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Amidinate Supporting Ligands Influence Molecularity in Formation of Uranium Nitrides

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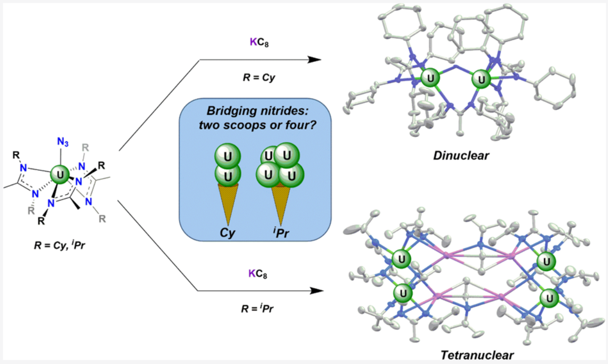

ABSTRACT: Uranium nitride complexes are attractive targets for chemists as molecular models for the bonding, reactivity, and magnetic properties of next-generation nuclear fuels, but these molecules are uncommon and can be difficult to isolate due to their high reactivity. Here, we describe the synthesis of three new multinuclear uranium nitride complexes, $[U(BCMA)_2]_2(\mu\text{-N})(\mu\text{-}\kappa^1{:}\kappa^1\text{-BCMA})$ (**7**), $[(U(BIMA)_2)_2(\mu\text{-N})(\mu\text{-N}^i\text{Pr})(K_2(\mu\text{-}\eta^3{:}\eta^3\text{-CH}_2\text{CHN}^i\text{Pr})]_2$ (**8**), and $[U(BIMA)_2]_2(\mu\text{-N})(\mu\text{-}\kappa^1{:}\kappa^1\text{-BIMA})$ (**9**) (BCMA = *N*,*N*-bis(cyclohexyl)-methylamidinate, BIMA = *N*,*N*-bis(*iso*-propyl)methylamidinate), from U(III) and U(IV) amidinate precursors. By varying the amidinate ligand substituents and azide source, we were able to influence the composition and size of these nitride complexes. ^{15}N isotopic labeling experiments confirmed the bridging nitride moieties in **7**–**9** were formed via two-electron reduction of azide. The tetra-uranium cluster **8** was isolated in 99% yield via reductive cleavage of the amidinate ligands; this unusual molecule contains nitrogen-based ligands with formal 1−, 2−, and 3− charges. Additionally, chemical oxidation of the U(IV) precursor $U(N_3)(BCMA)_3$ yielded the cationic U(V) species $[U(N_3)(BCMA)_3][OTf]$. Magnetic susceptibility measurements confirmed a U(IV) oxidation state for the uranium centers in the three nitride-bridged complexes and provided a comparison of magnetic behavior in the structurally related U(III)-U(IV)-U(V) series $U(BCMA)_3$, $U(N_3)(BCMA)_3$, and $[U(N_3)(BCMA)_3][OTf]$. At 240 K, the magnetic moments in this series decreased with increasing oxidation state, i.e., U(III) > U(IV) > U(V); this trend follows the decreasing number of 5f valence electrons along this series.

■ INTRODUCTION

Uranium nitride molecules and materials have been the subject of intense study in recent years due to the diverse reactivity profile of actinide-ligand multiple bonds[1−8] and the utility of these compounds as model systems for next-generation nuclear fuels.[8−11] Molecular uranium nitride complexes have been shown to facilitate a wide range of chemical transformations, such as C−H activation,[12−15] C−N bond formation,[16−18] and activation of small molecules such as N_2, H_2, CO, and CO_2.[19−22] Haber first discovered that bulk uranium nitrides could be used as effective catalysts for the conversion of N_2 to NH_3 in 1909,[23] and molecular models containing uranium nitride linkages have more recently been shown to undergo nitrogen fixation and conversion to NH_3.[24] In addition to their versatile reactivity, uranium nitride complexes and clusters have also gathered interest as single-molecule magnets, and the degree of magnetic communication between metal centers has been found to vary substantially based on the ligand environment in these species.[25−29]

Research in uranium nitride chemistry is often motivated by the goal of synthesizing dimensionally confined analogues that can be used to model the properties of bulk uranium mononitride (UN) fuels.[30−32] UN possesses a higher energy density and greater thermal conductivity than UO_2, conferring higher power output per unit mass and enhanced safety margins against thermal meltdown.[10,33] However, the chemical reactivity and the electronic and magnetic structure of uranium nitrides are still poorly studied in comparison to transition metal analogues, motivating the need for well-behaved models that can be used to investigate these fundamental properties.[34,35] Molecular uranium nitrides and related uranium-nitrogen complexes can be developed as versatile models for the physical and chemical properties of UN fuel materials, enabling us to study the electronic/magnetic structure and reactivity of uranium−nitrogen bonds in well-defined homogeneous systems.

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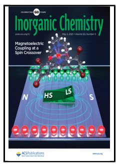
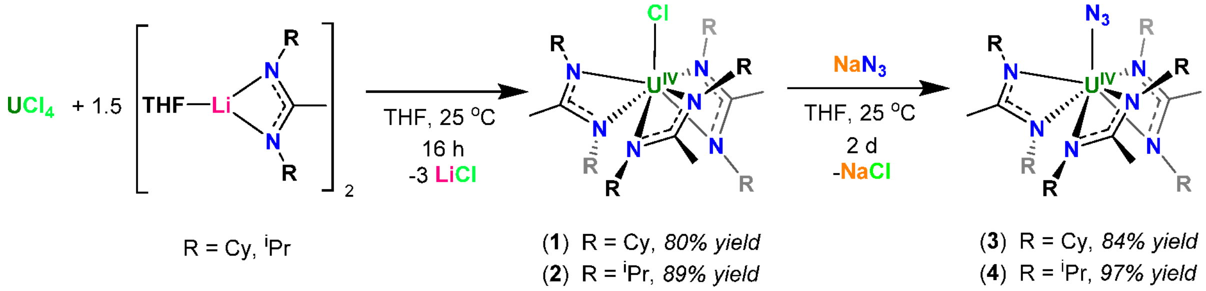


Scheme 1. Synthesis of UCl(BCMA)$_3$ (1), UCl(BIMA)$_3$ (2), U(N$_3$)(BCMA)$_3$ (3), and U(N$_3$)(BIMA)$_3$ (4)



Several ligand systems have been demonstrated to provide support for uranium nitride complexes, including azides,[32,36] siloxides,[21,22,28] cyclopentadienyls,[2] amides,[15,37] and triamidoamines.[3,25,26] Despite these advances, synthetic outcomes appear to be highly dependent upon small changes in the supporting ligand environment.[8] Our aim in this present work was to develop new nitride precursors with easily tunable supporting ligands to determine whether we could influence the pathways to—and composition of—any resulting nitride complexes. We chose amidinate ligands for this purpose because of their well-established steric and electronic tunability and because of their precedent as supporting ligands in actinide chemistry for a variety of chemical transformations.[38−47] As recently demonstrated by März and coworkers,[42] careful tuning of uranium coordination using amidate ligands provides new opportunities to isolate and characterize reactive nitride moieties. In addition, amidinate ligands bind to metals only through nitrogen atoms, the latter property being potentially useful in longer term efforts aimed at using these complexes as single-source precursors to uranium nitride materials.[48−52]

RESULTS AND DISCUSSION

Synthesis of U(IV) Azide Precursors. The uranium tris(amidinate) complexes UCl(BCMA)$_3$ (**1**) (BCMA = *N*,*N*-bis(cyclohexyl)methylamidinate)[53] and UCl(BIMA)$_3$ (**2**) (BIMA = *N*,*N*-bis(*iso*-propyl)methylamidinate) were synthesized in good (80−89%) yields via reaction of UCl$_4$ with 1.5 equiv of [Li(BCMA)(THF)]$_2$ and [Li(BIMA)(THF)]$_2$, respectively. Salt metathesis of **1** and **2** with NaN$_3$ generated the azide complexes U(N$_3$)(BCMA)$_3$ (**3**) and U(N$_3$)(BIMA)$_3$ (**4**) in 84% and 97% yield, respectively (Scheme 1).

The solid-state structures of the tris(amidinate) chloride complex **2** and the azide complexes **3** and **4** displayed pseudo-C_3 symmetry with a chloride or azide moiety bound to uranium along the pseudo-C_3 axis and κ^2-N,N coordination of all amidinates to the uranium center (Figures 1 and S1). The U−Cl distance of 2.673(6) Å in **2** is similar to the reported U−Cl distance of 2.678(1) Å in complex **1**.[53] Comparison of the U−N$_{\text{amidinate}}$ distances in **3** and **4** (2.366(6)−2.502(2) Å), as well as the U−N$_{\text{azide}}$ distances (2.340(6) Å in **3** and 2.335(3) Å in **4**; see Table S3 for full analysis), shows no significant difference in U−N bond lengths for these two ligand systems. The U−N$_{\text{amidinate}}$ and U−N$_{\text{azide}}$ bond lengths in **1**−**4** are comparable to the analogous U−N distances in the uranium amidinate complexes UCl(S-PEBA)$_3$ and U(N$_3$)(S-PEBA)$_3$.[42]

Reduction of the U(IV) chloride complexes **1** and **2** with metallic sodium in THF gave the dark blue homoleptic U(III) tris(amidinate) complexes U(BCMA)$_3$ (**5**)[53] and U(BIMA)$_3$ (**6**), respectively, in excellent (95−100%) yields (Scheme 2).

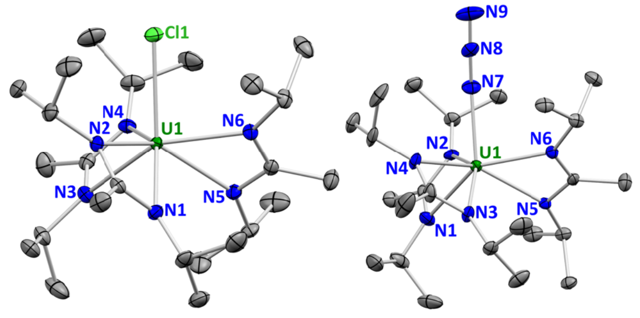
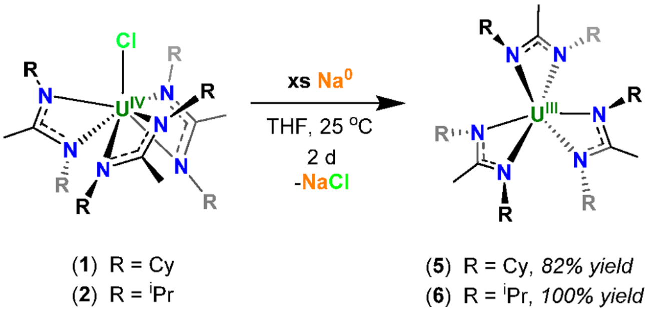


Figure 1. X-ray crystal structure of **2** (left) and **4** (right) shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. See Figure S1 for structure of **3**.

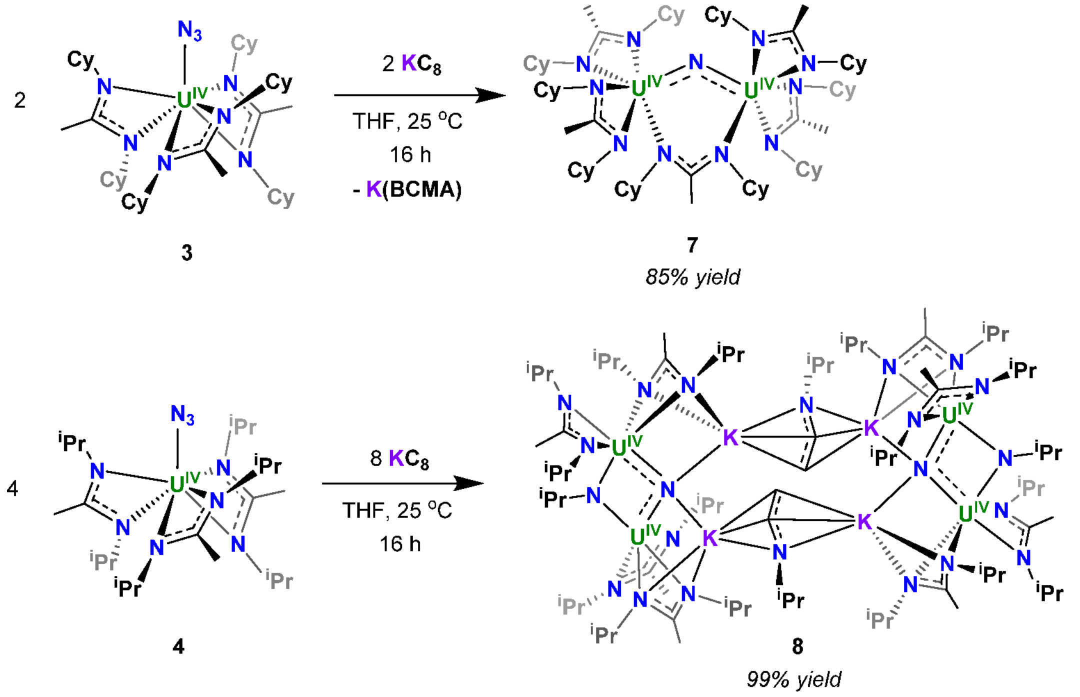
Scheme 2. Synthesis of U(BCMA)$_3$ (5) and U(BIMA)$_3$ (6)



Synthesis of Uranium Nitrides. We next sought to determine if reduction of the azide moieties on **3** and **4** could facilitate the formation of molecular uranium nitride species by loss of N$_2$. Photolysis of **3** and **4** with ultraviolet light yielded an intractable mixture of products, so we turned next to redox reactions. To investigate the redox behavior of **3** and **4**, we performed cyclic voltammetry in THF using [(^{n}Bu)$_4$N][PF$_6$] as the supporting electrolyte. Complex **3** was found to undergo a reversible oxidation at $E_{1/2}$ = −0.49 V vs Fc/Fc$^+$ (ΔE = 0.17 V) and an irreversible reduction at E_{pc} = −3.42 V, while complex **4** underwent a reversible oxidation at $E_{1/2}$ = −0.29 V vs Fc/Fc$^+$ (ΔE = 0.15 V) and an irreversible reduction at E_{pc} = −3.21 V (Figures S3−S5).

Consistent with these findings, chemical reduction of **3** with 1 equiv of KC$_8$ in THF did not result in a simple electron transfer, instead yielding a new red product (**7**). X-ray crystallography revealed **7** to be an unusual dinuclear uranium complex, with the two metals bridged by a nitride moiety and an amidinate. An interesting oxidative route and details of the X-ray structure of **7** will be discussed below (Scheme 4). When 2 equiv of KC$_8$ were added to a THF solution of **3**, the tris(amidinate) U(III) species **5** was isolated as the major

Scheme 3. Synthesis of the Bridging U(IV)−U(IV) Nitride $[U(BCMA)_2]_2(\mu\text{-}N)(\mu\text{-}\kappa^1{:}\kappa^1\text{-}BCMA)$ (7) and the Tetra-U(IV) Cluster $[(U(BIMA)_2)_2(\mu\text{-}N)(\mu\text{-}N^iPr)\text{-}(K_2(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2CHN^iPr)]_2$ (8) by Reaction of the U(IV) Azides 3 and 4, Respectively, with KC_8



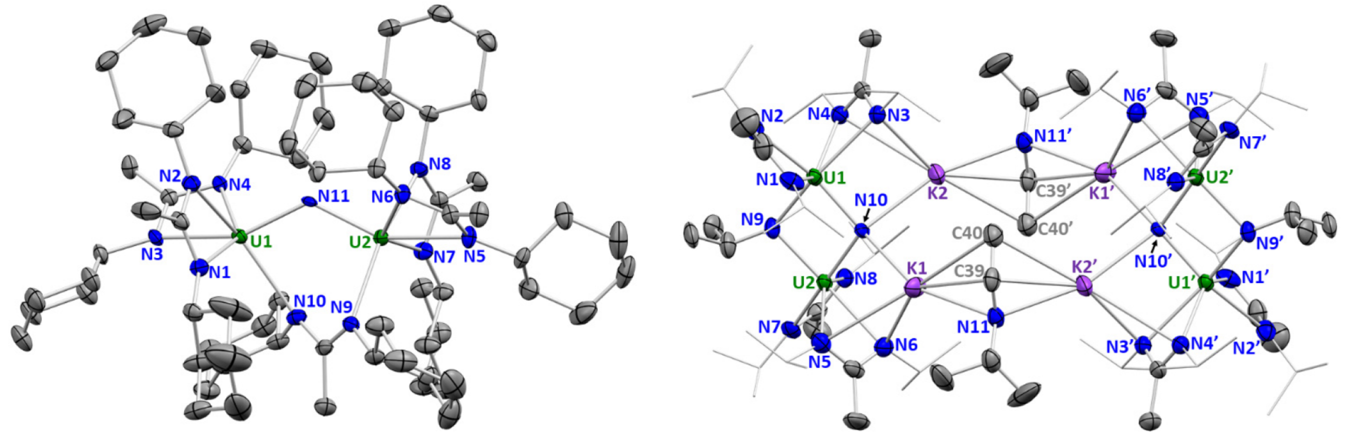


Figure 2. X-ray crystal structures of $[U(BCMA)_2]_2(\mu\text{-}N)(\mu\text{-}\kappa^1{:}\kappa^1\text{-}BCMA)$ (7) (left) and $[(U(BIMA)_2)_2(\mu\text{-}N)(\mu\text{-}N^iPr)(K_2(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2CHN^iPr)]_2$ (8) (right) shown with 50% probability ellipsoids. Hydrogen atoms are omitted, and amidinate isopropyl groups in 8 are shown in wireframe for clarity.

product (70% yield, Scheme 3), and 7 was also isolated in 11% yield by fractional crystallization from hexane. In contrast, reduction of the ^{i}Pr analogue **4** with 1 equiv of KC_8 in THF gave an intractable mixture of products. However, when 2 equiv of KC_8 was added to **4** in THF, the solution quickly changed color from green to blue, then again to red within 15 min. X-ray diffraction studies of the resulting product revealed an octametallic cluster (**8**) containing four uraniums, four potassiums, and two bridging nitrides (99% yield, Scheme 3). Of particular interest in the structure of **8** was the presence of imido ($(N^iPr)^{2-}$) and vinylamido ($(CH_2CHN^iPr)^-$) fragments, no doubt formed by reductive cleavage of the amidinate ligands, which results in a unique structure in which all four uranium atoms are N-bound to ligands having formal mono-, di-, and tri-anionic character. Related fragmentation of amidinate ligands, though rare, has been documented in zirconium systems.[54]

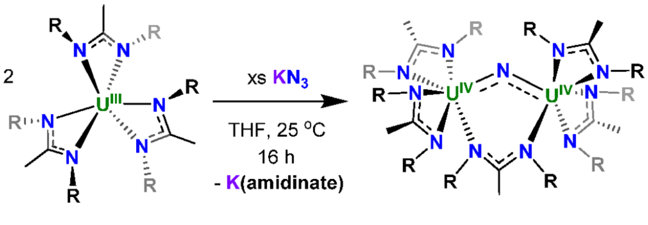
Complex **8** crystallizes on an inversion center in the space group $P\bar{1}$ with an asymmetric unit containing two uranium and two potassium atoms connected through bridging vinylamido moieties (Figure 2). Each uranium atom has two amidinate ligands coordinated in a κ^2-N,N geometry with $U-N_{amidinate}$ distances of 2.452(7)−2.618(7) Å, although one of these ligands on each uranium displays inequivalent bridging κ^2-N,N contacts to a potassium atom, with $K-N_{amidinate}$ distances ranging from 2.839(8) to 3.342(5) Å. The imido fragment bridging the uranium centers displays U1−N9 and U2−N9 distances of 2.187(7) and 2.233(5) Å, respectively, and a U1−N9−U2 angle of 100.1(2)°. The nitride moiety bridges the uranium centers as well, with slightly shorter U1−N10 and

U2−N10 distances of 2.132(5) and 2.101(6) Å, respectively, and a U1−N10−U2 angle of 106.4(2)°. These U−$N_{nitride}$ bonds are slightly (0.01−0.08 Å) longer than the reported values for U−$N_{nitride}$ bonds in the octa-U(IV) nitride cluster $[(C_5Me_4R)_2U(\mu\text{-}N)U(\mu\text{-}N_3)(C_5Me_4R)_2]_4$[32] and the U(IV)−U(V) bridging nitride cluster $[K(DME)_4][\{K(DME)(Et_8\text{-}calix[4]tetrapyrrole)U\}_2(\mu\text{-}NK)_2]$,[55] which also contains four potassium atoms in the coordination sphere. Similarly, the nitride ligands in **8** are in contact with two potassium atoms each, with K−N10 distances of 2.779(6) and 2.789(6) Å. In addition to interactions with amidinate and nitride ligands, each potassium is also bound to the bridging vinylamido fragments in a μ-η^3:η^3 coordination mode.

Following isolation of these distinctly different uranium nitride compounds via KC_8 reduction of **3** and **4**, we sought to investigate whether a dinuclear uranium nitride analogous to **7** could be isolated, as this would provide access to a second uranium nitride complex stabilized by the BIMA ligand system and also demonstrate control over product nuclearity.

Direct oxidation of **6** with KN_3 proved effective, giving the dinuclear uranium nitride $[U(BIMA)_2]_2(\mu\text{-}N)(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-BIMA})$ (**9**) in 93% yield. Similarly, oxidation of **5** with KN_3 resulted in the formation of **7**, giving the desired product in 61% yield (Scheme 4). In these reactions, 2 equiv of the U(III) amidinates **5** or **6** reacts with 1 equiv of KN_3, forming the dinuclear U(IV)−U(IV) nitrides **7** and **9** by reduction of the azide to a nitride and N_2, with concomitant precipitation of K(BCMA) or K(BIMA).

Scheme 4. Synthesis of the Bridging U(IV)−U(IV) Nitrides $[U(BCMA)_2]_2(\mu\text{-}N)(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-BCMA})$ (7) and $[U(BIMA)_2]_2(\mu\text{-}N)(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-BIMA})$ (9) by Oxidation of the Homoleptic U(III) Amidinates 5 and 6 with KN_3



(5) R = Cy
(6) R = ^{i}Pr

(7) R = Cy, *61% yield*
(9) R = ^{i}Pr, *93% yield*

The solid-state structures of **7** (Figure 2) and **9** (Figure S2) are very similar, with two uranium centers bridged by a nitride and a μ-κ^1:κ^1 bound amidinate ligand (see Table S4 for full comparison). Compounds **7** and **9** contain U−$N_{nitride}$ bond lengths ranging from 2.023(3) to 2.057(3) Å and U1−N11−U2 angles of 127.0(2)° and 133.6(2)°, respectively; these metrics are within the typical range reported for U(IV)−U(IV) bridging nitrides.[1,8]

The bridging amidinate ligands in both **7** and **9** adopt a μ-κ^1:κ^1 coordination mode, with each nitrogen atom bound to distinct uranium centers and U1−N10 and U2−N9 distances ranging from 2.485(3) to 2.563(2) Å. In the κ^2-N,N bound amidinates, U−$N_{amidinate}$ bond distances range from 2.422(4) to 2.577(4) Å.

Although we were able to synthesize both the BCMA- and BIMA-supported dinuclear complexes **7** and **9** via direct oxidation of **5** and **6** with KN_3, the different outcomes from reduction of the azide complexes **3** (R = Cy) versus **4** (R = ^{i}Pr) are pronounced and were surprising at first given the similarity of the amidinate ligands used. We note, however, that the cyclohexyl substituents on the BCMA ligand in **3** result in an overall much larger steric profile than the *iso*-propyl substituents on the BIMA ligand, thereby hindering formation of an analogous tetra-uranium cluster. The tetra-uranium cluster **8** could also be accessed in 68% yield by reduction of **9** (R = ^{i}Pr) with 2 equiv of KC_8, but no new uranium products were formed when **7** (R = Cy) was used instead. These findings further confirm the notion that small differences in ligand sterics may lead to rather different product outcomes in uranium chemistry.[56]

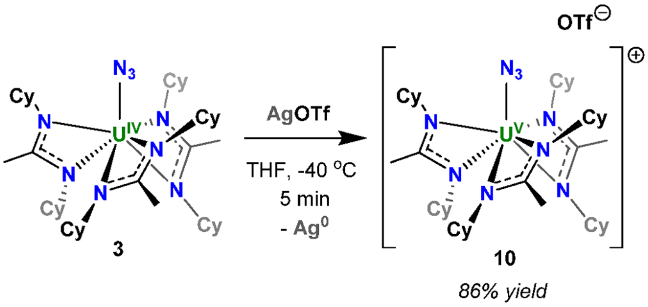
Acid Hydrolysis and ^{15}N Labeling. Since the structural parameters of bridging uranium nitrido and oxo complexes determined by X-ray diffraction are often quite similar,[1] we sought to confirm the identity of the nitride moieties through chemical means. In particular, we recognized that simple acid hydrolysis of **7**−**9** would be expected to form ammonium salts from bridging nitride but not from bridging oxo moieties.[25,57] Excess HCl (4.0 M in 1,4-dioxane) was added to Et_2O solutions of **7**−**9**, giving nearly colorless mixtures of decomposition products from each compound. After removal of the solvent, the soluble products were extracted into d_6-DMSO. The characteristic 1:1:1 triplet of NH_4Cl was evident in the ^1H NMR spectra for all three nitrides, confirming ammonium formation via acid hydrolysis of **7**−**9** (see Supporting Information (SI) for further details).

To provide additional evidence that the nitride moieties in these complexes were formed via reduction of azide, we prepared the labeled nitride complexes **7-^{15}N** and **9-^{15}N** by stirring **5** and **6** in THF with ^{15}N-labeled NaN_3 labeled solely at one terminal position. Similarly, we prepared **8-^{15}N** via reduction of **4-^{15}N** (formed by salt metathesis of **2** with ^{15}N-labeled NaN_3) with KC_8. If the nitride moieties in **7-^{15}N**, **8-^{15}N**, and **9-^{15}N** were indeed formed by reduction of the azide substituents, these complexes would be expected to contain approximately 50% ^{15}N for each nitride atom, corresponding to a roughly equal chance that the ^{15}N-labeled atom in each equivalent of NaN_3 would be incorporated as a nitride or lost as N_2. Accordingly, one U−N stretch would be expected in the IR spectra of **7**, **8**, and **9**, and two U−N stretches would be expected in the IR spectra of **7-^{15}N**, **8-^{15}N**, and **9-^{15}N**, with the U−^{15}N stretches at slightly lower energies than the U−^{14}N stretches.

To avoid overlap with Nujol in the pertinent regions, the labeled and unlabeled versions of each complex were dissolved in pentane and drop-cast onto KBr plates. The U−^{14}N stretches in **7**, **8**, and **9** were observed at 740, 730, and 729 cm^{-1}, respectively, and additional U−^{15}N stretches in **7-^{15}N**, **8-^{15}N**, and **9-^{15}N** were also observed at 724, 704, and 711 cm^{-1}, respectively (Figures S31−S36). In addition to yielding rare quantitative data regarding the energy of U−N stretching frequencies in bridging uranium nitrides, these results also provide further evidence for the formation of the nitride moieties in **7**−**9** through an azide reduction mechanism. Following these IR studies, **7-^{15}N**, **8-^{15}N**, and **9-^{15}N** were hydrolyzed with HCl as described above, and a multiplet corresponding to a statistical mixture of $^{15}NH_4Cl$ and $^{14}NH_4Cl$ was observed in the ^1H NMR spectra of these complexes (see SI for further details).

Magnetism. Following the synthesis of the uranium nitride complexes **7**−**9**, we sought to develop a series of related U(III), U(IV), and U(V) complexes that could be used as a benchmark for the magnetic behavior in these amidinate systems, therefore allowing us to accurately assign the oxidation state of the uranium atoms in **7**−**9** and enabling us to distinguish structure-based effects from oxidation state-dependent magnetic behavior. Upon addition of a THF solution of silver(I) triflate to the U(IV) azide complex **3**, the solution immediately changed from green to black. The cationic U(V) complex $[U(N_3)(BCMA)_3](OTf)$ (**10**) was isolated as a black crystalline solid in 86% yield (Scheme 5).

Scheme 5. Synthesis of $[U(N_3)(BCMA)_3](OTf)$ (10)



Complex **10** was found to be thermally unstable, undergoing complete decomposition to an intractable mixture of unidentified products within 1 h at room temperature as observed by ^1H NMR; nonetheless, storage of solid samples at −40 °C was sufficient to prevent any noticeable degradation over a period of months. Similarly to **3** and **4**, photolysis of **10** in THF resulted in an intractable mixture of products.

Single-crystal X-ray crystallographic data for **3** and **10** revealed that both possess distorted C_3 symmetry, each with all three of their amidinate ligands displaying κ^2-N,N chelation to the uranium center and an azide moiety protruding outward along the pseudo-C_3 axis (Figure 3). Although the connectivity in these two complexes is identical, the U−N bond lengths in **10** are all roughly ~0.1 Å shorter than those in **3** (Table 1), likely due to the increased charge and decreased ionic radius of U(V) versus U(IV).[58]

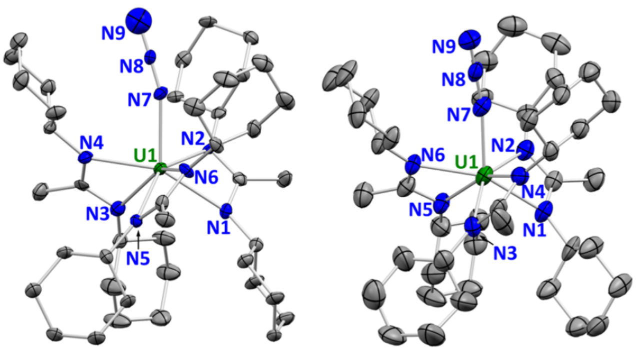


Figure 3. X-ray crystal structures of the neutral U(IV) azide **3** (left) and its cationic U(V) analogue **10** (right) shown with 50% probability thermal ellipsoids. Hydrogen atoms and an outer-sphere triflate counteranion in **10** are omitted for clarity. Complex **10** crystallizes with two formula units in the asymmetric unit; both formula units exhibit similar bond metrics. Only one formula unit is depicted here.

Table 1. Selected Atomic Distances (Å) for 3 and 10

atoms	3	10
U1−N1	2.478(5)	2.365(8)
U1−N2	2.392(4)	2.290(7)
U1−N3	2.441(6)	2.328(8)
U1−N4	2.366(6)	2.318(9)
U1−N5	2.502(2)	2.351(9)
U1−N6	2.373(5)	2.302(7)
U1−N7	2.340(6)	2.269(8)
N7−N8	1.154(8)	1.22(2)
N8−N9	1.17(1)	1.13(2)

Magnetic susceptibility data for the U(III), U(IV), and U(V) BCMA complexes **5**, **3**, and **10** are shown as plots of μ_{eff} as a function of temperature in Figure 4 (left). While room-temperature magnetic moments are known to be insufficient to distinguish U(IV) and U(III) in most cases,[59] it is worth noting that the μ_{eff} value of **5** (2.84 μ_B) is lower than most reported values for U(III) species, and only slightly larger than **3**, which is consistent with U(IV).[59−61] The data for **10** were collected only up to 240 K due to the compound's thermal sensitivity; the μ_{eff} value at 240 K (1.33 μ_B) is comparable to reported values for other U(V) complexes.[59−61] The low-temperature data are more informative, as the moment of a $5f^2$ U(IV) complex should decrease sharply toward a diamagnetic ground state at low temperature.[4,59]

Upon cooling, the μ_{eff} values decreased steadily to 1.13 and 0.76 μ_B at 2 K for **5** and **10**, respectively, but more drastically to 0.58 μ_B for **3**. This behavior is consistent with a decrease in moments upon cooling resulting from the depopulation of crystal field levels of the uranium ions. No saturation of the magnetization in the field-dependent measurement was observed at 5 K for **3**, also characteristic of a U(IV) species (Figure S6).[62−64] In addition, no significant difference in moments was observed between the BCMA and BIMA complexes, showing that the specific supporting ligand system minimally affects the resulting magnetic properties of these structurally similar molecules (Figures S6 and S7). As a result, the magnetic data indicate the oxidation states of **3**, **5**, and **10** as U(IV), U(III), and U(V), respectively.

Magnetic susceptibility curves for the uranium nitride complexes are shown in Figure 4 (right). No significant difference in magnetic moments (per uranium) was observed between the three nitrides **7**−**9** in the temperature range of 2−300 K. The room-temperature moments (2.74 μ_B) for all three complexes were consistent with the values of the monomeric U(IV) tris(amidinate) azide complexes **3** and **4**. No saturation of the magnetization in the field-dependent measurement was observed at 5 K.

■ CONCLUSIONS

With the discovery of these three new uranium nitrides resulting from amidinate-supported uranium precursors, we have built on the burgeoning body of recent work in this area in several significant aspects. Two different synthetic strategies were employed to access these nitride complexes: (i) chemical reduction of a U(IV) azide with KC_8 and (ii) reaction of a U(III) starting material with an alkali metal azide. These two methods led to the same di-uranium nitride product when the BCMA ligand was used as a supporting ligand, but they yielded distinct di- and tetranuclear uranium complexes from the less bulky BIMA-supported precursors. In addition, ^{15}N labeling, IR spectroscopy, and acid hydrolysis experiments confirmed the presence of the bridging nitride moieties in all three complexes. Magnetic susceptibility measurements showed oxidation state-dependent magnetic behavior for a series of

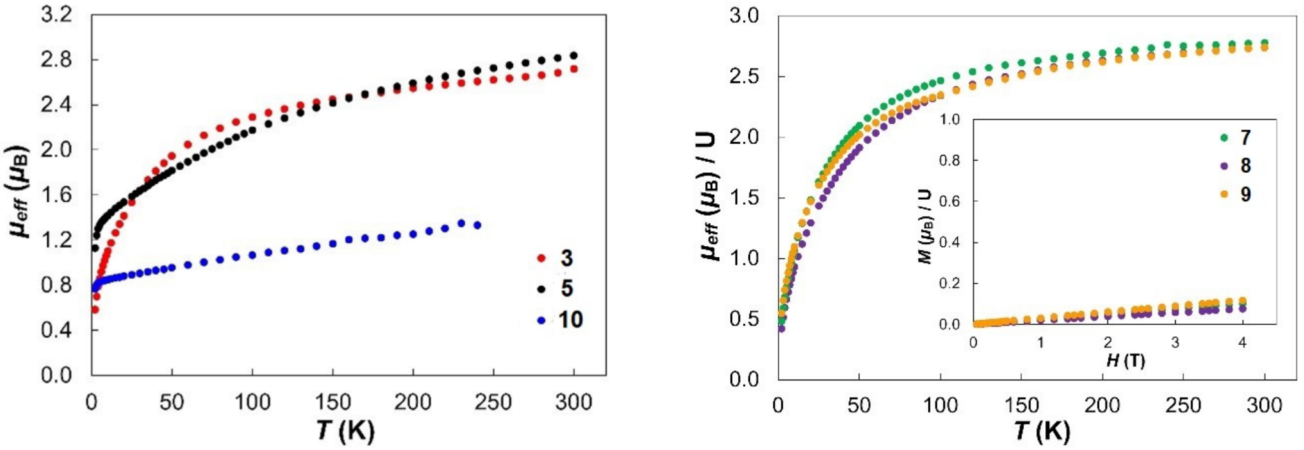


Figure 4. Variable-temperature molar magnetic data (μ_{eff}) for **3** (red), **5** (black), and **10** (blue) (left). Variable-temperature molar magnetic data (μ_{eff}) for **7** (green), **8** (purple), and **9** (orange) (per uranium ion) and variable field data collected at 5 K (inset) (right).

related U(III), U(IV), and U(V) amidinates and confirmed a U(IV) oxidation state for the uranium atoms in all three nitrides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00471.

> Listings of experimental details, crystallographic metrics, electrochemistry and magnetism figures, NMR and IR spectra (PDF)

Accession Codes

CCDC 2050796–2050802 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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