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The Crucial Role of the f Electrons in the Bent or Linear Configuration of Uranium Cyanido Metallocenes**

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The uranium complexes $[Cp^*_2U(NCMe)_5]X_2$ ($Cp^* = C_5Me_5$; X = I, OTf, BPh_4) are unique examples of linear metallocenes containing auxiliary ligands in their equatorial girdle.[1] Their formation from the bent precursors $[Cp^*_2UX_2]$ was found to be critically dependent on the nature of the solvent, the counterion, and the metal oxidation state.[1b] It was then desirable to extend this novel class of π-sandwich complexes to get a better insight into the factors which determine their structure. One approach was to replace the MeCN ligands with anionic groups. The cyanide anion was particularly attractive since, like MeCN, its suitable size and shape would permit the complete filling of the equatorial girdle of the $\{Cp^*_2U\}^{2+}$ moiety. The choice of this ligand was also motivated by the possibility of developing the cyanide chemistry of the f elements, which has received little attention[2–4] in contrast to that of the d transition metals.[5] Herein we report on the U^{III}–U^{V} complexes $[Cp^*_2U(CN)_3][NR_4]_n$ ($n = 1, 2$) and $[Cp^*_2U(CN)_5][NR_4]_n$ ($n = 2, 3$), which adopt a bent and linear configuration, respectively. These results raise the fundamental question of the nature of the metal–ligand interaction and the influence of the number of f electrons on the geometry of the complexes. The crucial role of the f orbitals is evidenced by density functional theory (DFT) analysis.

In contrast to the $[Cp^*_2U(NCMe)_5]X_2$ complexes,[1a,b] the synthesis of the cyanido compounds presented herein is independent of the counterion and solvent. However, a major difficulty in their preparation came from the elimination of the salts formed during the reaction. Pure compounds were obtained with a proper choice of reactants and solvent for controlling the relative solubility of the products.

Successive addition of one equivalent of KCN and two equivalents of $NnBu_4CN$ to $[Cp^*_2UI(py)]$ in MeCN led to the formation of a brown solution of $[Cp^*_2U(CN)_3][NnBu_4]_2$ (**1**), which was isolated as a brown powder in 83 % yield; crystals were obtained upon slow diffusion of Et_2O into the MeCN solution. Crystals of the U^{IV} counterpart $[Cp^*_2U(CN)_3][NnBu_4]\cdot 1.5\,THF$ (**2**·1.5 THF) were formed from $[Cp^*_2UI_2]$ and $NnBu_4CN$ in THF, while the analytically pure complex $[Cp^*_2U(CN)_3][NEt_4]$ (**2′**) was synthesized in good yield by reaction of $[Cp^*_2UI_2]$ with NEt_4CN in THF.

The crystal structures of the anions of **1** and **2** (Figure 1) are very similar. The complexes adopt the familiar bent-sandwich configuration, with the C-coordinated CN ligands in the equatorial girdle. The average U−C(Cp*) and U−C(CN) bond lengths in **2** are smaller by about 0.1 Å than those in **1**, in agreement with the variation in the radii of the U^{4+} and U^{3+} ions.[6] The U−C(CN) bond lengths in **2** are larger than those in $[(C_5H_2tBu_3)_2U(OSiMe_3)(CN)]$ (2.415(6) Å)[3] and in $[(C_5HMe_4)_3U(CN)_{0.6}(Cl)_{0.4}]$ (2.31(4) Å),[4] thus reflecting the higher coordination number and negative charge of the anionic compound.

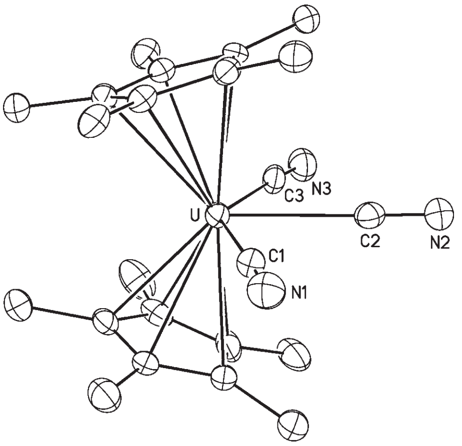

Figure 1. View of the anion of **2**. Selected bond lengths [Å] and angle [°] (the corresponding values of the U^{III} counterpart **1** are in square brackets): av U-C(Cp*) 2.727(15) [2.808(16)], U-C1 2.504(7) [2.636(5)], U-C2 2.541(6) [2.643(3)], U-C3 2.515(7) [2.643(3)]; Cg-U-Cg 144.6 [142.0] (Cg = Cp* centroid).

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The U^{III} complex **1** was inert towards an excess of CN^- ions, whereas its U^{IV} counterpart **2** or **2′** was readily transformed into the pentacyanido derivative $[Cp^*_2U(CN)_5][NR_4]_3$. The orange compound $[Cp^*_2U(CN)_5][NEt_4]_3$ (**3**) was isolated in 75 % yield from $[Cp^*_2U(OTf)_2]$ and NEt_4CN. Slow diffusion of Et_2O into a MeCN solution of $[Cp^*_2UI_2]$ and NEt_4CN gave crystals of $[Cp^*_2U(CN)_5][NEt_4]_3{\cdot}MeCN$ (**3**·MeCN).

Similarly, in one attempt to synthesize $[Cp^*_2U(CN)_5][N\mathit{n}Bu_4]_3$, brown crystals of the U^V derivative $[Cp^*_2U(CN)_5][N\mathit{n}Bu_4]_2$ (**4**) were obtained, likely resulting from oxidation of the parent U^{IV} metallocene by adventitious traces of air; further work is in progress for controlling the synthesis of **4**. The structures of the anions of **3** and **4** are very similar; a view of the anion $[Cp^*_2U(CN)_5]^{2-}$ of **4** is shown in Figure 2. The geometry of the linear metallocene is identical to that of the dication $[Cp^*_2U(NCMe)_5]^{2+}$, with the Cp* rings equidistant from and parallel to the plane defined by the metal center and the five CN groups. The pentagon of the CN carbon atoms is in a staggered conformation with respect to the eclipsed Cp* rings. As expected from the variation in the radii of the U^{4+} and U^{5+} ions,[6] the mean U−C(Cp*) and U−C(CN) bond lengths in **4** are about 0.1 Å smaller than those in **3**. These results demonstrate that $[Cp^*_2U(CN)_5]^{q-}$ anions are formed with U^{IV}/U^V centers but not with U^{III}, thus evidencing that the number of f electrons is prevailing in the stability of linear versus bent metallocenes.

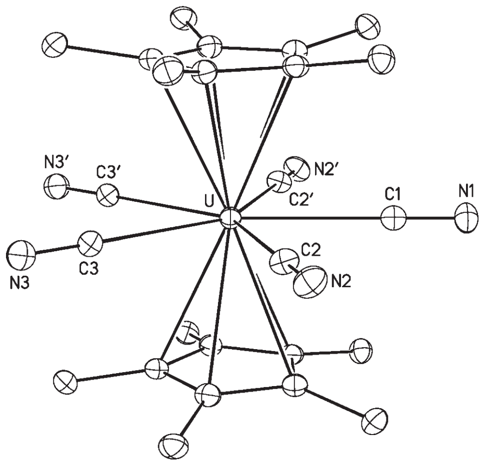

Figure 2. View of the anion of **4**. Symmetry code (atoms denoted with ′): −*x*, *y*, 1.5−*z*. Selected bond lengths [Å] and angle [°]. (the corresponding values of the U^{IV} counterpart **3** are in square brackets): av U-C(Cp*) 2.795(12) [2.86(2)], av U-C(CN) 2.548(7) [2.62(2)]; Cg-U-Cg 179.1 [178.6] (Cg = Cp* centroid).

The relationship between electronic structure, bonding, and coordination geometry of the cyanido metallocenes **1**–**4** was elucidated by relativistic DFT analysis. Calculations were carried out on model compounds in which the ring substituents have been replaced with H atoms. Regardless of the metal oxidation state, both a bent and a linear configuration could be optimized. The computed geometries of the U^{III} and U^{IV} bent metallocenes $[Cp^*_2U(CN)_3]^{q-}$ ($q = 2, 1$) and the U^{IV} and U^V linear ones $[Cp^*_2U(CN)_5]^{(q+2)-}$ ($q = 1, 0$) are very similar to the experimental crystal structures of **1**–**4**. The largest difference between theoretical and experimental bond lengths is less than 0.1 Å, while the major angular deviation of 23° in the Cg-U-Cg angle (Cg = Cp* centroid) in the bent compounds is explained by the less sterically demanding Cp ligand (C_5H_5) favoring larger bending.

A first explanation of the preferred formation of the bent or linear metallocenes **1**–**4** was provided by considering the hypothetical reaction $[Cp^*_2U(CN)_3]^{q-} + 2\,CN^- \rightarrow [Cp^*_2U(CN)_5]^{(q+2)-}$. The computed absolute energies for these reactions have no meaning, but their trend from U^{III} ($q = 2$) to U^V ($q = 0$) is informative. The reaction enthalpies in the gas phase are equal to +256, +92, and −75 kcal mol^{-1} for the complexes in the +3, +4, and +5 oxidation state, respectively. These values should be smaller in solution, owing to the more efficient solvation of the more negatively charged linear complex. The stability of the linear configuration thus increases with the metal oxidation state, in agreement with the experimental observations.

The MO diagrams of the bent and linear $\{Cp_2U\}$ fragments (Figure 3) imply the participation of the f orbitals. For the linear $\{Cp_2U\}$ fragment, seven nonbonding orbitals (five f and two d) are still accessible, with five of them in the equatorial plane and the two others (f orbitals) out of the equatorial plane. In the linear U^{III} complex, the five CN^-

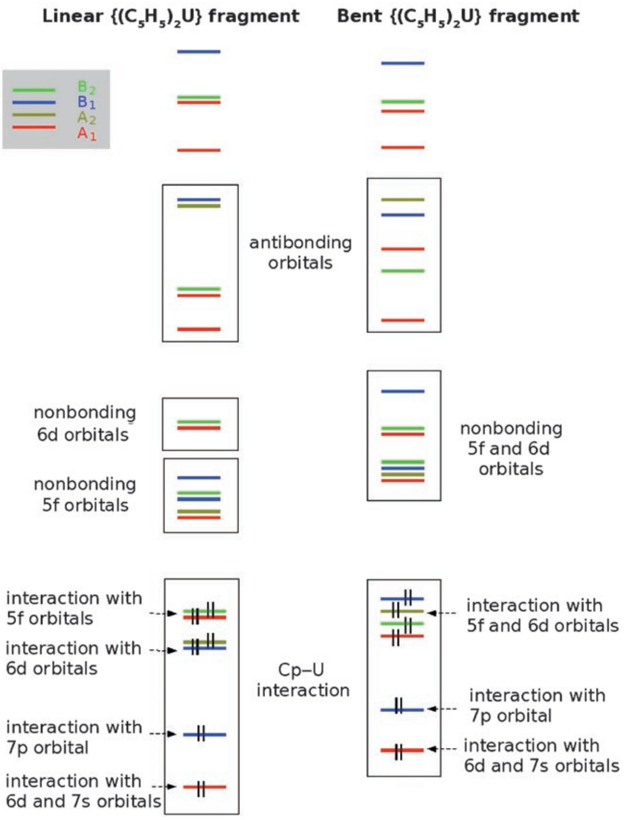

Figure 3. Molecular orbital diagrams of the $\{Cp_2U\}$ fragment in both linear and bent forms. For clarity, both diagrams are given in C_{2v} symmetry. The labels A_1, A_2, B_1, and B_2 refer to the irreducible representation of the C_{2v} point group.

ligands can interact with the in-plane orbitals, and the remaining three unpaired electrons occupy the two out-of-plane orbitals and an antibonding one. This complex should not be stable and the bent form will be adopted since after rehybridization only three orbitals (mainly of d character) point towards the equatorial girdle. With the same analysis, the U^{IV} complex can adopt a linear structure since only two unpaired electrons remain after coordination of the CN^- ions; however, a bent complex can also exist. A deeper analysis of the MO diagrams shows that the highest occupied MOs are energetically lower in the linear than in the bent complex, so that the former should be slightly favored. However, the two unpaired electrons induce an electronic repulsion for the CN^- lone pair that is higher for the linear (5 CN) than for the bent complex (only 3 CN). Both structures could thus be adopted by the U^{IV} complex, depending on the experimental conditions. In the U^V complex, only one out-of-plane f orbital is occupied in the linear complex, and the electronic repulsion between the CN^- lone pair and the unpaired electron is smaller, thus rendering the linear form more stable. These results suggest that linear metallocenes of early actinides with $5f^0$ configuration would be stable.

Experimental Section

Full details on the synthesis, characterization including X-ray data of **1**–**4**, and computational calculations on the model complexes are given in the Supporting Information.

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