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The First f-Element Ketimido Complex: Synthesis and Characterization of $(C_5Me_5)_2U(-N{=}CPh_2)_2$

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Summary: The first example of an f-element ketimido complex has been prepared. Complex **2** *is surprisingly unreactive and displays unusual electronic properties. The physical properties and chemical stability of this complex suggest higher U−N bond order due to significant ligand to metal π-bonding in the uranium ketimido interactions.*

The reactivity of the uranium−nitrogen σ-bond has played a central role in the development of modern organometallic uranium chemistry.[1] Uranium amide complexes, like their transition-metal counterparts, constitute an important class of compounds that have been exploited as valuable precursors for the synthesis of a large array of coordination compounds due to their propensity to undergo protonolysis[2] with acidic substrates and insertion reactions[3] with small polar molecules. In fact, recent work has capitalized on the highly reactive nature of the U−N linkage in complexes of the type $(C_5Me_5)_2U(NHR)_2$ to develop organouranium-catalyzed chemistry.[4]

We have been interested in the development of new synthetic entries toward uranium complexes containing multiply bonded functional groups.[5] One particular target of interest has been the ketimido, or azavinylidene, functionality ($-N{=}CR_2$), which has much precedence within the d-block metals but is less known for the f-elements.[6] The ketimido ligand is attractive from the standpoint that it can serve not only as a σ-donor but also as a π-donor. The ability of the ketimido ligand to function as a π-base to an actinide metal center is of interest, since the resulting metal complex might be expected to experience enhanced stability due to higher bond order between the metal and ligand. Thus, the preparation of actinide ketimido complexes could shed light on the importance of f-orbital participation in bonding schemes for actinide metals in lower oxidation states (III, IV). To this end, we have developed a direct route to access uranium complexes possessing the ketimido functional group. Herein, we report the syn-

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[1] Berthet, J. C.; Ephritikhine, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 83−116 and references therein.

[2] (a) Jamerson, J. D.; Takats, J. *J. Organomet. Chem.* **1974**, *78*, C23−C25. (b) Arduini, A. L.; Edelstein, N. M.; Jamerson, J. D.; Reynolds, J. G.; Schmid, K.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2470−2474.

[3] (a) Bagnall, K. W.; Yanir, E. *J. Inorg. Nucl. Chem.* **1974**, *36*, 777−779. (b) Arduini, A. L.; Jamerson, J. D.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2474−2479. (c) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206−2220.

[4] (a) Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541−2546. (b) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017−5035 and references therein.

[5] (a) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448−9460 and references therein. (b) Arney, D. S. J.; Schnabel, R. C.; Scott, B. L.; Burns, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 6780−6781. (c) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959−960. (d) Duval, P. B.; Burns, C. J.; Clark, D. L.; Morris, D. E.; Scott, B. L.; Thompson, J. D.; Werkema, E. L.; Jia, L.; Andersen, R. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3358−3361.

[6] (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E., Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291−1300. (b) Erker, G.; Frömberg, W.; Krüger, C.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400−2405. (c) Zippel, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429−4437 and references therein.

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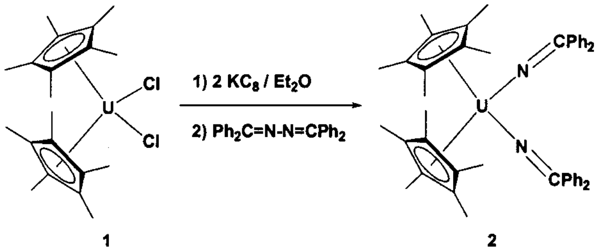
thesis and characterization of the first actinide ketimido complex, $(C_5Me_5)_2U(-N{=}CPh_2)_2$.

Entry into this new class of organouranium complexes is achieved by treatment of a diethyl ether solution of $(C_5Me_5)_2UCl_2$ (**1**) with 2 equiv of a reducing species (provided by KC_8), followed by reaction with 1 equiv of benzophenone azine, $Ph_2C{=}NN{=}CPh_2$. Filtration and removal of solvent furnishes a brown powder, which may be recrystallized from hot hexanes to provide $(C_5Me_5)_2U(-N{=}CPh_2)_2$ (**2**) in 68% yield (eq 1).[7] Our convenient synthetic route into the bis(amide) ligand system takes advantage of KC_8 for the reduction of **1** to generate the uranium(III) complex $(C_5Me_5)_2UCl(KCl)$, which is known to function as an uranium(II) synthetic equivalent.[5c,d] Reductive cleavage of the N−N bond in benzophenone azine affords **2** in high yield.



(1)

The modest isolated yield reflects the high solubility of the complex rather than the formation of any byproducts. When the reaction is monitored by ^1H NMR spectroscopy, **2** is the only observable uranium-containing product and is formed in >95% yield. Also, the NMR spectrum of **2** is sharp and paramagnetically shifted, which suggests that the complex is a U(IV) species.

The identity of complex **2** as a uranium(IV) bis(ketimido) complex was unambiguously ascertained by a single-crystal X-ray diffraction study (Figure 1).[8] The molecular structure of **2** reveals a typical bent-metallocene framework with a pseudotetrahedral coordination environment about the uranium atom. Within the metallocene wedge lie the two ketimido ligands, which are terminally bound via nitrogen to the uranium metal center (U(1)−N(1) = 2.179(6) Å, U(1)−N(2) = 2.185(5) Å, and N−U−N = 107.2(2)°). Importantly, the uranium−nitrogen bond distances in **2** are significantly shorter compared to other structurally characterized uranium(IV) bis(amido) complexes (e.g.: $(C_5Me_5)_2U\{NH(2,6\text{-}Me_2C_6H_3)\}_2$, U−N = 2.267(6) Å;[4a] $(C_5Me_5)_2U\{NH(4\text{-}ClC_6H_4)\}_2$, U−N = 2.269(4) Å[9]).

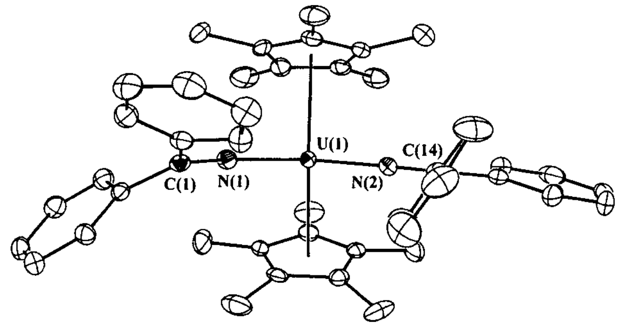


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): U(1)−N(1), 2.179(6); U(1)−N(2), 2.185(5); N(1)−C(1), 1.293(8); N(2)−C(14), 1.281(8); U(1)−N(1)−C(1), 173.4(6); U(1)−N(2)−C(14), 176.5(5); N(1)−U(1)−N(2), 107.2(2).

The most striking aspects of the structure are the nearly linear U−N−C bond angles (U(1)−N(1)−C(1) = 173.4(6)° and U(1)−N(2)−C(14) = 176.5(5)°), which may be consistent with the formulation of the ligands as ketimido groups with the uranium metal center accepting density from the nitrogen 2p lone pairs. Complex **2** is reminiscent of high-valent uranium(VI) bis(imido) complexes which have significant uranium−imido multiple bond character, as typified by the complex $(C_5Me_5)_2U({=}N-Ph)_2$, which exhibits a U−N−C bond angle of 177.8(6)° and U−N = 1.952(7) Å.[10] The metal center in complex **2** is not U(VI), which is evident upon comparison of the U−N bond distances in the two systems as well as the NMR and UV−visible−near-IR spectra.

In addition, the planes defined by $N(1){=}C(1)(C_{ipso})_2$ and $N(2){=}C(14)(C_{ipso})_2$ are essentially orthogonal (111.1 and 85.1°, respectively) to the Cp(centroid)−U−Cp(centroid) (Cp = C_5Me_5) plane. The two N=C fragments each have bond lengths (N(1)−C(1) = 1.293(8) Å, N(2)−C(14) = 1.281(8) Å) typical for an sp^2 carbon−nitrogen double bond.[11] The N=C bond distances compare well with those found in other structurally characterized ketimido complexes.[6] All of the combined structural features suggest that there is significant ligand to metal π-bonding in both uranium ketimido interactions.

The bis(ketimido) complex **2** is rather interesting in that it is an f^2 system and yet it does not behave chemically or electronically like known U(IV) amido complexes.[12] Perhaps the most distinguishing chemical property of complex **2** is that it displays no reaction chemistry with substrates such as benzophenone, phenylacetylene, diphenylacetylene, carbon monoxide, pyridine *N*-oxide, or dihydrogen. This is in marked contrast with observations reported by Marks and Eisen, who have shown that uranium(IV) amide complexes of the type

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[7] A flask was charged with **1** (0.952 g, 1.64 mmol), KC_8 (0.493 g, 3.65 mmol), and diethyl ether (60 mL) and the mixture was stirred at room temperature for 6 h. To this green slurry was added $Ph_2C{=}NN{=}CPh_2$ (0.542 g, 1.50 mmol) in diethyl ether (40 mL). The resultant mixture was stirred at room temperature for 12 h and then filtered through a Celite-padded frit to remove the charcoal and KCl byproducts, and the volatiles were removed under reduced pressure to afford a brown solid. This solid was taken up in toluene (30 mL) and filtered through a Celite-padded frit to remove any residual KCl. The filtrate was collected, and the volatiles were removed under reduced pressure to give crude **2** as a dark yellow crystalline solid. Analytically pure samples of **2** were obtained by recrystallization from hot hexanes (0.888 g, 1.02 mmol, 68%). ^1H NMR (toluene-d_8, 300 MHz, −75 °C): δ 88.88 (br s, 4H, Ar *H*), 26.32 (br s, 2H, Ar *H*), 24.49 (br s, 4H, Ar *H*), 9.18 (br s, 2H, Ar *H*), −4.34 (br s, 4H, Ar *H*), −4.70 (s, 30H, Cp*−CH_3), −10.89 (br s, 4H, Ar *H*). UV−vis−near-IR (ϵ, $M^{-1}\,cm^{-1}$, toluene): 323 (15 860), 465 (2210), 615 (680), 700 (210), 940 (35), 985 (61), 1111 (249), 1185 (295), 1245 (426), 1355 (150), 1381 (160), 1529 (196). MS (EI, 70 eV): *m/z* 868 (M^+), 733 (M^+ − Cp*), 688 (M^+ − N=CPh$_2$). Anal. Calcd for $C_{46}H_{50}N_2U$ (mol wt 868.91): C, 63.58; H, 5.80; N, 3.23. Found: C, 63.51; H, 5.85; N, 3.27.

[8] Data for brown crystal of **2**: triclinic, $P\bar{1}$, $Z = 4$, $a = 10.544(1)$ Å, $b = 20.260(3)$ Å, $c = 20.501(3)$ Å, $\alpha = 64.548(2)°$, $\beta = 83.120(3)°$, $\gamma = 82.388(3)°$, $V = 3909.9(9)$ Å^3, $T = 203$ K, $R(I > 2\sigma) = 0.0376$, and GOF = 1.242.

[9] Peters, R. G.; Scott, B. L.; Burns, C. J. Unpublished results.

[10] Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 10068−10069.

[11] Allen, F. H.; Kennard, P.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

[12] Complex **2** also exhibits an unusually high melting point (201−203 °C). The mass spectrometry fragmentation pattern reveals loss of C_5Me_5 rather than loss of N=CPh$_2$, providing further evidence for the robust character of the $U(-N{=}CPh_2)_2$ core.

$(C_5Me_5)_2U(NR'R)_2$ readily insert carbon monoxide to form bis(carbamoyl) complexes, $(C_5Me_5)_2U(\eta^2\text{-CONR'R})_2$,[3c] as well as undergo amine elimination upon reaction with phenylacetylene to generate the bis(acetylide) complex $(C_5Me_5)_2U(-C{\equiv}CPh)_2$.[4a] Although steric arguments are often made to account for the variability in reactivity between different amido groups, such an argument cannot be made in the case with the bis(ketimido) complex, since the phenyl groups are one atom removed from the nitrogen atom, thereby providing easier access to the metal center compared to amido ligands. Thus, the lack of reactivity evinced by complex **2** simply reflects the stronger bond in the uranium−ketimido interaction.

The U(IV) bis(ketimido) complex shows interesting electrochemistry. Two reversible reduction processes can be observed at $E_{1/2} = -2.51$ and -2.79 V, and a reversible oxidation step is found at -0.48 V (vs $[FeCp_2]^{0/+}$). This is in contrast to the electrochemistry typically observed for other $(C_5Me_5)_2UX_2$ (X = Me, CH_2Ph, Cl) systems, which display a reversible redox wave at ~ -2 V attributable to the U(IV/III) couple and only irreversible oxidative chemistry.[13] In comparison to the simple U(IV) metallocene systems, the metal center in the bis(ketimido) complex has become more difficult to reduce and easier to oxidize (both the U(IV/III) and U(V/IV) couples are shifted to more negative potentials), which is consistent with a more electron-rich U(IV) metal center sustained by donation of electron density from the ketimido ligand.

The novelty in the electronic structure is also manifest in the electronic absorption spectrum for complex **2**. The room-temperature UV−visible−near-IR spectrum, recorded in toluene solution from 1600 to 300 nm, displays relatively few near-IR electronic transitions, the most prominent of which occur at 1185 and 1245 nm, with ϵ values (295 and 425 M^{-1} cm^{-1}, respectively) being rather large for nominally parity forbidden transitions. This is clearly distinct from the electronic absorption spectra typically observed for actinide complexes with f^2 electronic configurations, which are rich with narrow line width, low molar absorptivity (<100 M^{-1} cm^{-1}) transitions derived from the ^3H ground state.[14]

In summary, the first ketimido complex of an f-element has been isolated. The structural features of the complex suggest a model of bonding that involves significant stabilization of the ligand π-electron pairs by metal-based orbitals, resulting in higher bond order in the uranium−ketimido interactions. That the nitrogen lone pairs strongly interact with the uranium metal center is manifested in the chemistry (or lack thereof) and unusual electronic properties of this complex. Interestingly, the combined data are suggestive of electronic delocalization throughout the N−U−N core and indicate that the f-electrons in mid-valent organouranium complexes might play a considerable role in bonding and reactivity. The synthetic methodology presented in this contribution can be applied to the preparation of a wide variety of uranium(IV) ketimido complexes. We are currently exploring the generality of this chemistry as well as the behavior of this new class of actinide complexes.

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Supporting Information Available: Figures giving voltammetric data and UV−vis−near-IR electronic spectrum for **2** and tables giving X-ray crystallographic information for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020381K

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[13] Morris, D. E.; Kiplinger, J. L.; Burns, C. J. Manuscript in preparation.

[14] Carnall, W. T.; Crosswhite, H. M. Optical Spectra and Electronic Structure of Actinide Ions in Compounds and in Solution; Argonne National Laboratory Report ANL-84-90; August 1985.