Uranium Complexes

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A Nitrido-Centered Uranium Azido Cluster Obtained from a Uranium Azide**

*Grégory Nocton, Jacques Pécaut, and Marinella Mazzanti**

Metal nitrides are a particularly interesting class of compounds owing to their potential application in catalysis or materials science.[1,2] In particular, uranium nitrides have been proposed as suitable materials for the development of nuclear fuel in light of their stability, high thermal conductivity, and high melting point.[3] Accordingly, molecular uranium nitrides would be very useful reagents for the synthesis of highly pure uranium nitrides, which are difficult to obtain under the extreme reaction conditions of conventional ceramics synthesis.[4] Moreover, nitrides have been shown to play an important template role in the assembly of metal clusters[5,6] and could therefore provide a new route to expand actinide cluster chemistry, which remains limited in spite of the high current interest.[7–12]

Despite their relevance, nitrides remain elusive in molecular actinide chemistry, and only three examples of molecular uranium nitrides have been reported. A dimeric uranium nitrido complex was obtained from the reduction of nitrogen by a tetrapyrrole complex of low-valent uranium,[13] while the recent isolation of a large polymetallic, nanometer-sized nitrido/azido uranium ring[14,15] suggests that nitrido compounds can be used to expand the supramolecular chemistry of the f elements.[16] These fascinating compounds were prepared by using a classic synthetic method which involves the two-electron reduction of azide to nitride and N_2 by a reducing metal complex.[2] However, for low-valent uranium this method appears very sensitive to the nature of the ancillary ligands and has in other cases resulted only in the isolation of stable uranium azido complexes,[17–21] including a structurally characterized binary heptaazido anion.[22]

We have recently shown the versatility of the oxidation reactions of trivalent uranium iodide to produce high-nuclearity clusters.[7] We are now investigating the synthesis of polymetallic nitrido compounds that are very dense in uranium and nitrogen from uranium triiodide in the absence of stabilizing ancillary ligands. In a previous study the reaction of $[UI_3(thf)_4]$ with an alternative nitride source was found to yield a unique hexakisamido complex of U^{V} [23] instead of the expected nitride. Conversely we found that the direct reaction of $[UI_3(thf)_4]$ with the more reactive azides CsN_3 or Bu_3SnN_3 is difficult to control and leads only to intractable solids. These results highlight the need for alternative nitride sources. Herein we show that the use of the tetravalent uranium azide "$Cs_3[U(N_3)_7]$" (**1**) as a nitride source provides a convenient route for the synthesis of the tetranuclear azido/nitrido U^{IV} cluster $\{[(Cs(CH_3CN)_3][U_4(\mu_4\text{-}N)(\mu\text{-}N_3)_8(CH_3CN)_8I_6]\}_\infty$ (**3**) from trivalent uranium iodide according to Equation (3).

$$[UI_4(PhCN)_4] + 7\,CsN_3 \xrightarrow[CH_3CN]{-4\,CsI} \text{“}Cs_3[U(N_3)_7]\text{”}\ (\mathbf{1}) \qquad (1)$$

$$\text{“}Cs_3[U(N_3)_7]\text{”} \xrightarrow[pyridine]{-3\,CsN_3} \mathbf{2} \qquad (2)$$

$$2\,\text{“}Cs_3[U(N_3)_7]\text{”} + 2\,[UI_3(thf)_4] \xrightarrow[CH_3CN]{-5\,CsN_3/-N_2} \mathbf{3} \qquad (3)$$

The tetravalent uranium azide precursor was prepared in situ by treating $[UI_4(PhCN)_4]$[24] with seven equivalents of CsN_3 in acetonitrile according to Equation (1). The instability of the azide complex **1** in acetonitrile solution prevented its isolation; the nature of the decomposition products is under investigation. The formula of the intermediate was assigned in analogy to the recently reported heptaazido complex $(Bu_4N)_3[U(N_3)_7]$ prepared from the reaction of the tetravalent $(Bu_4N)_2[UCl_6]$ with AgN_3 in acetonitrile.[22] The difference in stability of the two compounds is probably due to the presence of a very different counterion. However, the neutral pyridine adduct $[U(N_3)_4(py)_4]$ (**2**) is sufficiently stable to allow its isolation from pyridine and its crystallographic characterization. The crystal structure of complex **2** shows the presence of a tetravalent uranium center that is eightfold coordinated by four pyridine ligands and four terminal azido ligands with a distorted dodecahedral geometry (Figure 1).

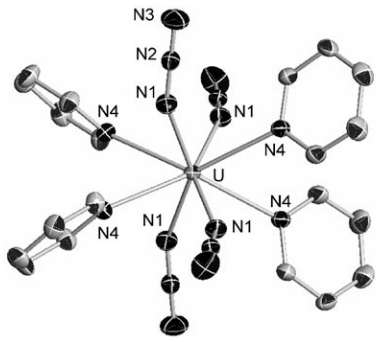

Figure 1. ORTEP view of **2** with thermal ellipsoids at the 30% probability level.

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[*] G. Nocton, Dr. J. Pécaut, Dr. M. Mazzanti
Laboratoire de Reconnaissance Ionique et Chimie de Coordination
Laboratoire de Chimie Inorganique et Biologique
(UMR-E 3 CEA-UJF), INAC, CEA-Grenoble
17 rue des Martyrs, 38054 Grenoble, Cedex 09 (France)
Fax: (+33) 4-3878-5090
E-mail: marinella.mazzanti@cea.fr

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The complex **2** has an S_4 crystallographic axis relating each of the four pyridine ligands and each of the four azido ligands. The U$-$N$_{azide}$ bond lengths (2.314(3) Å) fall in the range of the U$-$N bond lengths found in the few other crystallographically characterized U^{IV} azido complexes (2.219(6) to 2.564(1) Å).[14,17,20–22,25]

The addition of [UI$_3$(thf)$_4$] to the unstable green intermediate "Cs$_3$[U(N$_3$)$_7$]" is accompanied by gas evolution and leads to the isolation of the azido/nitrido cluster **3** in 47% yield. Cluster **3** is very reactive towards oxygen and water but is stable in acetonitrile solution at room temperature for several weeks. The molecular structure of **3** was elucidated by X-ray diffraction, which shows the presence of 1D polymeric chains of tetranuclear uranium clusters connected through cesium ions binding the coordinated iodide atoms (Figure 2).

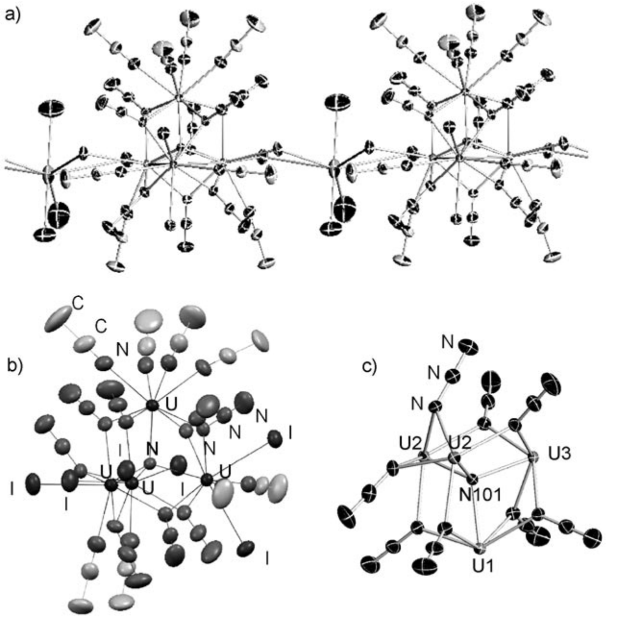

Figure 2. ORTEP views of a) 1D polymer **3**, b) the anion [U$_4$(μ_4-N)(μ-1,1-N$_3$)$_8$(CH$_3$CN)$_8$I$_6$]$^-$, and c) the azido/nitrido cluster core {U$_4$(μ_4-N)(μ-1,1-N$_3$)$_8$} with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å]: U1-N101 2.316(5), U2-N101 2.271(3), U3-N101 2.399(5), mean U1-N$_{azide}$ 2.453(7), mean U2-N$_{azide}$ 2.46(2), mean U3-N$_{azide}$ 2.49(2), mean U2-I 3.15(5), mean U3-I 3.20(5), mean U1-N$_{MeCN}$ 2.59(3), U2-N$_{MeCN}$ 2.599, U3-N$_{MeCN}$ 2.594.

The structure exhibits three symmetrically independent uranium atoms, and a symmetry plane passing through U3, U1, and N101 relates the two equivalent U2 ions. In **3** four uranium cations are connected by eight 1,1-end-on bridging azido ligands to form a slightly distorted tetrahedron (two edges are bridged by two azido ligands, four edges by one azido ligand). The U$-$N$_{azide}$ bond lengths range from 2.441(4) Å to 2.511(4) Å. These values are very similar to those found for the 1,3-end-to-end bridging azido ligands in previously reported U^{IV} azido/nitrido polymetallic rings (2.449(14)–2.525(7) Å),[14] while the end-on azido bridging mode results in shorter U$-$U separations (3.55 vs. 3.90 Å). A quadruply bridging nitrido ligand is included in the tetrahedron and binds the four uranium ions in an asymmetric mode with bond lengths ranging from 2.271(3) to 2.399(5) Å. These values are close to that reported for six-coordinate uranium nitride (U$-$N = 2.444(9) Å),[26] while a shorter U$^{IV}-$(μ_3-N^{3-}) bond length (2.15(3) Å) was found for a trinuclear U^{IV} complex containing a triply bridging nitrido ligand (μ_3-N^{3-}) that was isolated from the reduction of azide by a U^{III}(cyclopentadienyl) iodide species.[15] N^{3-}-centered tetrahedra are found in the crystal structures of quaternary nitride tellurides of lanthanides prepared by a high-temperature, solid-state reaction;[27] the reported anisotropic thermal parameters are very similar to those found in the structure refinement of **3**. The UV/Vis/NIR spectrum of **3** shows absorption maxima only at 694 and 1153 nm, which is typical for U^{IV} species. The overall cluster charge is balanced with an interstitial N^{3-} ligand and four tetravalent uranium ions. Notably, the observed gas formation during the reaction in Equation (3) is in agreement with nitride formation as a result of the two-electron reduction of one azido ligand by two U^{III} ions.

Temperature-dependent magnetic susceptibility data were collected for **3** in the temperature range from 6 to 300 K (Figure 3). The χ vs. T values increase with decreasing temperature and level off to a constant temperature-independent value at $T < 45$ K. A temperature-independent paramagnetism (TIP) is a typical magnetic response of molecular U^{IV} compounds at low temperature owing to coupling between a nonmagnetic ground state and low-lying excited states through a Zeeman perturbation.[28] This type of magnetic response is not observed in mixed-valence U^{III}/U^{IV} complexes, in which the χ vs. T values continue to increase at low temperature.[29] The measured room-temperature magnetic moment ($\mu_{eff} = 3.44\,\mu_B$ at 300 K) is in the range of the values previously reported for mononuclear U^{IV} complexes (2.5–3.55 μ_B).[28,30] The observed low-temperature field dependency of the magnetization shows a small response of less than 0.9 μ_B, which is typical for U^{IV} compounds (Figure S6 in the Supporting Information).[31] These magnetic data provide clear evidence that complex **3** contains only U^{IV} ions.

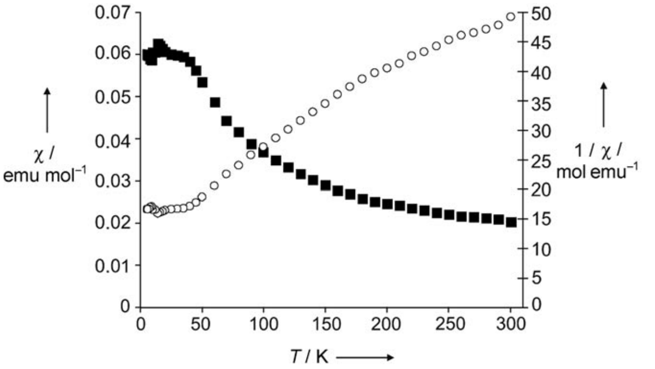

Figure 3. Temperature-dependent magnetic susceptibility data for **3** from 6 to 300 K. ■: χ (left-hand axis); ○: 1/χ (right-hand axis).

The existence of mixed uranium nitrido/azido species had been predicted by quantum chemical calculations,[32] but only one example of such species has been previously isolated in the presence of supporting cyclopentadienyl ligands.[14] Complex **3** is thus a very rare example of a molecular azido/nitrido uranium cluster and is the first prepared without stabilizing ancillary ligands. Moreover, **3** is the first example of a low-valent uranium complex containing 1,1-end-on bridging azido ligands. The isolation of cluster **3** shows that polymetallic assemblies that are very dense in uranium and nitrogen can be prepared from simple U^{III} iodide salts by using an appropriate nitride source, which is likely to play an important role in the cluster formation by exerting an organizational or template effect. Work is in progress to explore the possibility of obtaining larger clusters by using different reaction conditions. The two-step synthetic strategy presented here opens new perspectives for the preparation of uranium clusters and could provide a versatile route for the incorporation of low-valent uranium into heterodimetallic f–f azido clusters.

Experimental Section

3: In an argon-filled glovebox, a solution of $[UI_4(PhCN)_4]$ (75.0 mg, 64.8 μmol, 1 equiv) in acetonitrile (1 mL) was added to a suspension of cesium azide (79.4 mg, 454 μmol, 7 equiv) in acetonitrile (1 mL). The resulting brown solution was stirred for 20 min until the solution became deep green. A brown precipitate (CsI) formed and was removed by filtration. The green filtrate was added to a solution of $[UI_3(thf)_4]$ (58.8 mg, 64.8 μmol, 1 equiv) in acetonitrile (2 mL). The reaction was accompanied by gas evolution and a slow color change from deep green to the final deep red (after 25 h; see Figure S3 in the Supporting Information). A white precipitate formed (CsN_3), and the mixture was filtered. When the reaction between the intermediate and $[UI_3(thf)_3]$ was carried out with stirring, the reaction time decreased to 5 h. The slow diffusion of diisopropyl ether into the filtrate led to the isolation after several days of **3** as a microcrystalline deep red solid, which was recrystallized from acetonitrile and diisopropyl ether (1:4) to remove CsI and CsN_3 salts. Yield: 40.3 mg, 47%. Elemental analysis (%) calcd for $Cs[U_4(\mu_4\text{-}N)(\mu\text{-}N_3)_8(CH_3CN)_7I_6]\cdot 0.8\,i\text{Pr}_2O$ ($U_4C_{18.8}H_{32.2}N_{32}CsI_6O_{0.8}$, $M_r = 2565.7\ \text{g mol}^{-1}$): C 8.80, H 1.27, N 17.47; found: C 8.82, H 1.12, N 17.21.

Crystal data for **2**: $C_{20}H_{20}N_{16}U$, $M_r = 722.55$, tetragonal, space group $I4_1/a$, $a = 15.6286(19)$, $b = 15.6286(19)$, $c = 10.168(2)$ Å, $V = 2483.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.933\ \text{g cm}^{-3}$, $\mu = 6.581\ \text{mm}^{-1}$, $T = 223(2)$ K. Of the 4164 reflections collected, 1439 were unique ($R_{int} = 0.0187$). Refinement on all data converged at $R_1 = 0.0262$, $wR2 = 0.0560$. Max/min residual density 0.327/−1.969 e Å^{-3}. Crystal data for **3**: $C_{22}H_{33}CsI_6N_{36}U_4$, $M_r = 2648.27$, monoclinic, space group $P21m$, $a = 12.1065(9)$, $b = 13.3965(10)$, $c = 19.9014(15)$ Å, $\beta = 99.9690(10)°$, $V = 3179.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.767\ \text{g cm}^{-3}$, $\mu = 13.686\ \text{mm}^{-1}$, $T = 223(2)$ K. Of the 18229 reflections collected, 7842 were unique ($R_{int} = 0.0200$). Refinement on all data converged at $R_1 = 0.0343$, $wR2 = 0.0502$. Max/min residual density 1.783/−2.987 e Å^{-3}. CCDC-670287 (**2**) and CCDC-670286 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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