C, 54.79; H, 5.22; N, 3.86.

(8) 2 crystallizes in the orthorhombic space group $Pna2_1$ with $a = 10.001(2)$ Å, $b = 22.555(3)$ Å, $c = 13.172(2)$ Å, $V = 2971.1(8)$ Å$^3$, $d_{calc} = 1.622$ mg/m$^3$, and $Z = 4$. The limits of data collection were $0 \le 2\theta \le 50°$ (Mo K$\alpha$). The structure was solved by Patterson and direct-methods techniques and refined by full-matrix least squares. Final discrepancy indices were $R_F = 3.20\%$ and $R_{wF} = 4.21\%$.

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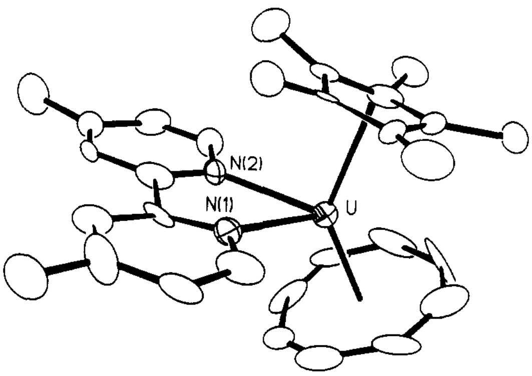

**Figure 1.** ORTEP drawing of complex 2. Selected distances and angles: U(1)–$C_8H_8$(1) (centroid), 2.01 Å; U(1)–$C_5Me_5$(1) (centroid), 2.49 Å; U(1)–N(1), 2.429(11) Å; U(1)–N(2), 2.423 (11) Å; $C_8H_8$(1) (centroid)–U(1)–$C_5Me_5$ (centroid), 138.2°; N(1)–U(1)–N(2), 64.6(4)°.

slightly longer than that found for several $U^{IV}$–COT half-sandwich complexes,[3b,11] as expected on the basis of the larger ionic radius of U(III). The $U^{III}$–N distances of 2.429 and 2.423 Å are in the range of other structurally characterized U(III) complexes containing pyridine-type ligands.[12] Although there are no other structurally characterized mixed-ring uranium systems with which to compare, the Cp–U–COT angle of 138.2° is essentially identical with the Cp–Th–COT angle in the mixed-ring thorium(IV) systems $(C_8H_8)(C_5Me_5)Th(\mu\text{-}Cl)_2Mg(CH_2CMe_3)(THF)$[3a] and $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$,[3a] where the Cp–Th–COT angles are 138.0 and 138.1°, respectively. The centroid–metal–centroid angle in 2 also compares well with those of several Lewis base adducts of the mixed-ring lanthanide complexes.[2]

Similar reactions of $Yb(C_5Me_5)_2(OEt_2)$ with bipyridine do not form simple adducts of Yb(II). Instead, paramagnetic complexes are formed where the radical anion of bpy is coordinated to a Yb(III) center.[13] This assignment was confirmed by the visible spectrum of the Yb–bpy complex, which contained three broad absorption bands between 800 and 900 nm, characteristic of the 2,2′-bipyridine radical anion. No such absorptions are observed in the visible spectrum of complex 2. Furthermore, in the $^1H$ NMR of 2, we see no appreciable shift of the COT resonance (−53.4 ppm) relative to 1 (−52.3 ppm) that would indicate a change from U(III) to U(IV)[15] upon coordination of bpy. The absence of any observed redox chemistry in the $U^{III}$–bpy complex can be rationalized on the basis of the oxidation potential of complex 2 versus that of $(C_5Me_5)_2Yb^{II}$. The redox potential, $E°$, for complex 2 is −0.69 V (vs SHE in THF),[16] and the redox potential of $(C_5Me_5)_2YbL$ is 1.40 V (vs SHE in $CH_3CN$),[14] indicating that the mixed-ring uranium(III) complex is much more stable with respect to oxidation and bipyridine radical anion formation than the Yb complex. These data, together with the visible spectrum, $^1H$ NMR data, and structural data, support the assignment of 2 as a simple Lewis base adduct of a mixed-ring uranium(III) complex.

Complexes 1 and 2 represent the first examples of mixed-ring uranium(III) complexes. Reactivity studies of complex 1 with a variety of organic substrates are currently in progress.

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**Supplementary Material Available:** Tables of data collection constants, atomic positional parameters, anisotropic thermal parameters, selected bond lengths and angles, and hydrogen atom positions and a figure giving additional atom labeling for 2 (12 pages). Ordering information is given on any current masthead page.

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[15] The few $U^{IV}$–COT complexes that have appeared in the literature have reported $C_8H_8^{2-}$ resonances in the range $\delta$ −24 to −38 ppm.[3b,11] We have also prepared several U(IV) mixed-ring complexes where the $C_8H_8^{2-}$ resonances fall in this range, typically around $\delta$ −35 ppm.

[16] $E°$ was determined by cyclic voltammetry using a platinum-disk working electrode and using ferrocene as an internal potential reference. The measurements were made in THF containing 0.1 M tetrabutylammonium tetraphenylborate as supporting electrolyte. A reversible one-electron-oxidation wave was observed at a scan rate of 0.2 V/s.