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Cation-Cation Interactions, Magnetic Communication and Reactivity of the Pentavalent Uranium Ion $[\text{U}(\text{NR})_2]^+$

Liam P. Spencer, Eric J. Schelter, Ping Yang, Robyn L. Gdula, Brian L. Scott, Joe D. Thompson, Jacqueline L. Kiplinger, Enrique R. Batista, and James M. Boncella*

Pentavalent uranium complexes have long attracted attention as a means to probe the role of the f^1 -electronic configuration in actinide chemistry. Studies of the $[\text{UO}_2]^+$ ion have been essential to this area as a result of its role in nuclear fuel reprocessing, its speciation in the environment, and its potential to perform electrochemical catalysis.¹ Despite this interest, well-characterized examples of $[\text{UO}_2]^+$ are exceedingly rare, which has limited their use to illustrate important fundamental concepts in actinide chemistry. While some of the structurally characterized $[\text{UO}_2]^+$ complexes are monomeric,^{2a,b} many are oligomeric, for example, the U(V) coordination polymer $\{[\text{UO}_2\text{py}_3][\text{Kl}_2\text{py}_2]\}$,^{2c,d} the tetrameric complex $\{[\text{UO}_2(\text{dbm})_2][\text{K}_6\text{py}_{10}]\cdot 12\text{py}_3\}^{2e}$ (py = pyridine, dbm = dibenzoylmethanate) and the dimeric complex $[\text{UO}_2(\text{dbm})_2\text{K}(\text{18C6})]_2$ (18C6 = 18-crown-6).^{2f} These oligomers demonstrate that the $[\text{UO}_2]^+$ ion can assume many oxygen-bridged architectures. While these complexes have been used to probe the role of 'cation-cation' oligomeric interactions in structural uranyl(V) chemistry, very little is known about the reactivity and magnetic interactions between such f^1 -actinide centers in polynuclear complexes. These properties can be further addressed by the study of other families of pentavalent actinide complexes that are similar in molecular and electronic structure to the $[\text{UO}_2]^+$ ion.

Despite the potential that $[\text{U}(\text{NR})_2]^+$ ions offer to pentavalent uranium chemistry, imido analogues of the $[\text{UO}_2]^+$ ion are unknown. Herein, we describe the synthesis of the dimeric pentavalent bis(imido) uranium complex $[\text{U}(\text{N}^t\text{Bu})_2(\text{I})(^t\text{Bu}_2\text{bpy})]_2$ ($^t\text{Bu}_2\text{bpy}$ = 4,4'-di-*tert*-butyl-2,2'-bipyridyl), the first complex of the $[\text{U}(\text{NR})_2]^+$ ion. We demonstrate with magnetic susceptibility measurements and Density Functional Theory (DFT) calculations that this f^1 - f^1 system displays magnetic coupling at low temperatures. Furthermore, this dimeric species can undergo two-electron oxidative addition reactions to form new bis(imido) uranium(VI) complexes, which are inaccessible by other synthetic procedures.

Our recent work has described the synthesis and reactivity of the bis(imido) uranium(VI) ion, $[\text{U}(\text{NR})_2]^{2+}$, in particular towards imido exchange and iodide metathesis reactions.^{3b,c} During studies on the organouranium(VI) complex $(\text{C}_5\text{Me}_5)_2\text{U}(\text{N}^t\text{Bu})_2$,^{3d} we discovered that the reaction between two equivalents of $\text{Na}(\text{C}_5\text{Me}_5)$ and $\text{U}(\text{N}^t\text{Bu})_2(\text{I})_2(^t\text{Bu}_2\text{bpy})$ (**1**) ($^t\text{Bu}_2\text{bpy}$ = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) does not provide the expected uranium(VI) species. The addition of a toluene solution of $\text{Na}(\text{C}_5\text{Me}_5)$ to **1** provides the

bis(imido) uranium(V) dimer complex $[\text{U}(\text{N}^t\text{Bu})_2(\text{I})(^t\text{Bu}_2\text{bpy})]_2$ (**2**) in reasonable yield, in addition to the coupled cyclopentadienyl species $(\text{C}_5\text{Me}_5)_2$ (Equation 1). The use of the C_5Me_5 anion as a reductant has precedent in the reduction of $[\text{UO}_2]^{2+}$ to $[\text{UO}_2]^+$ and in complexes like $\text{U}(\text{C}_5\text{Me}_5)_3$ that can engage in sterically induced reduction reactions to eliminate $(\text{C}_5\text{Me}_5)_2$.^{2d,4} Complex **2** was identified by ^1H NMR spectroscopy, single crystal X-ray diffraction, and elemental analysis. The ^1H NMR spectrum of **2** is consistent with a paramagnetic uranium(V) complex with broad resonances at -18.54 ppm and 44.42 ppm indicative of the *tert*-butyl imido resonances. There are also two broad singlets at -3.11 ppm and 2.32 ppm attributable to the *tert*-butyl groups on the bipyridyl ligand.

The solid-state molecular structure of **2** is shown in Figure 1 and features the first structurally characterized pentavalent bis(imido) uranium(V) ion. This dinuclear motif is not common in uranium chemistry; there are only a few reported dinuclear, dimeric derivatives.^{2f,5} Interestingly, the solid state molecular structure of **2** displays a cation-cation interaction between $[\text{U}(\text{NR})_2]^+$ units that to our knowledge represents the first structurally characterized example of an actinide complex that possess two bridging $\text{An}=\text{N}(\text{R})-\text{An}$ units and two $\text{An}=\text{N}(\text{R})$ ligands. These interactions are reminiscent of the $\text{An}=\text{O}$ bridging interactions found in the dimeric uranyl(V) species $[\text{UO}_2(\text{dbm})_2\text{K}(\text{18C6})]_2$.^{2f} Complex **2** possesses a *pseudo*-octahedral geometry at each uranium center as represented by two axial bis(imido) ligands and bipyridyl, iodide, and bridging imido equatorial ligands. A near linear bis(imido) $\text{N}=\text{U}=\text{N}$ bond angle (ave = $170.1(2)^\circ$) is present in **2** along with a non-bridging $\text{U}-\text{N}_{\text{imido}}$ bond length (ave = $1.898(5)$ Å) that is slightly longer than the $\text{U}-\text{N}_{\text{imido}}$ bond distances found in *trans*-bis(imido) uranium(VI) complexes³ and shorter than $\text{U}-\text{N}_{\text{imido}}$ bond lengths found in other uranium(V)-imido complexes.⁶ The U_2N_2 core features a set of $\text{U}-\text{N}$ bonds, $\text{U1}-\text{N4}$ ($2.067(5)$ Å) and $\text{U2}-\text{N5}$ ($2.078(5)$ Å), that are on average ~ 0.3 Å shorter than $\text{U1}-\text{N5}$ ($2.380(5)$ Å) and $\text{U2}-\text{N4}$ ($2.387(5)$ Å). This shorter bond distance is slightly longer than many of the $\text{U}-\text{N}_{\text{imido}}$ bond distances found in other uranium(V) imido complexes ($1.910(6)$ – $2.047(8)$ Å)⁶ but significantly shorter than the $\text{U}-\text{N}_{\text{amido}}$ bond length found in the uranium(V)-amido complex $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{U}=\text{N}(\text{SiMe}_3)$ ($\text{U}-\text{N}_{\text{amido}}$ = $2.295(10)$ Å).^{6d} This suggests that there is metal-ligand multiple bond character present in this set of $\text{U}-\text{N}$ bonds. In contrast, the average bond length in the other set of uranium-nitrogen bond distances, $\text{U1}-\text{N5}$ and $\text{U2}-\text{N4}$ (ave $2.384(5)$ Å), is slightly longer than the $\text{U}-\text{N}_{\text{amido}}$ bond lengths observed in $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{U}=\text{N}(\text{SiMe}_3)$ and is consistent with a $\text{U}-\text{N}$ bond that possesses single bond character. Furthermore, the U_2N_2

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parallelogram defined by the atoms U1-N4-U2-N5 is nearly planar ($\text{N4-U1-N5-U2} = 2.8(2)^\circ$) as are the bridging nitrogen imido atoms as defined by the sum of the angles (360°) about atoms N4 and N5.

Figure 1. Solid-state molecular structure of $[\text{U}(\text{N}'\text{Bu})_2(\text{l})(\text{Bu}_2\text{bpy})]_2$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles ($^\circ$): U1-N1 2.536(5), U1-N2 2.650(5), U1-N3 1.895(5), U1-N4 2.067(5), U1-N5 2.380(5), U2-N4 2.387(5), U2-N5 2.078(5), U2-N6 1.901(5), U1-I2 3.1385(6), N3-U1-N4 170.6(2), U1-N4-U2 106.7(2), U1-N4-C23 130.5(4), U2-N4-C23 122.8(4), N4-U1-N5-U2 2.8(2).

Temperature dependent magnetic data were collected for complex **2** in the temperature range from 2-300 K to detect the presence of interacting $^2\text{F}_{5/2}$ U(V)- $5f^1$ spin centers (Figure 2). The molar χT vs T data achieve a value of $1.48 \text{ emu K mol}^{-1}$ at 300 K, close to the expected value of $2 \times 0.69 = 1.38 \text{ emu K mol}^{-1}$ for a $J = 5/2$, $g_J = 0.857$ ion, which assumes complete population of the crystal field (CF) doublets at this temperature. The slightly larger than expected value is due to Van Vleck Temperature Independent Paramagnetism (TIP) from excited-state mixing, as evidenced by the positive slope in the high temperature region of χT vs T . Ignoring any effects of magnetic coupling (*vide infra*), the TIP for **1** can be roughly estimated from the slope of χT vs T between 140-300 K at $7.7 \times 10^{-4} \text{ emu mol}^{-1}$. Recently reported organometallic uranium(V)-imido complexes also exhibit such TIP.^{6b}

Figure 2. Molar temperature dependent magnetic behavior for **2** recorded from 2-300 K.

The χ vs T data clearly indicate the presence of an antiferromagnetic interaction between the metal ions by the appearance of a maximum at 13 K. Observation of a clear signature

of magnetic coupling is exceedingly rare in actinide molecular chemistry, as the magnetic response of paramagnetic actinide complexes is usually dominated by single ion magnetic effects. The interaction in **2** is reminiscent of magnetic data reported for the bimetallic $5f^1$ - $5f^1$ benchmark complex $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-1,4-N}_2\text{C}_6\text{H}_4]$ (**3**),⁶ⁱ as well as the structurally related $[\text{UO}_2(\text{dbm})_2\text{K}(\text{18C6})]_2$ (**4**).^{2f} As with **3**, data for **2** in the range of 140-280 K of $1/\chi$ vs T are linear, allowing for Curie-Weiss fitting, $\chi = C/(T-\theta)$. Parameters per uranium ion (for ease in comparison) obtained from a linear fit the $1/\chi$ vs T data in this range are: $C = 0.80 \text{ emu K mol}^{-1}$, $\mu_{\text{eff}} = 2.53 \mu_B$, and $\theta = -27 \text{ K}$ (see Supporting Information for the linear fit of $1/\chi$ vs T , Figure S1). Table 1 shows a comparison of these results with **3**. Both the larger μ_{eff} value and smaller negative Weiss constant between **2** and **3** provide evidence that the magnetic coupling interaction in **2** is weaker than that observed in **3**. The $1/\chi$ vs T data for **4** are not linear over this temperature range making comparison of **2** with this complex difficult, however a similar temperature dependent character of the χ vs T data (*vide infra*) is present in **2** and **4**.

Table 1. Results of magnetism studies for complexes **2** and **3**.

	$C^{a,b}$	$\mu_{\text{eff}} (\mu_B)^a$	$\theta (\text{K})^a$	$J (\text{cm}^{-1})$
2	0.80	2.53	-27	-12 ^c
3	0.54	2.08	-147	-19

[a] Determined on a per mole-U basis from a linear fit of $1/\chi$ vs T from 280-40 K. [b] $\text{emu K mol per mole-U}$. [c] Estimate based on uniaxial crystal field of **3**; see text.

The nominal uniaxial crystal field present in **2** allows for modeling of the χT data to estimate the exchange energy in a similar way to that reported for **3**. The truncation of parameters by this symmetry assumption is supported by reported uranium(V)-imido complexes, whose magnetic properties are rather insensitive to the identity of auxiliary ligands.^{6b} The data were modeled according to the following effective spin, Ising expression ($\hat{S}_{z1} = \hat{S}_{z2} = 1/2$, $g_{\perp} = 0$) (Eqns 2 and 3, Figure 2, inset).⁷

$$\hat{H} = -2J \hat{S}_{z1} \hat{S}_{z2} + g_{\parallel} \mu_B H_z (\hat{S}_{z1} + \hat{S}_{z2}) \quad (2)$$

$$\chi T = \left(\frac{1}{3} \right) \frac{N g_{\parallel}^2 \mu_B^2}{2k} \left(1 + e^{-\frac{J}{kT}} \right)^{-1} + \chi_{\text{TIP}} T \quad (3)$$

This produced best fit parameters of: $g_{\parallel} = 4.52$, $J = -12 \text{ cm}^{-1}$ using $\chi_{\text{TIP}} = 3.85 \times 10^{-4} \text{ emu per mol-U}$. Critically, the $g_{\parallel}$ obtained is close to the expected value for the $\pm 5/2$ Kramer's doublet as the ground state: $g_{\parallel} = 5g_J = 4.29$. The appearance of this g -value provides validation of the symmetry assumption and assignment of the ground state $\pm 5/2$ doublet. The data indicate a smaller exchange interaction in **2** than **3** (Table 1), despite the shorter U-U distance in **2**, 3.58 Å, compared to **3**, ~9.6 Å, estimated from twice the metal to aryl-ring-centroid distance in $[\text{1,2,4-(Me}_3\text{C)}_3\text{-C}_5\text{H}_2)_2\text{U=N}(p\text{-tolyl})]$.⁸ This is consistent with the very different exchange pathways operative in these molecules; dative interactions of side-on U-N coordination interactions in **2** (Figure 1), versus a covalent 1,4-phenylenediimide bridging ligand that is aligned directly with the uranium ions' magnetic easy axes in **3**.

Temperature dependent magnetic susceptibility data reported for **4** also indicate the presence of an antiferromagnetic interaction.^{2f} Given our success using the Ising model described above, the approach could also reasonably be applied to **4** to ascertain the strength of the magnetic coupling interaction in that complex. Qualitatively, the interaction in **4** appears weaker than **2** as judged by the appearance of a maximum at ~5 K in that complex compared to 13 K in **2**.

Further insight on the antiferromagnetic interaction between metal centers was attained from hybrid density functional theory

(DFT) calculations. These calculations were performed on the model complex $[U(N^tBu)_2(I)_2(bpy)]_2$ (**5**) to investigate the molecular orbital interactions in the U_2N_2 core, the relative energy differences and spin densities of the singlet and triplet spin states. The structure of **5** predicted by DFT calculations is in good agreement with the experimental values of **2** (Table S3), with deviations between experimental and theoretical values similar to other uranium(V)-imido complexes at a similar level of computational theory.^{6a,b} The ground state of **5** at its optimal configuration (0 K) was calculated to be a broken-symmetry singlet state, and the lowest triplet was found to be 1.6 kcal mol⁻¹ higher in energy. A natural orbital analysis shows that the unpaired spin density is localized in the uranium center as $f^1_{\phi}-f^1_{\phi}$ (Figure S2). The Mulliken spin density population analysis of the singlet and triplet state of **5** is shown in Table 2. The singlet state of **5** possesses 1.13 unpaired electrons on both uranium centers with oppositely oriented spins whereas the triplet state exhibits the same number of electrons but with parallel spins. The spin density so close to 1 indicates that most of it comes from the unpaired electrons and the bonding orbitals contribute only a small amount to the net spin polarization. Furthermore, the bridging and non-bridging imido nitrogen atoms possess very little spin density, as do the iodide and nitrogen-containing bpy ligands. The spin density in the bridging nitrogen atoms is reduced in the singlet state because the two uranium centers compete out of phase for the bonding interaction while this does not happen to the non-bridging atoms that can change the spin state.

Table 2. Net spin density calculations for singlet- and triplet-state configurations for $[U(N^tBu)_2(I)_2(bpy)]_2$ (**5**). The labels follow those of Figure 1.

	U1	U2	N4 ^b	N5 ^b	N3 ^a	N6 ^a
Singlet	+1.13	-1.13	+0.09	-0.09	-0.12	+0.12
Triplet	+1.14	+1.12	-0.13	-0.12	-0.12	-0.12

[a] Terminal imido ligands. [b] Bridging imido ligands.

Figure 3. Decomposition of a natural bonding orbital of **5** in atomic and molecular components: (A) three atomic orbitals involved in forming the π_u orbital of the U-N bond, (B) hybridized fragment orbital forming the U-N bonds, and (C) full molecular orbital result of the symmetric combination of the two fragments shown in B.

The bonding interaction between the two $[U(NR)_2]^+$ ($R = ^tBu$) centers consists in symmetric and anti-symmetric combinations of the six U-N molecular bonding orbitals of $[U(NR)_2]^{2+}$ (Figure S3). The natural orbital with largest interaction (symmetric combination of π_u molecular orbitals) is shown in Figure 3 decomposed into its fragments. Figure 3A indicates the $[U(NR)_2]^{2+}$ orbital is composed of U(5f_u) and N(2p). Each $[U(NR)_2]^{2+}$ unit forms the molecular orbitals shown in Figure 3B and the symmetric combination of the two is shown in Figure 3C. The U=N bond in one $[U(NR)_2]^{2+}$ unit has triple bond character presenting one σ and two π bonding orbitals.³ This triple bond breaks into a double bond and a single bond in the dimer complex in order to form the bridging bond, i.e., U1=N4 and U2=N4, U2=N5 and U1=N5 respectively. DFT calculations show that the double bond at 2.073 Å consists of one σ and one π bonding orbitals, whereas, the bridging bond at 2.384 Å is a single π bond.

The coupling between the two units is weak due not only to the long U-N distance and the interaction between the side lobes, which

are smaller, (as shown in Figure 3) but also to the fact that 6 of the 12 orbitals consist of anti-symmetric combinations which place a node along the U-N bond. This weak interaction between these orbitals leads to the observed weak magnetic communication between the two uranium centers.

The addition of 1 equivalent of 4-methyl morpholine *N*-oxide to **2** yields the dinuclear oxo-bridged uranium(VI) complex **6** (Equation 4) in reasonable yield. The ¹H NMR of **6** is consistent with a diamagnetic uranium(VI) complex with asymmetric bpy resonances at 7.94 ppm, 8.19 ppm, 8.64 ppm, 8.72 ppm, 11.19 ppm and 11.59 ppm and a singlet at 0.21 ppm that confirms the presence of a *tert*-butyl imido ligand.

The solid state molecular structure of **6** is shown in Figure S3 (Supplemental Information) and features both uranium centers in a *pseudo*-octahedral geometry. Complex **6** features U-O bond distances (avg. 2.104(9) Å) that are significantly shorter than observed in other uranium(VI) phenolate complexes⁹ and a near linear U-O-U bond angle (173.3(6)°). The U-O bond distance in **6** is also significantly longer than U-O(oxo) bond lengths found in many $[UO_2]^{2+}$ complexes. The uranyl(VI) complex $[UO_2(O-2,6-Ph_2C_6H_3)(THF)_2]$ is representative of many complexes of the $[UO_2]^{2+}$ ion and features a U-O(oxo) bond distance of 1.759(14).^{9a} Taken together, these structural features suggest that there is some measure of U-O multiple bond character present in the solid state in **6**. Furthermore, the U-N(imido) and U-I bond distances in **6** are similar to other reported *trans*-bis(imido) uranium(VI) complexes.³

We have described the synthesis of a new stable pentavalent bis(imido) uranium(V) complex. This finding offers significant impact for the expansion of the small number of uranium complexes with well-defined magnetic coupling and for the formation of new uranium(V) imido architectures. The oxidation of this compound also offers a rich chemistry for the synthesis of new bis(imido) uranium(VI) complexes that are otherwise inaccessible.

Experimental details for the synthesis of **1**, **2**, and **6**, details of the magnetism studies and DFT calculations are given in the Supporting Information. Complexes **2** and **6** have been deposited in the Cambridge Crystallographic Data Centre (**2**: 713660; **6**: 713661).

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Cation-Cation Interactions, Magnetic Communication and Reactivity of the Pentavalent Uranium Ion $[U(NR)_2]^+$

Communication is important! The dimeric bis(imido) uranium complex $[U(N^tBu)_2(I)(^tBu_2bpy)]_2$ has been synthesized and displays cation-cation interactions between $[U(NR)_2]^+$ ions. This f^1-f^1 system also displays f-orbital communication between uranium(V) centers at low temperatures and can be oxidized to generate uranium(VI) bis(imido) complexes.