

Bending of “Uranocene” ($(\eta^8\text{-C}_8\text{H}_8)_2\text{U}$): Synthesis and Crystal Structure of the Cyanido Complex $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}(\text{CN})][\text{NEt}_4]$

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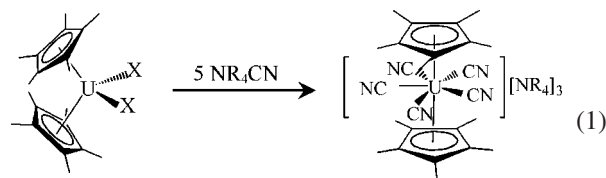
Summary: The two parallel, eight-membered rings of uranocene were forced to bend upon addition of CN^- to give the title compound.

The discovery in 1968 of the uranium compound $(\eta^8\text{-C}_8\text{H}_8)_2\text{U}$ (**1**), the first linear sandwich complex of an f element, was a milestone in the history of actinide chemistry.^{1,2} This compound, which was called “uranocene” in reference to ferrocene, boosted the development of organo-f-element chemistry and induced much theoretical debate on the nature of the metal–ligand bond.² The surprisingly great stability of **1** was accounted for by covalent stabilization originating from overlap of 5f orbitals with a symmetry-allowed combination of the highest occupied orbitals in the dianionic ligand.^{2,3}

This novel class of π -sandwich complexes expanded rapidly with the synthesis of the tetravalent “actinocenes” $(\eta^8\text{-C}_8\text{H}_8)_2\text{An}$ (An = Th, Pa, Np, Pu, Am),^{2,4} $(\eta^8\text{-C}_8\text{H}_8)_2\text{Ce}$,^{3a,4} the trivalent lanthanide derivatives $[(\eta^8\text{-C}_8\text{H}_8)_2\text{Ln}]^+$,^{5,6} and the multiple-decker sandwich complexes $\text{Ln}_m(\text{C}_8\text{H}_8)_m$.^{6,7} Substituted cyclooctatetraenyl dianions⁸ were used to increase the solubility and reactivity of these complexes,⁹ favoring in particular the

characterization of trivalent 5f species.^{4,10} However, the chemical transformations of **1** remained disappointingly poor, and this inertness was explained by the inaccessibility of the uranium center to supplementary ligands due to the steric constraints imposed by the two cyclooctatetraenyl rings. This situation was observed with all the π -sandwich compounds of the type $(\eta^8\text{-C}_8\text{H}_8)_2\text{M}$, and no example of a $[(\eta^8\text{-C}_8\text{H}_8)_2\text{M}(\text{L})]^{q-}$ derivative (L = neutral or anionic ligand) was reported, whatever the charge, oxidation state, or nature of the metal center; therefore, it is a generally accepted idea that a bis($\eta^8\text{-C}_8\text{H}_8$) complex cannot adopt a bent configuration.

In face of the rather limited chemistry of **1** and substituted uranocenes, the half-sandwich complexes of the type $(\eta^8\text{-C}_8\text{H}_8)\text{AnX}_2(\text{L})_n$ opened new vistas for cyclooctatetraenyl–actinide chemistry. Among the various synthetic routes to such compounds,¹¹ the displacement of one $\text{C}_8\text{H}_8^{2-}$ ligand of **1** by anionic ligands such as NR_2^- and OR^- ^{11c} suggests the formation of the anionic transient intermediate $[(\eta^8\text{-C}_8\text{H}_8)_2\text{UX}]^-$. It seemed to us that such compounds could be detectable or attainable by the use of ligands with suitable size and strong coordinating capacity. That the cyanide ion fulfills these criteria was recently demonstrated by the reaction of the bent metallocenes Cp^*_2UX_2 ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, X = OTf, I) with NR_4CN leading to $[\text{Cp}^*_2\text{U}(\text{CN})_5][\text{NR}_4]_3$ (eq 1),¹² which represents a novel type of linear metallocene containing auxiliary ligands in its equatorial girdle.¹³



X = CF_3SO_3 , I

Here we report that the cyanide ion is an efficient and convenient wedge for bending the linear uranocene **1** toward the formation of the monoanionic derivative $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}$

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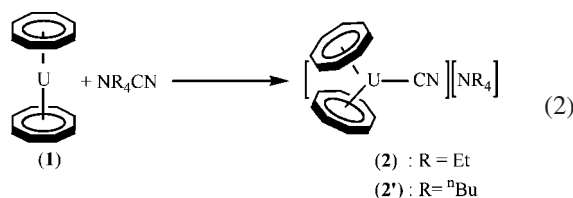
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(CN)] $[\text{NR}_4]$ (R = Et (**2**), ^nBu (**2'**)), which is the first complex with two $\eta^8\text{-C}_8\text{H}_8$ ligands in a bent configuration.

Addition of slightly less than 1 molar equiv of NEt_4CN to a suspension of **1** in pyridine at 50 °C gave rapidly a clear solution of color varying from green to red upon lighting conditions, from which thin brown needles of **2** crystallized on cooling to room temperature (eq 2);¹⁴ after evaporation of the mother liquor, another crop of **2** was obtained, leading to a total yield of 86%. The ^1H NMR spectrum of **2** in pyridine- d_5 exhibits a singlet at δ -32.18 (16 H) characteristic of a C_8H_8 ligand bound to uranium(IV) and two signals at δ +4.49 (8 H) and +1.96 (12 H) due to a single NEt_4^+ group. The narrow resonance of the C_8H_8 ligand in **2** is shifted downfield by comparison with the broad signal at δ -37.65 for **1**.



While the IR vibrational frequency of the cyanide ion in NEt_4CN is 2050 cm^{-1} ,^{10c} the infrared spectrum of **2** displays a strong $\nu(\text{CN})$ stretching frequency at 2073 cm^{-1} , suggesting the absence of π -back-bonding from the U^{4+} ion to the cyanide ligand. This value is relatively low when compared with the corresponding absorptions in other uranium(IV) cyanido compounds, 2091 cm^{-1} in $[\text{Cp}^*\text{U}(\text{CN})_5][\text{NEt}_4]_3$, 2134 cm^{-1} in $\text{Cp}^*\text{U}(\text{CN})_2$, and 2053 and 2188 cm^{-1} in $[\text{Cp}^*\text{U}(\text{CN})_3][\text{NEt}_4]$,^{12b} indicating a weaker σ -donating interaction. The strong bands in the 600–1000 cm^{-1} region can be assigned to the (cyclooctatetraenyl)uranium(IV) linkage.^{5,11a}

The structure of the anion in **2** (Figure 1)¹⁵ shows the coordination of a single carbon-bound cyanide ligand in the equatorial girdle of a bent “uranocene”. In contrast with the $[(\eta^8\text{-C}_8\text{H}_8)_2\text{M}]^{q-}$ ($q = 0, 1$) complexes, where the Cnt-M-Cnt angles (Cnt = ring centroid) deviate from linearity by a

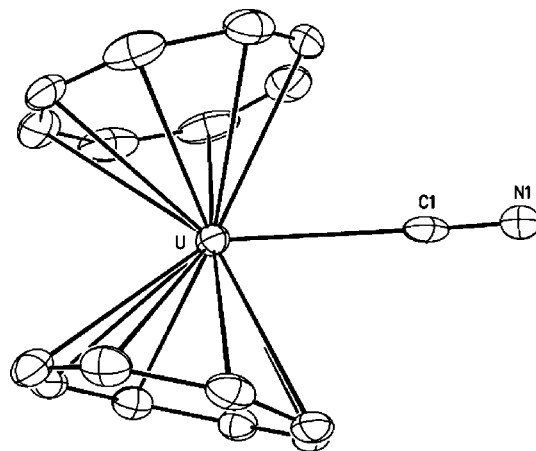


Figure 1. View of the anion $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}(\text{CN})]^-$ in **2**. Selected bond lengths (\AA) and angles (deg) (Cnt = C_8H_8 centroid): $\langle \text{U-C}(\text{C}_8\text{H}_8) \rangle = 2.73(2)$, $\text{U-C}(1) = 2.626(4)$, $\text{C}(1)\text{-N}(1) = 1.158(4)$, $\text{U-Cnt}(1) = 2.032$, $\text{U-Cnt}(2) = 2.033$; $\text{Cnt}(1)\text{-U-Cnt}(2) = 153.3$, $\text{C}(1)\text{-U-Cnt}(1) = 102.5$, $\text{C}1\text{-U-Cnt}(2) = 104.2$, $\text{U-C}(1)\text{-N}(1) = 177.7(3)$.

maximum of 4°, the $(\eta^8\text{-C}_8\text{H}_8)_2\text{U}$ moiety in **2** adopts an unprecedented bent configuration with a Cnt-U-Cnt angle of 153.3°. The Cnt-U-Cnt angle in **2** is identical with the Cnt-Sc-Cnt angle (152.9(3)°) in the dinuclear compound $\text{Li}(\text{THF})_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_8\text{H}_8)\text{Sc}(\eta^8\text{-C}_8\text{H}_8)$,¹⁶ where the bridging, nonplanar C_8H_8 ligand is η^4 -coordinated to the metal centers. This value can be compared with those found in the bent bis(C_5Me_5) U^{IV} complexes and mixed-ring $(\eta^8\text{-C}_8\text{H}_7\text{R}_{8-n})\text{-}(\text{Cp}^\dagger)\text{An}^{\text{IV}}$ derivatives (An = U, Th; Cp^\dagger = substituted cyclopentadienyl), where the Cnt-U-Cnt angles are in the ranges 127–152 and 125–140°, respectively.¹⁷ The two eight-membered rings in **2** are planar with rms deviations of 0.036 and 0.041 \AA and form a dihedral angle of 27.04(10)°. The average $\text{U-C}(\text{C}_8\text{H}_8)$ distance of 2.73(2) \AA in **2** is larger than that of 2.648(5) \AA in **1**, reflecting the variation in the coordination number and the charge of the complex. The $\text{U-C}(\text{CN})$ distances in **2** (2.626(4) \AA) and the linear metallocene $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{CN})_5][\text{NEt}_4]_3$ (average 2.62(2) \AA)^{12a,b} are identical, being ca. 0.10 \AA larger than in the 9-coordinate tricyanido complex $[(\text{C}_5\text{Me}_5)_2\text{U}(\text{CN})_3][\text{NBu}_4]$ (average 2.520(16) \AA),^{12b} in agreement with the increase in coordination number. The C–N distance of 1.158(4) \AA is identical with those measured in the free cyanide anion.¹⁸

While it is insoluble in THF and toluene, **2** is soluble in dichloromethane; dissociation of the cyanide ligand was

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(14) Synthesis of $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}(\text{CN})][\text{NEt}_4]$ (**2**): all reactions were carried out under argon (<5 ppm of oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. A flask was charged with **1** (190 mg, 0.42 mmol) and NEt_4CN (94% purity, 67 mg, 0.40 mmol), and pyridine (20 mL) was condensed in. After the mixture was stirred for 10 h at 50 °C, the dark green solution was filtered. The volume of the solution was reduced by evaporation to ca. 7 mL, and upon cooling to 0 °C, a dark brown microcrystalline powder was deposited. Filtering, washing of the powder with ca. 2 mL of cold pyridine, and drying under vacuum gave an analytically pure sample of **2** (130 mg, 0.21 mmol, 51%). A second crop of **2** was obtained by evaporation of the mother liquors and extraction of the slight excess of **1** by repeated washings with THF (20 mL) by the Soxhlet technique (90 mg, 0.15 mmol). Total yield: 86%. Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{N}_2\text{U}$: C, 49.83; H, 6.02; N, 4.65. Found: C, 49.24; H, 5.90; N, 4.70. ^1H NMR (200 MHz, pyridine- d_5 , 23 °C): δ 4.47 (s, 8 H, NCH_2CH_3), 1.96 (s, 12 H, NCH_2CH_3), -32.18 (s, 16 H, C_8H_8). IR spectrum (in Nujol mulls between KBr round cell windows): 2073 (s), 1172 (s), 1002 (s), 908 (s), 901 (s), 791 (s) 704 (vs) cm^{-1} .

(15) Crystallography: the data were collected at 100(2) K on a Nonius Kappa-CCD area-detector diffractometer with Mo $K\alpha$ radiation and were treated with HKL2000.¹⁹ The structure was solved with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.²⁰ Absorption effects were corrected empirically with SCALEPACK.¹⁹ *Crystal data for 2*: $\text{C}_{25}\text{H}_{36}\text{N}_2\text{U}$, $M_r = 602.59$, monoclinic, space group $P2_1/c$, $a = 7.1745(4)$ \AA , $b = 12.4979(9)$ \AA , $c = 24.8907(16)$ \AA , $\beta = 93.569(4)^\circ$, $V = 2227.5(2)$ \AA^3 , $Z = 4$, $\mu(\text{Mo } K\alpha) = 7.299$ mm^{-1} , 85 789 measured reflections, 4221 independent ($R_{\text{int}} = 0.058$), 3625 with $I > 2\sigma(I)$, 257 parameters, $R1 = 0.021$, $wR2 = 0.045$, $S = 0.975$; $\Delta\rho_{\text{min}} = -0.94$ $\text{e } \text{\AA}^{-3}$, $\Delta\rho_{\text{max}} = 0.62$ $\text{e } \text{\AA}^{-3}$.

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observed in acetonitrile, leading to crystals of **1**. The quantitative study of the equilibrium between **1** and **2** was impeded by the poor solubility of the complexes in organic solvents. A much more soluble analogue of **2** was obtained by changing the nature of the ammonium salt. The derivative $[(\eta^8\text{-C}_8\text{H}_8)_2\text{U}(\text{CN})][\text{N}^n\text{Bu}_4]$ (**2'**) was prepared in quantitative yield by addition of 1 mol equiv of $\text{N}^n\text{Bu}_4\text{CN}$ to a suspension of **1** in THF. In contrast to the anions $[(\eta^8\text{-C}_8\text{H}_8)\text{UX}_3]^-$ ($\text{X} = \text{O}^i\text{Pr}, \text{NR}_2$), which were obtained by treatment of **1** with 3 mol equiv of LiNEt_2 or NaO^iPr ,^{11e,f} addition of excess NR_4CN to a pyridine solution of **2** did not induce the displacement of the $\text{C}_8\text{H}_8^{2-}$ ligands; the C_8H_8 NMR signal of **2** was, however, shifted by 1 ppm to ca. $\delta -31$, but only crystals of **2** were recovered.

Future investigations are planned in order to extend the variety of bent $(\eta^8\text{-C}_8\text{H}_8)_2\text{M}$ complexes, by changing either the donor ligands in the equatorial girdle or the metal and its oxidation state; theoretical calculations are also in progress.

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Supporting Information Available: CIF file giving crystallographic data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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