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## Dinitrogen cleavage by a dinuclear uranium(III) complex†

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Understanding the role of multimetallic cooperativity and of alkali ion-binding in the second coordination sphere is important for the design of complexes that can promote dinitrogen (N<sub>2</sub>) cleavage and functionalization. Herein, we compare the reaction products and mechanism of N<sub>2</sub> reduction of the previously reported K<sub>2</sub>-bound dinuclear uranium(III) complex, [K<sub>2</sub>{U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-O)}], **B**, with those of the analogous dinuclear uranium(III) complexes, [K(2.2.2-cryptand)][K{U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-O)}], **1**, and [K(2.2.2-cryptand)]<sub>2</sub>{U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-O)}], **2**, where one or two K<sup>+</sup> ions have been removed from the second coordination sphere by addition of 2.2.2-cryptand. In this study, we found that the complete removal of the K<sup>+</sup> ions from the inner coordination sphere leads to an enhanced reducing ability, as confirmed by cyclic voltammetry studies, of the resulting complex **2**, and yields two new species upon N<sub>2</sub> addition, namely the U(III)/U(IV) complex, [K(2.2.2-cryptand)][U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-O){U<sup>IV</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>}], **3**, and the N<sub>2</sub> cleavage product, the bis-nitride, terminal-oxo complex, [K(2.2.2-cryptand)]<sub>2</sub>{U<sup>V</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(μ-N)<sub>2</sub>{U<sup>VI</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(κ-O)}], **4**. We propose that the formation of these two products involves a tetranuclear uranium–N<sub>2</sub> intermediate that can only form in the absence of coordinated alkali ions, resulting in a six-electron transfer and cleavage of N<sub>2</sub>, demonstrating the possibility of a three-electron transfer from U(III) to N<sub>2</sub>. These results give an insight into the relationship between alkali ion binding modes, multimetallic cooperativity and reactivity, and demonstrate how these parameters can be tuned to cleave and functionalize N<sub>2</sub>.

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## Introduction

Multimetallic cooperativity plays an important role both in the biological and industrial reduction and cleavage of dinitrogen (N<sub>2</sub>) to ammonia (NH<sub>3</sub>), but the involved mechanisms remain ambiguous.<sup>1,2</sup> Although the binding and reduction of N<sub>2</sub> by molecular metal complexes have been intensively studied, in most cases only a few compounds have been reported that can cleave N<sub>2</sub> without the assistance of supporting ligands, or the addition of external reducing agents.<sup>2–4</sup>

The first example of N<sub>2</sub> cleavage by a metal complex was reported more than 20 years ago when Cummins and coworkers showed that the Mo(III) complex, [Mo<sup>III</sup>(N<sup>t</sup>Bu)Ar<sub>3</sub>] (Ar = 3,5-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>), cleaves N<sub>2</sub> to yield a Mo(VI) nitride *via* an end-on

bridging intermediate.<sup>5,6</sup> An analogous reactivity was reported recently for a Mo(III) siloxide complex, [Mo<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>].<sup>7</sup> Remarkably to date, these complexes remain the only examples of N<sub>2</sub> cleavage involving mononuclear metal complexes in the absence of reducing agents. A low-valent heteromultimetallic Nb<sub>x</sub><sup>III</sup>/Na<sub>y</sub> complex was also reported that can cleave N<sub>2</sub>, but the inner sphere cation was proposed to be key in the binding and polarization of N<sub>2</sub>.<sup>8,9</sup>

Alkali metals are often employed as external reducing agents in combination with metal complexes, and their key role in the binding, activation, and cleavage of N<sub>2</sub> has been demonstrated by many recent studies.<sup>10–19</sup> In particular, it was proposed that alkali ions are key in promoting the assembly of multimetallic iron complexes that effect the cleavage of N<sub>2</sub>, but the hypothesis was difficult to verify due to the absence of key intermediates.<sup>14</sup> More recently, Holland and coworkers showed that removing the potassium (K<sup>+</sup>) cation from the K-bridged, dinuclear FeNNFe complex, led to a high degree of activation of the N<sub>2</sub> in the resulting mononuclear Fe(N<sub>2</sub>)<sub>2</sub> complex.<sup>20</sup>

Although the number of studies reporting binding and reduction of N<sub>2</sub> by uranium complexes has significantly increased in recent years,<sup>3,18,19,21–35</sup> only a handful of examples of N<sub>2</sub> cleavage to nitrides by uranium have been identified, in which all required the use of an external reducing agent,<sup>18,19,24,33,36</sup> or assistance from a non-innocent ligand,<sup>34</sup>

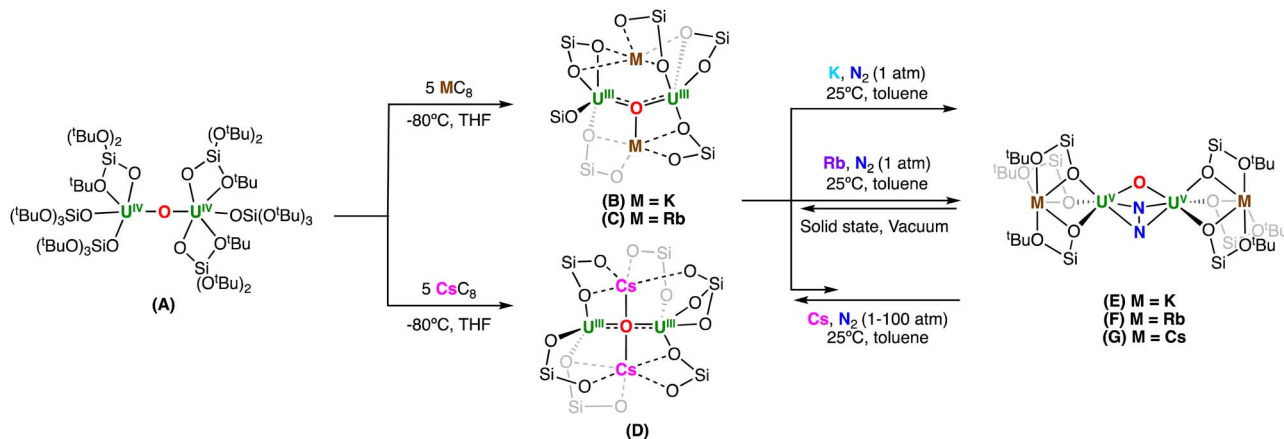
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Scheme 1 Previous works on dinitrogen ( $N_2$ ) reduction by multimetallic  $U(III)$ -alkali metal ion complexes bearing tris(*tert*-butoxy)siloxide ligands.<sup>19,30</sup>

although very small amounts of a  $N_2$  cleavage side product were identified in one case in the reaction of a putative  $U(III)$  with  $N_2$ .<sup>35</sup> We previously reported the reactivity of  $N_2$  with a series of dinuclear  $U(III)$  oxo-bridged complexes supported by (tris-*tert*-butoxy)siloxide ligands which contained different alkali metal ions,  $[M_2\{U^{III}(OSi(O^tBu)_3)_2(\mu-O)\}]$  ( $M = K, Rb, Cs$ ) **B–D** (Scheme 1).<sup>19,30</sup> We demonstrated that  $N_2$  binding is less favored with larger cations by steric factors, but that in all the  $N_2$  complexes, a four-electron reduction of  $N_2$  occurs. Full cleavage of  $N_2$  could only be effected by further reduction of the bound  $N_2^{4-}$  moiety with an external reducing agent, leading to dinuclear and tetranuclear uranium nitride complexes.<sup>18,19</sup>

However, the role of the alkali metal ions in the  $N_2$  cleavage by these multimetallic systems remained ambiguous, and in particular, we were interested in understanding if the presence of the alkali metal ions is indeed essential for  $N_2$  cleavage, or if  $U(III)$  ions can cooperatively cleave  $N_2$ .

Herein, we demonstrate that removal of the alkali metal ion from the second coordination sphere has an unexpected outcome on the reactivity of the diuranium(III) complexes with  $N_2$ . Removal of one alkali metal ion forming complex,  $[K(2.2.2\text{-cryptand})][K\{U^{III}(OSi(O^tBu)_3)_2(\mu-O)\}]$ , **1**, and further reactivity with  $N_2$ , resulted in the formation a highly activated  $(N_2)^{4-}$  species. In contrast, both the reaction of the full alkali metal ion-sequestered complex,  $[K(2.2.2\text{-cryptand})]_2\{U^{III}(OSi(O^tBu)_3)_2(\mu-O)\}$ , **2**, with  $N_2$ , and removal of the  $K^+$  cation from the isolated  $(N_2)^{4-}$  complex, **E**, resulted in the immediate cleavage of  $N_2$ . Overall, this study provides the first example of direct stoichiometric  $N_2$  cleavage by an isolated uranium(III) compound without the assistance of the supporting ligand or external alkali metal reducing agents.

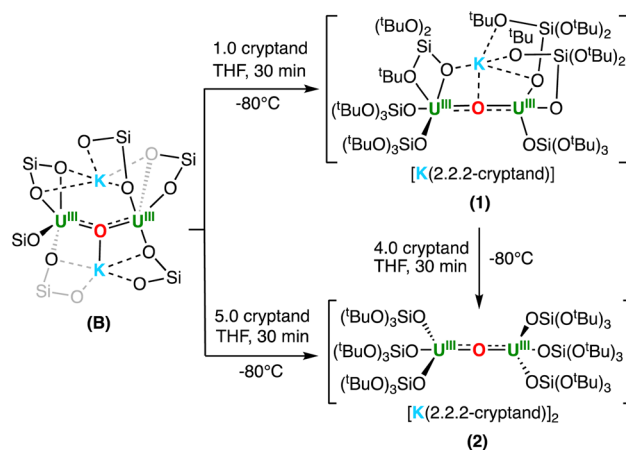
## Results and discussion

### Synthesis of anionic diuranium(III) complexes

To investigate how the presence of  $K^+$  cations in the second coordination sphere may affect the reaction of dinuclear  $U(III)$  complexes with  $N_2$ , we first pursued the synthesis of  $K^+$  cation-sequestered complexes.

The addition of 1 equiv. of 2.2.2-cryptand to a  $d_8$ -THF solution of **B** at  $-80^\circ C$  resulted in the consumption of **B**, with the appearance of a new resonance at  $-0.27$  ppm, and signals corresponding to  $[K(2.2.2\text{-cryptand})]^+$ , as evidenced by  $^1H$  NMR spectroscopy (Fig. S1b<sup>†</sup>). Single crystals suitable for XRD analysis of  $[K(2.2.2\text{-cryptand})][K\{U^{III}(OSi(O^tBu)_3)_2(\mu-O)\}]$ , complex **1**, were obtained from layering a concentrated THF solution with *n*-hexanes at  $-40^\circ C$  in 72% yield (Scheme 2).

Similarly, addition of 1 equiv. of 2.2.2-cryptand to **1** in  $d_8$ -THF at  $-80^\circ C$ , led to the disappearance of **1**, with the appearance of a single new resonance at 1.03 ppm and signals corresponding to  $[K(2.2.2\text{-cryptand})]^+$ , as observed by  $^1H$  NMR spectroscopy (Fig. S1c<sup>†</sup>). Dark red single crystals suitable for X-ray diffraction studies of  $[K(2.2.2\text{-cryptand})]_2\{U^{III}(OSi(O^tBu)_3)_2(\mu-O)\}$ , complex **2**, were isolated by layering a concentrated THF solution with *n*-hexanes at  $-40^\circ C$  in 76% yield (Scheme 2). It is important to note that the complete removal of the second  $K^+$  cation proved more difficult, and the isolation of analytically pure **2** in high yields required an excess (5 equiv.) of 2.2.2-cryptand.



Scheme 2 Sequestration of the  $K^+$  cations from complex **B**.



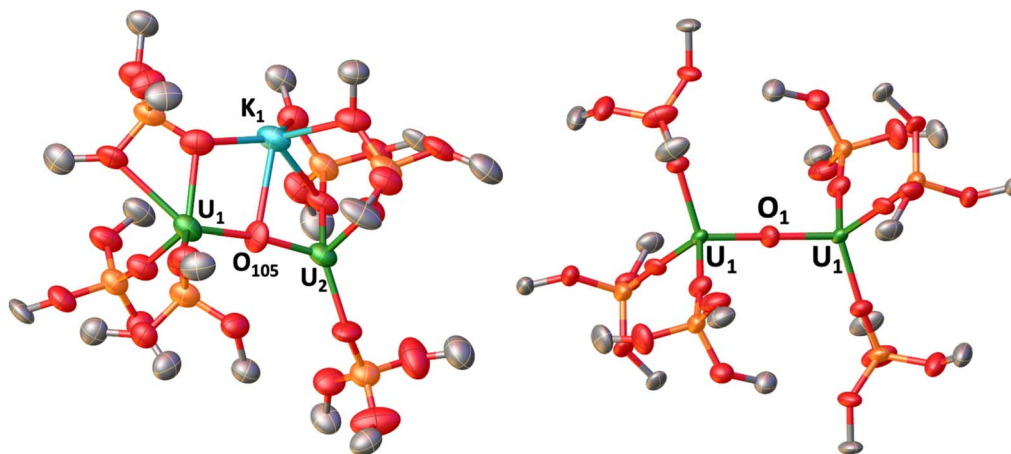


Fig. 1 Solid-state molecular structures of the anion of (left) **1** and (right) **2** with 50% probability ellipsoids. Color code: uranium (green), potassium (light blue), oxygen (red), carbon (grey), silicon (orange). Hydrogen atoms and methyl groups on the  $-\text{OSi}(\text{O}^t\text{Bu})_3$  ligands were omitted for clarity.

Complexes **1** and **2** are insoluble in toluene and showed low thermal stability in THF solutions at 25 °C, resulting in complete decomposition after 6 hours. Removal of one or two  $\text{K}^+$  cations in complexes **1** and **2** results in a decreased stability when compared to the previously reported  $\text{K}^+$  cation-bound complex, **B**, which is stable in THF at 25 °C for 12 hours.

The solid-state molecular structure of complex **1** (left, Fig. 1) shows an anionic complex with two  $\text{U}(\text{III})$  ions bridged by an oxo ligand. The inner-sphere  $\text{K}^+$  cation (2.851(15) Å) is coordinated to the bridging oxo moiety and by four oxygen atoms of three siloxide ligands, at a shorter distance than that reported for **B** (2.913(4) Å), suggesting a stronger  $\text{K1-O}_{\text{oxo}}$  interaction.<sup>30</sup> The presence of a stronger  $\text{K-O}_{\text{oxo}}$  bonding is consistent with the fact that an excess of 2.2.2-cryptand is required to fully remove the  $\text{K}^+$  cations to yield complex **2**. In **2**, the second  $\text{K}^+$  cation is coordinated by 2.2.2-cryptand as a  $[\text{K}(2.2.2\text{-cryptand})]^+$  counterion. The values of the  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  bond distances ( $\text{U1-O105}$ : 2.123(13) and  $\text{U2-O105}$ : 2.155(13) Å) in **1** are slightly longer than those found in the  $\text{U}^{\text{IV}}\text{-O-U}^{\text{IV}}$  complex **A** (2.085(1), 2.137(1) Å),<sup>30</sup> and compare well with those found in the  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  complexes, **B-D** (2.100(5)–2.178(3) Å).<sup>19,30</sup> The  $\text{U1-O105-U2}$  core is slightly bent (172.7(8)°), and is consistent with the previously reported  $\text{K}^+$  cation-bound  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  complex, **B** (167.4(2)°).<sup>30</sup>

The solid-state molecular structure of **2** (right, Fig. 1) shows an anionic complex with two  $\text{U}(\text{III})$  ions bridged by an oxo ligand, with two outer-sphere  $[\text{K}(2.2.2\text{-cryptand})]^+$  counterions. The values of the  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  bond distances ( $\text{U1-O1}$  and  $\text{U2-O1}$ :

2.1061(3) Å) are identical, and longer than those found for the  $\text{U}^{\text{IV}}\text{-O-U}^{\text{IV}}$  complex **A** (2.085(1), 2.1376(13) Å), but shorter than those observed in **1** (2.123(13) Å, 2.155(13) Å), while comparing well with the previously reported  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  complexes, **B-D** (2.100(5)–2.178(3) Å). Additionally, the  $\text{U}^{\text{III}}\text{-O-U}^{\text{III}}$  bond angle in **2** is linear (180°; Table 1).

### Electrochemical studies

To determine and compare the reducing ability of complexes, **2** and **1**, with those of the previously reported complexes **B-D**, cyclic voltammetry studies were carried out under argon with  $[\text{Bu}_4\text{N}][\text{BPh}_4]$  (0.1 M in THF) as the supporting electrolyte (Fig. 2).

As previously observed for complexes **B-D** (ref. 19) distinctive irreversible oxidation events at  $E_{\text{pa}} = -1.89$  V and  $-2.25$  V are observed in the cyclic voltammograms of **1** and **2**, respectively, which are assigned to the  $\text{U}(\text{III})/\text{U}(\text{IV})$  couple (Fig. 2). The corresponding reduction events at  $E_{\text{pc}} = -3.23$  V and  $-3.48$  V, respectively, are only observed after initial oxidation, in which these redox events can be attributed to the  $\text{U}(\text{IV})/\text{U}(\text{III})$  couple. The reduction potentials for **1** and **2** are more negative compared to the previously reported complex **B** (Table 2), with  $E_{\text{pc}}$  values comparable to that observed for **D**. This suggests that partial and full sequestration of the  $\text{K}^+$  cations by use of 2.2.2-cryptand results in a higher reducing ability for both **1** and **2**, and is comparable to what was previously observed when the  $\text{K}^+$  cation is replaced by a weaker Lewis acid, such as  $\text{Cs}^+$ .

Table 1 Average values of selected bond lengths (Å) and angles (°) in the complexes

Complex	U-U	U1-O <sub>oxo</sub>	U2-O <sub>oxo</sub>	U1-O-U2	M1-O <sub>oxo</sub>	M2-O <sub>oxo</sub>
<b>A</b> <sup>a</sup>	4.2128(9)	2.0852(13)	2.1376(13)	172.19(8)	—	—
<b>B</b> <sup>a</sup>	4.2619(10)	2.178(3)	2.120(3)	167(4)	2.913(4)	3.392(4)
<b>1</b>	4.2697(12)	2.123(12)	2.155(13)	172.7(8)	2.851(15)	—
<b>2</b>	4.2123(8)	2.1061(3)	2.1061(3)	180	—	—
<b>D</b> <sup>a</sup>	4.247(1)	2.137(7)	2.126(7)	177.9(4)	3.336(8)	3.434(8)

<sup>a</sup> Values from ref. 19 and 30.



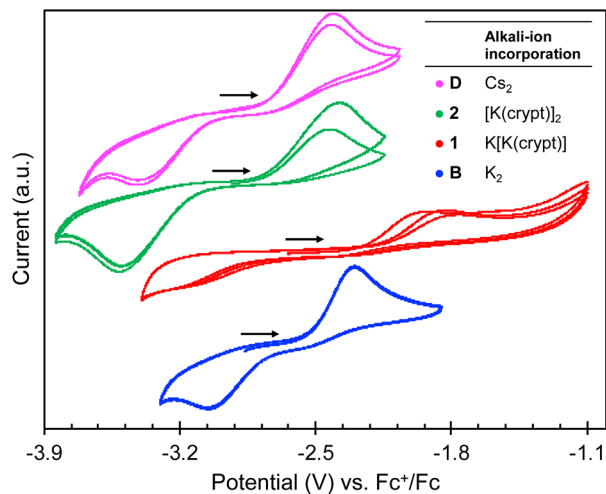


Fig. 2 [−3.9 V; −1.1 V] region of cyclic voltammogram of 3.0 mM THF solutions of complexes **D** (pink),<sup>19</sup> **2** (green), **1** (red), and **B** (blue)<sup>19</sup> recorded in 0.1 M [NBu<sub>4</sub>][BPh<sub>4</sub>] under Ar (scan rate = 100 mV s<sup>−1</sup>; referenced against [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+0</sup>).

Table 2 Reduction potentials assigned to the U(v)/U(III) couples measured for **1** and **2** compared to values reported for **B** and **D**

Complex	<i>E</i> <sub>pc</sub> (V)	<i>E</i> <sub>pa</sub> (V)	Δ <i>E</i> (V)
<b>B</b> <sup>a</sup>	−3.07	−2.30	0.77
<b>1</b>	−3.23	−1.89	1.34
<b>2</b>	−3.48	−2.25	1.23
<b>D</b> <sup>a</sup>	−3.4	−2.41	0.99

<sup>a</sup> From ref. 19.

The higher oxidation potential observed for **1** (*E*<sub>pa</sub> = −1.89 V) compared to complexes, **2** (*E*<sub>pa</sub> = −2.25 V) and **B** (*E*<sub>pa</sub> = −2.30 V), could be attributed to the stronger K–O<sub>oxo</sub> interaction, which renders the removal of the K<sup>+</sup> cation from the inner coordination sphere more difficult, and therefore the overall process more irreversible.

### Dinitrogen binding and cleavage

Considering the high reducing ability of complexes **1** and **2**, we set out to investigate how removal of one or two K<sup>+</sup> cations from the inner coordination sphere of the complex could affect the reactivity with N<sub>2</sub>, when compared to the previously reported **B–D** complexes.

First, exposing a dark red solution of **2** in THF to N<sub>2</sub> at −40 °C, resulted in an immediate color change to dark orange. Analysis by <sup>1</sup>H NMR spectroscopy of the reaction mixture at −40 °C revealed the consumption of **2**, and the formation of a <sup>1</sup>H NMR silent species, with the appearance of the signal corresponding to [K(2.2.2-cryptand)][OSi(O<sup>t</sup>Bu)<sub>3</sub>] (formation of 0.5 equiv. determined by quantitative <sup>1</sup>H NMR spectroscopy) (Fig. S11<sup>†</sup>). Instead, analysis of the same reaction mixture at −80 °C by <sup>1</sup>H NMR spectroscopy revealed refined resonances at δ = 35.48, 6.61, and −14.81 ppm (Fig. S12<sup>†</sup>), corresponding to the U(III)/U(IV) anion, [U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>](μ-O){U<sup>IV</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>}<sup>−</sup>. The assignment of the

putative, K-sequestered U(III)/U(IV) species, [K(2.2.2-cryptand)][U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>](μ-O){U<sup>IV</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>}, **3**, was confirmed by the independent synthesis of the U(III)/U(IV) complex, [K{U<sup>III</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>}(μ-O){U<sup>IV</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>}, **3-K**, and further addition of 2.2.2-cryptand (Scheme S1<sup>†</sup>). Notably, the <sup>1</sup>H NMR spectrum of complex **3-K** in the presence of 1 equiv. 2.2.2-cryptand in d<sub>8</sub>-THF at −80 °C, displayed identical resonances (Fig. S10<sup>†</sup>) as observed in the reaction mixture obtained after addition of N<sub>2</sub> to **2**.

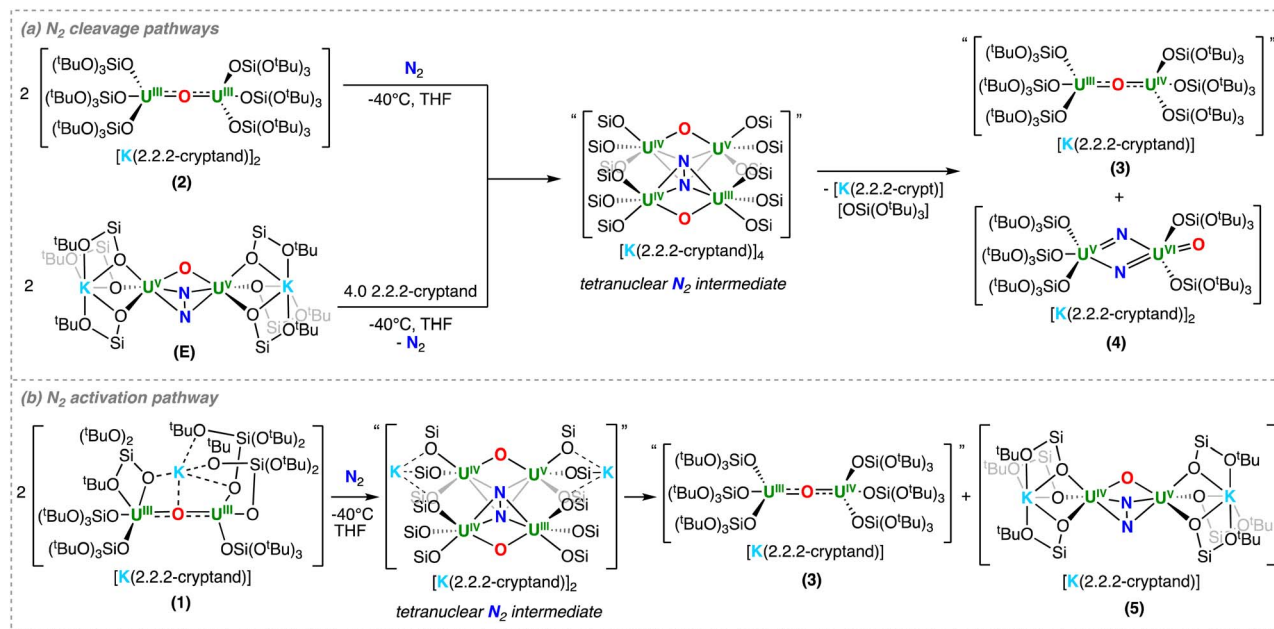
From the reaction mixture obtained after exposing **2** to N<sub>2</sub>, golden crystals suitable for XRD analysis of the bridging bis-nitride, terminal-oxo complex, [K(2.2.2-cryptand)]<sub>2</sub>[-U<sup>V</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>3</sub>](μ-N)<sub>2</sub>{U<sup>VI</sup>(OSi(O<sup>t</sup>Bu)<sub>3</sub>)<sub>2</sub>(κ-O)}], **4**, were isolated from a mixture of *n*-hexanes and THF (10 : 1) at −40 °C in 67% yield (yield is provided considering the reaction stoichiometry in Scheme 3). The <sup>1</sup>H NMR spectrum of **4** in d<sub>8</sub>-THF is silent at −40 °C and −80 °C, and the complex is insoluble in non-polar solvents.

X-Band EPR studies of the *in situ* reaction mixture obtained after addition of N<sub>2</sub> to **2** (20 mM frozen THF/Et<sub>2</sub>O solution), showed two independent sets of signals at 6 K, in which the first is very intense and was fit to an axial set of *g*-values (*g*<sub>1</sub> = 2.35; *g*<sub>2</sub> = 2.05; *g*<sub>3</sub> = 2.05), whereas the second signal is at higher field (*g* = 1.13 and *g* = 1.09), and much less intense (Fig. S49<sup>†</sup>). The first signal was attributed to the U(III)/U(IV) complex, **3**, whereas the second signal could be assigned to the U(V)/U(VI) bis-nitride, terminal-oxo complex, **4**. These assignments were confirmed by independent measurement of the EPR spectra for the putative U(III)/U(IV) complex, **3**, and of isolated **4**, both in frozen THF : Et<sub>2</sub>O solutions (Fig. S52–S58<sup>†</sup>) and are consistent with *g*-values reported for U(III) complexes<sup>37,38</sup> and U(V) terminal oxo complexes.<sup>39–41</sup>

The solid-state molecular structure of **4** (Fig. 3) shows the presence of a dinuclear complex, in which there are two molecules per asymmetric unit, where the two uranium ions are bridged by two nitrides, and are overall bound by five –OSi(O<sup>t</sup>Bu)<sub>3</sub> ligands, indicating the loss of one ligand.

The overall charge of complex **4** is consistent with the presence of U(V)/U(VI) centers. The two U ions are penta-coordinated and display a distorted square pyramidal geometry, and are bridged by two nitride ligands with a short U⋯U distance of 3.3672(5) Å. The U1 ion is coordinated by three siloxide ligands and the two nitrides, while U2 is coordinated by two siloxide ligands, two nitrides, and a terminal oxo moiety. The U<sub>2</sub>N<sub>2</sub>O core is planar, with a N1–N2 separation of 2.543(11) Å, ruling out the presence of a bond between the two nitrogen atoms. The bridging U–N bond distances are asymmetric, featuring a combination of short (U1–N2: 1.950(7) Å, U2–N1: 1.892(8) Å) and elongated (U1–N1: 2.315(8) Å, U2–N2: 2.251(7) Å) bond distances. This is consistent with the presence of U=N multiple bonds and singly bound U–N, respectively, as observed in previously reported U(VI)/U(VI) and U(VI)/U(V) bis-nitride bridged complexes.<sup>35,42</sup> The bond valence sum analysis and the computational data (*vide infra*), suggest that U1 and U2 are formally +5 and +6, respectively; however, a delocalized valence cannot be fully ruled out. Overall, the solid-state molecular structure of **4** displays a unique nitride-





Scheme 3 (a) Dinitrogen cleavage by 2 and upon addition of 2.2.2-cryptand to E. (b) Dinitrogen activation by 1.

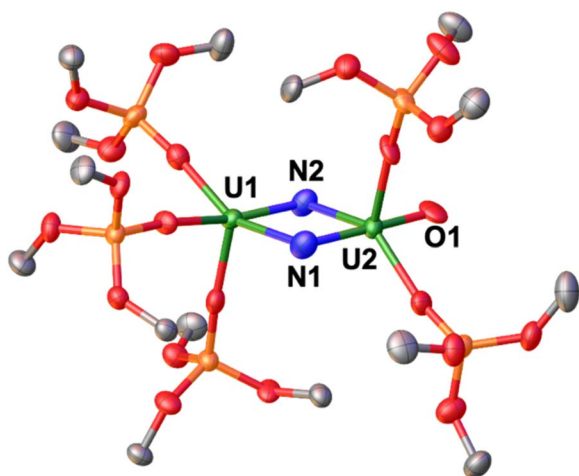


Fig. 3 Solid-state molecular structure of the anionic moiety  $\{[U^V(OSi(O^tBu)_3)_3](\mu-N)_2[U^VI(OSi(O^tBu)_3)_2(\kappa-O)]\}^{2-}$ , **4**, (50% probability ellipsoids). Color code: uranium (green), oxygen (red), carbon (grey), nitrogen (blue), and silicon (orange). Hydrogen atoms, solvent molecules and methyl groups the  $-OSi(O^tBu)_3$  were omitted for clarity.

substituted analogue of the uranyl(VI) ion, which is only the third example of such  $O=U=N$  motif. The distances observed in the trans oxo-nitrido moiety  $[O=U=N]$  found in **4** ( $U2-O1$ : 1.845(6) Å;  $U2-N1$  = 1.892(8) Å) are significantly longer than those found in the trans sodium-capped oxo-nitrido U(VI) complex reported by Hayton and coworkers ( $U-O_{oxo}$  = 1.797(7) Å;  $U-N_{nitride}$  = 1.818(9) Å),<sup>43</sup> and are comparable to those found in the analogous cesium-capped  $[O=U=N]$  motif in the previously reported complex,  $[Cs_3\{U(OSi(O^tBu)_3)_3\}(\mu-N)_2\{U(OSi(O^tBu)_3)_2(\kappa-O)\}][CsOSi(O^tBu)_3]$ , ( $U-O_{oxo}$ : 1.856(4) Å;  $U2-N2_{nitride}$  = 1.85(1) Å).<sup>19</sup>

The molecular structure of **4** is similar to that of the bis-nitride, terminal-oxo U(VI)/U(V) complex,  $[Cs_3\{U(OSi(O^tBu)_3)_3\}(\mu-N)_2\{U(OSi(O^tBu)_3)_2(\kappa-O)\}][CsOSi(O^tBu)_3]$ . However, it should be noted that in order to promote full cleavage of  $N_2$  from **D**, the addition of 2 equiv. of an alkali metal reducing agent ( $CsC_8$ ) under  $N_2$  atmosphere were required, despite the similar redox potentials measured for **2** and **D**. In contrast, the diuranium(III) complex, **2**, is able to effect the direct, stoichiometric cleavage of  $N_2$  without further addition of reducing agent or assistance from supporting ligand, which is unprecedented in f elements chemistry. Additionally, it is remarkable that one uranium ion is able to transfer three electrons to  $N_2$ , yielding a U(VI) ion, as these multielectron transformations still remain rare for uranium.

The formation of the U(VI)/U(V) bridging bis-nitride, terminal-oxo complex, **4**, requires the binding and reduction of  $N_2$  by two molecules of complex **2**, most likely through a proposed tetranuclear intermediate, which is supported by the isolation of **4** and the formation of **3** as observed by  $^1H$  NMR spectroscopy (Scheme 3a).

In our previous works, the reaction of the alkali metal-bound diuranium(III) complexes, **B–D** were shown to form the diuranium(V)- $N_2^{4-}$  **E–G** complexes (Scheme 1), in which each had different binding constants; however, no direct  $N_2$  cleavage was observed. Considering that the measured reduction potentials for **1** and **2** by cyclic voltammetry studies were greater than for **B**, but very similar to that of **D**, the observed differences in reactivity can be interpreted in terms of unfavorable steric interactions for the alkali ion-bound complexes, which most likely prevent the formation of the tetranuclear intermediate. To further verify this hypothesis, we next studied how removal of the  $K^+$  cation from complex **E** could affect the bound hydrazido ( $N_2^{4-}$ ) moiety.



The addition of 2 equiv. of 2.2.2-cryptand to complex **E** in  $d_8$ -THF at  $-40$  °C, resulted in an immediate color change from dark brown to dark orange. Analysis by  $^1\text{H}$  NMR spectroscopy indicated the formation of  $[\text{K}(2.2.2\text{-cryptand})][\text{OSi}(\text{O}^t\text{Bu})_3]$  and **3** (Fig. S15 $\dagger$ ), similar to the reaction mixture of **2** and  $\text{N}_2$ . Golden crystals of **4** were isolated in 50% yield (per 1.0 equiv. of **E**) by leaving a concentrated hexane : toluene (10 : 1) solution at  $-40$  °C over the course of two days.

Overall, these results suggest that removal of the coordinated  $\text{K}^+$  cations from complex **E**, results in an important structural change which promotes further reactivity of the bound  $\text{N}_2$ . The cleavage of  $\text{N}_2$ , and the formation of the putative  $\text{U}^{\text{III}}\text{-O-U}^{\text{IV}}$  complex **3**, requires two dimers to fully reduce one molecule of  $\text{N}_2$ . We propose that due to steric factors, removal of the  $\text{K}^+$  cations results in a weaker binding of  $\text{N}_2$ , where an equilibrium between the  $\text{U}(\text{III})/\text{U}(\text{III})$  complex, **2**, and the  $\text{U}(\text{v})/\text{U}(\text{v})\text{-N}_2^{4-}$  complex, exists (*vide infra*), as previously observed for **D**. However, the removal of the bound alkali metal cations allows two dimeric complexes to interact and form the proposed tetranuclear intermediate, which can then effect the six-electron transfer and subsequent cleavage of one molecule of  $\text{N}_2$ , yielding the  $\text{U}(\text{VI})/\text{U}(\text{V})$  bis-nitride, terminal-oxo complex **4**.

We next investigated the reaction of **1** with  $\text{N}_2$  to assess if the tetranuclear intermediate may be accessible when one potassium is still bound in the second coordination sphere.

Exposing a dark red solution of **1** in THF at  $-40$  °C to  $\text{N}_2$ , resulted in an immediate color change to dark brown-orange. Analysis of the reaction mixture by  $^1\text{H}$  NMR spectroscopy in  $d_8$ -THF at  $-80$  °C, showed the complete consumption of **1** and the formation of the putative  $\text{U}(\text{III})/\text{U}(\text{IV})$  complex, **3**, suggesting a similar reaction pathway (Fig. S20 $\dagger$ ). However, the formation of  $[\text{K}(2.2.2\text{-cryptand})][\text{OSi}(\text{O}^t\text{Bu})_3]$ , which had been observed during  $\text{N}_2$  cleavage to form complex **4**, is not observed in this reaction mixture (Scheme 3a and b).

Indeed, the X-band EPR spectrum of the reaction mixture for **1** and  $\text{N}_2$  in a THF :  $\text{Et}_2\text{O}$  (1 : 1) frozen glass solution at 6 K shows the presence of the  $\text{U}(\text{III})/\text{U}(\text{IV})$  complex, **3**. However, there were no additional signals suggestive of a  $\text{U}(\text{v})$  species, indicating that **4** is most likely not formed in this reaction (Fig. S59 $\dagger$ ).

Attempts to isolate the N-containing species from this reaction mixture proved unsuccessful. However, through an alternative route, single crystals of a  $\text{U}(\text{v})/\text{U}(\text{IV})$  hydrazido ( $\text{N}_2^{4-}$ ) complex,  $[\text{K}(2.2.2\text{-cryptand})][\text{K}_2\{\text{U}^{\text{V}}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}\{\text{U}^{\text{IV}}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}(\mu\text{-O})(\mu\text{-N}_2)]$ , **5** (Fig. S39 $\dagger$ ), could be isolated upon addition of 1 equiv. of 2.2.2-cryptand to **E** in toluene at  $-40$  °C. It is important to note that complex **5** could only be obtained once, as attempts to isolate analytically pure material were unsuccessful due to the low solubility of the reactants and products in toluene. Isolation of the  $\text{U}(\text{IV})/\text{U}(\text{v})$   $\text{N}_2^{4-}$  complex, **5**, provides further support for the proposed tetranuclear intermediate (Scheme 3b).

Overall, the reaction of **1** with  $\text{N}_2$  also involves four uranium centers; however,  $\text{N}_2$  cleavage is not observed due the presence of  $\text{K}^+$  cations in the inner coordination sphere, decreasing the reducing ability of the U ions, preventing the transfer of one additional electron to reduce  $\text{N}_2$ . In contrast, the reaction of

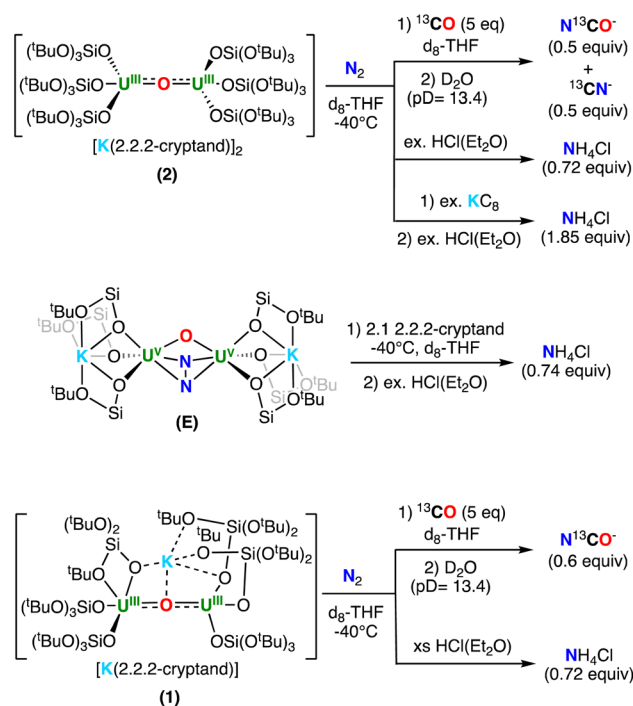
complexes **B-D** with  $\text{N}_2$  only involves two uranium centers due to steric hindrance.

### Reactivity of the N-containing complexes

To further investigate the N-containing species formed upon addition of  $\text{N}_2$  to complexes **2** and **1**, as well as the addition of 2.2.2-cryptand to **E**, we next pursued their reactivity with acids ( $\text{H}^+$ ) and CO.

The addition of excess  $\text{HCl}(\text{Et}_2\text{O})$  to the residue of the reaction mixture obtained from **2** and  $\text{N}_2$ , yielded  $\text{NH}_4\text{Cl}$  in 72% yield (per 1 equiv. of **2**). To further determine whether the  $\text{NH}_4\text{Cl}$  was unambiguously derived from  $\text{N}_2$ , the reactivity with labelled  $^{15}\text{N}_2$  was investigated, leading to the formation of isotopically enriched  $^{15}\text{NH}_4\text{Cl}$  as evidenced by  $^1\text{H}$  NMR spectroscopy (Fig. S24 $\dagger$ ). Similarly, addition of excess  $\text{HCl}(\text{Et}_2\text{O})$  to the residue of the reaction mixture obtained from **E** and 2.1 equiv. of 2.2.2-cryptand in THF, also yielded  $\text{NH}_4\text{Cl}$  in 74% yield (per 1 equiv. of **E**). Overall, these results are consistent with the formation of the bis-nitride, terminal-oxo complex, **4**, as the primary N-containing species (Scheme 4). Finally, the addition of excess  $\text{HCl}(\text{Et}_2\text{O})$  to isolated **4** resulted in the formation of  $\text{NH}_4\text{Cl}$  in 92% yield (1.84 equiv., 100% conversion corresponding to 2 equiv. of  $\text{NH}_4\text{Cl}$ ), consistent with the presence of the two nitride ligands (Scheme 4).

We also investigated the reactivity with  $^{13}\text{CO}$ . The addition of 5 equiv. of  $^{13}\text{CO}$  to the reaction mixture obtained after addition of  $\text{N}_2$  to **2**, led to an immediate color change from dark orange to brown. The products of the reaction could not be isolated; however, quenching the reaction mixture with basic ( $\text{pD} = 13.4$ )  $\text{D}_2\text{O}$ , revealed the presence of 0.5 equiv. of  $\text{N}^{13}\text{CO}^-$  and 0.5



Scheme 4 Reactivity of (top) **2**, (middle) **E** and 2.2.2-cryptand, and (bottom) **1**, after addition of  $\text{N}_2$  with  $\text{H}^+$  and  $^{13}\text{CO}$ .



equiv. of  $^{13}\text{CN}^-$  (per 1 equiv. of **2**), as evidenced by quantitative  $^{13}\text{C}$  NMR spectroscopy (Fig. S29†). The amount of  $\text{NCO}^-/\text{CN}^-$  is consistent with the formation of 0.5 equiv. of the bis-nitride, terminal-oxo complex, **4** (top, Scheme 4). The formation of  $\text{NCO}^-/\text{CN}^-$  has been previously observed in the reactivity of uranium nitride complexes with CO.<sup>18,19,42,44–46</sup> In particular, the previously reported dinuclear U(v) bis-nitride complex,  $[\text{K}_2\{\text{U}^{\text{V}}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})_2\}]$ , showed similar reactivity with CO yielding a 1 : 1 ratio of  $\text{N}^{13}\text{CO}^- : ^{13}\text{CN}^-$ .

Alternatively, the addition of 5 equiv. of  $^{13}\text{CO}$  to the reaction mixture obtained after addition of  $\text{N}_2$  to **1**, led to a series of color changes over 48 hours. The products of the reaction could not be isolated, but quenching the reaction mixture with basic (pD = 13.4)  $\text{D}_2\text{O}$ , revealed the presence of 0.5 equiv. of  $\text{N}^{13}\text{CO}^-$  (per 1 equiv. of **1**) by quantitative  $^{13}\text{C}$  NMR spectroscopy (Fig. S32† and Scheme 4). This reactivity is most consistent with the formation of 0.5 equiv. of the  $\text{N}_2^{4-}$  complex, **5**, as the formation of  $\text{NCO}^-$  with concomitant release of  $\text{N}_2$  was previously observed for the reaction of CO and the U(v)/U(v) hydrazido–amide complex,  $[\text{K}_2\{\text{U}^{\text{V}}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-NH})(\mu\text{-N}_2)\}]$ .<sup>29</sup> Interestingly, addition of excess  $\text{HCl}(\text{Et}_2\text{O})$  to the residue obtained from the reaction mixture of **1** with  $\text{N}_2$  yielded  $\text{NH}_4\text{Cl}$  in 74% yield (per 1 equiv. of **1**). Notably, the formation of  $\text{NH}_4\text{Cl}$  was not previously observed upon addition of  $\text{HCl}$  to the U(v)/U(v)  $\text{N}_2^{4-}$  complexes, **E–G**,<sup>19,30</sup> suggesting that the  $\text{N}_2^{4-}$  in the U(IV)/U(v) complex, **5**, is more activated.

### Computational studies

To gain insight into the  $\text{N}_2$  reduction pathways promoted by complexes, **1** and **2**, DFT calculations (B3PW91) were performed, including solvent and dispersion forces. Formation of the isolated U(v)/U(v) bis-nitride, terminal-oxo complex, **4**,

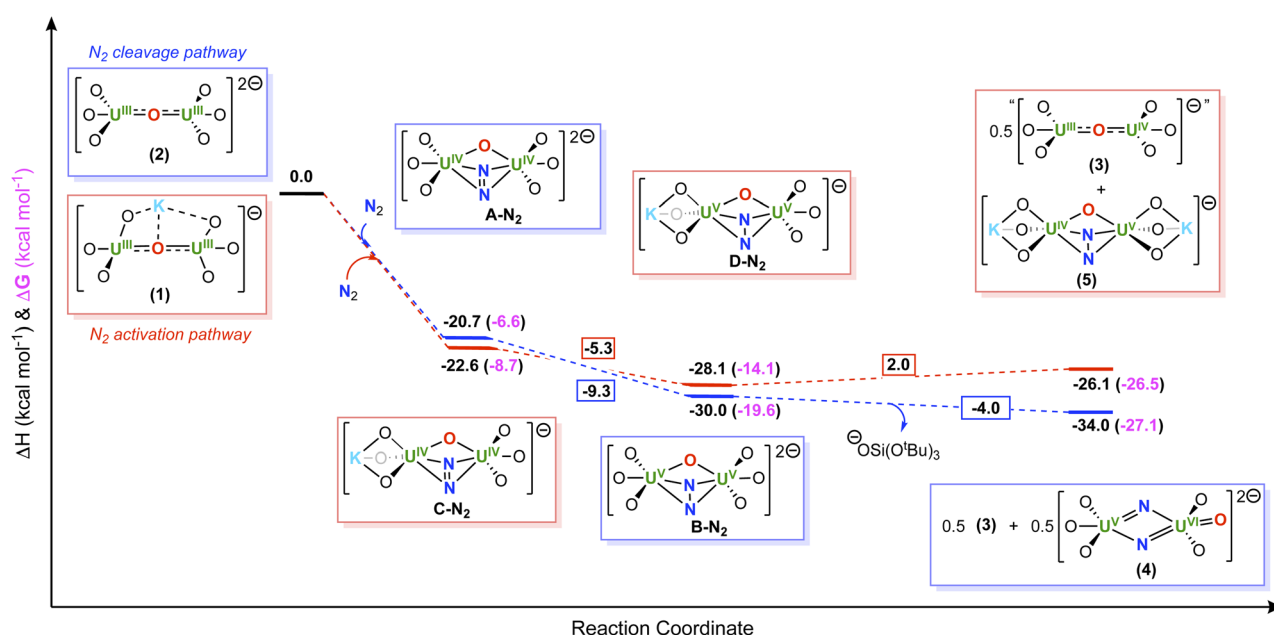
from the reaction of  $\text{N}_2$  and **2**, was shown to be thermodynamically favorable by  $-34.0 \text{ kcal mol}^{-1}$  ( $-26.5 \text{ kcal mol}^{-1}$  in Gibbs free energy) (Scheme 5). Unfortunately, the calculations of the proposed tetranuclear intermediate were intractable; however, the calculations demonstrate that complete reduction of  $\text{N}_2$  may involve two intermediate species, namely a U(IV)/U(IV)  $\text{N}_2^{2-}$  (**A–N<sub>2</sub>**) and a U(v)/U(v)  $\text{N}_2^{4-}$  complex (**B–N<sub>2</sub>**), in which both intermediate species involve a step-wise, two-electron reduction to  $\text{N}_2$ .

Interestingly, the first two-electron reduction of  $\text{N}_2$ , forming intermediate **A–N<sub>2</sub>**, is computed to be exothermic by  $-20.7 \text{ kcal mol}^{-1}$  ( $-6.6 \text{ kcal mol}^{-1}$  in Gibbs free energy), as well as the second two-electron reduction to yield the  $\text{N}_2^{4-}$  intermediate, **B–N<sub>2</sub>**, is exothermic by  $-9.3 \text{ kcal mol}^{-1}$  ( $-7.5 \text{ kcal mol}^{-1}$  in Gibbs Free energy). The final N–N bond cleavage step, which involves the proposed tetranuclear uranium intermediate, is also exothermic by  $-4.0 \text{ kcal mol}^{-1}$  ( $-12.4 \text{ kcal mol}^{-1}$  in Gibbs free energy).

Next, the oxidation states of the complexes, **2** and **4**, as well as the intermediates, **A–N<sub>2</sub>** and **B–N<sub>2</sub>**, were verified by computing the different spin states.

For complex **2**, the septet ( $s = 3$ ), quintet ( $s = 2$ ), and triplet ( $s = 1$ ) spin states were considered. As expected for a U(III)/U(III) system, the septet ( $s = 3$ ; six unpaired electrons) was found to be the ground state, with the other spin states higher than  $14.7 \text{ kcal mol}^{-1}$  in energy. The unpaired spin localization clearly shows that the unpaired electrons are fully localized at the uranium centers (Fig. 4).

The spin states for the  $\text{N}_2$ -bound intermediate species, namely, **A–N<sub>2</sub>** and **B–N<sub>2</sub>**, were also computed considering the quintet ( $s = 2$ ), triplet ( $s = 1$ ), and singlet ( $s = 1$ ) ground states. Interestingly, the quintet ( $s = 2$ ) is  $3.1 \text{ kcal mol}^{-1}$  higher in energy than the triplet ( $s = 1$ ), while the singlet ( $s = 0$ ) is higher



Scheme 5 Computed enthalpy and Gibbs free energy ( $\Delta\text{H}$  (black) and  $\Delta\text{G}$  (pink) in  $\text{kcal mol}^{-1}$ ) profiles for the formation of (blue) **4** and (red) **5**.



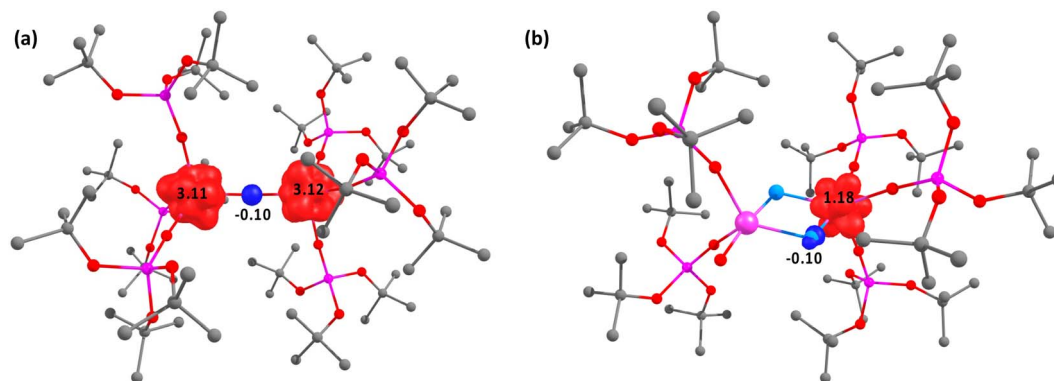


Fig. 4 Unpaired spin density plot for (a) 2 and (b) 4.

than  $44.0 \text{ kcal mol}^{-1}$  in energy. Scrutinizing the unpaired spin density on the U centers for the two lower spin states (quintet and triplet), clearly shows that the quintet ( $s = 2$ ) corresponds to the  $\text{U(IV)/U(IV)} \text{N}_2^{2-}$  (**A-N<sub>2</sub>**), whereas the triplet ( $s = 1$ ) corresponds to the  $\text{U(V)/U(V)} \text{N}_2^{4-}$  (**B-N<sub>2</sub>**) intermediate. Interestingly, in the quintet ( $s = 2$ ) spin-state, the SOMO-2 and the SOMO-3 (SOMO = singly occupied molecular orbital), indicates occupation of two degenerate N-N  $\pi^*$  ligand orbitals, suggesting that the  $\text{N}_2$  has undergone a two-electron reduction to a  $\text{N}_2^{2-}$  moiety, yielding formal  $\text{U(IV)/U(IV)} 5f^2$  centers. Therefore, some unpaired spin density is observed on the  $\text{N}_2$  moiety with a ferromagnetic coupling with the unpaired spins at the uranium.

For the bis-nitride, terminal-oxo complex, **4**, a doublet ( $s = 1/2$ ) spin state was calculated, which is consistent with a mixed-valent  $5f^1 \text{U(V)/U(VI)}$  complex. The unpaired spin density is located on only one uranium, suggesting that this is most likely the  $\text{U(V)} 5f^1$  ion, whereas the second uranium ion does not display any unpaired spin density, suggesting this is a  $\text{U(VI)} 5f^0$  ion (Fig. 4), which is in line with the observed bond valence sum analysis. Interestingly, the two bridging nitride moieties are negatively charged ( $-0.8$ ,  $-0.9$ ), indicating a nucleophilic character.

Similar analysis was performed for the reduction of  $\text{N}_2$  by complex **1**, in which calculations for the proposed tetranuclear intermediate were also intractable. In this system, the two step-wise, two-electron reductions of  $\text{N}_2$ , forming the intermediate,  $\text{U(IV)/U(IV)} \text{N}_2^{2-}$  (**C-N<sub>2</sub>**) and  $\text{U(V)/U(V)} \text{N}_2^{4-}$  (**D-N<sub>2</sub>**) species, were found to be thermodynamically favorable by  $-22.6$  and  $-5.3 \text{ kcal mol}^{-1}$  ( $-8.7$  and  $-10.9 \text{ kcal mol}^{-1}$  in Gibbs free energy, respectively) respectively. Whereas, subsequent formation of the bis-nitride, terminal-oxo complex, **4**, was endothermically unfavorable by  $34.6 \text{ kcal mol}^{-1}$ . Therefore, the overall six-electron reduction and cleavage of  $\text{N}_2$  is endothermic by  $6.7 \text{ kcal mol}^{-1}$ . In contrast, the formation of the  $\text{U(IV)/U(V)} \text{N}_2^{4-}$  complex, **5**, is slightly endothermic by  $2.0 \text{ kcal mol}^{-1}$  (exergonic by  $7.5 \text{ kcal mol}^{-1}$ ) leading to an overall thermodynamically favorable reaction pathway ( $-26.1 \text{ kcal mol}^{-1}$  in enthalpy,  $-27.1 \text{ kcal mol}^{-1}$  in Gibbs free energy). Overall, these results are consistent with the experimental findings, suggesting that generation of the  $\text{U(IV)/U(V)}$

$\text{N}_2^{4-}$  species, **5**, is more favorable when partial  $\text{K}^+$  cation sequestration has occurred, whereas  $\text{N}_2$  cleavage to the  $\text{U(V)/U(VI)}$  bis-nitride, terminal-oxo complex, **4**, is more favorable when all  $\text{K}^+$  cations have been removed from the inner coordination sphere.

## Conclusions

Herein, we have compared the mechanism and resulting products of  $\text{N}_2$  reduction by previously reported  $\text{K}_2$ -bound dinuclear uranium(III) complexes with those of the analogous uranium(III) dinuclear complexes, **1** and **2**, where one or two  $\text{K}^+$  ions have been removed from the inner coordination sphere by addition of 2.2.2-cryptand. The complete sequestration of the  $\text{K}^+$  cations resulted in an enhanced reducing ability of complex **2**, leading to the formation of two products upon  $\text{N}_2$  addition, namely, the  $\text{U(III)/U(IV)}$  complex, **3**, and the  $\text{U(V)/U(VI)}$  bis-nitride complex, **4**. The formation of these two products requires four uranium centers to be involved in  $\text{N}_2$  cleavage, and is proposed to occur *via* a tetranuclear  $\text{N}_2$  intermediate that can only form in the absence of coordinated alkali metal ions, resulting in a six-electron  $\text{N}_2$  cleavage. Removal of only one  $\text{K}^+$  cation and subsequent reactivity with  $\text{N}_2$  led to the formation of the  $\text{U(III)/U(IV)}$  complex, **3**, and to the formation of a  $\text{U(V)/U(IV)} \text{N}_2^{4-}$  complex, **5**, where the  $\text{N}_2^{4-}$  is more activated than in the analogous  $\text{U(V)/U(V)} \text{N}_2^{4-}$ , **E-G** complexes, as indicated by its high reactivity with electrophiles, such as acid ( $\text{H}^+$ ) and CO. Most notably, we had previously shown that  $\text{N}_2$  evolution occurred upon addition of a strong acid (HCl) to the complexes **E** and **F**, whereas in this study, we found HCl addition to complex **5** resulted in  $\text{NH}_4\text{Cl}$  formation. Additionally, computational studies indicate that  $\text{N}_2$  cleavage by **2**, with concomitant formation of the bis-nitride complex, **4**, is thermodynamically favored. Both the  $\text{U(V)/U(VI)}$  bis-nitride **4**, and the  $\text{U(V)/U(IV)} \text{N}_2^{4-}$ , **5**, complexes react with CO in ambient conditions leading to  $\text{CN}^-$  and  $\text{NCO}^-$  or solely  $\text{NCO}^-$ , respectively. Overall, these results provide an important insight into the relationship between alkali ion-binding modes and the multimetallic cooperativity and reactivity within a unique uranium system that cleaves and functionalizes  $\text{N}_2$ , demonstrating the possibility of a three-electron transfer from  $\text{U(III)}$  to  $\text{N}_2$ .





## Data availability

The data that support the findings of this study are openly available in the Zenodo repository at <https://doi.org/10.5281/zenodo.10044157>.

## Author contributions

N. J. designed and carried most experiments and analyzed the data; M. K. identified the conditions for the isolation of the key complex **4**. M. M. designed and supervised the project; T. R. and L. M. carried out the computational study; R. S. measured and analyzed the X-Ray data; N. J., M. K., and M. M. wrote the manuscript with contributions of all authors, and all authors have given approval for the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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