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Reductive disproportionation of nitric oxide mediated by low-valent uranium^{†‡}

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The reductive disproportionation of nitric oxide (1 atm) is mediated by the bulky U^{III} aryloxyde [U^{III}(OAr^{Ad,Ad,Me})₃] (Ar^{Ad,Ad,Me} = O-C₆H₂-2,6-Ad-4-Me) (1) to form the U^V terminal oxo species [(^{Ad,Ad,Me}ArO)₃U^V(O)] (2) and N₂O, as confirmed by single crystal X-ray diffraction and GC-MS measurements. The reaction is quantitative in the solid state. Mechanistic and theoretical studies of the reaction suggest that the N–N bond is formed by the coupling of an η¹-O bound nitric oxide ligand with gaseous NO to give an η¹-(N₂O)₂^{1–} intermediate prior to the spontaneous extrusion of N₂O to yield the U^V terminal oxo species 2.

The reactivity of nitric oxide (NO) with transition metal molecular complexes and solid-state materials is a key concern because of the role of NO as biological signaling molecule and its role as a potent greenhouse gas produced as the by-product of hydrocarbon combustion.^{1–4} Initial theoretical studies of the coordination of NO to U^{III} complexes suggested that distinct reaction pathways with NO are accessible to uranium and the early actinides, based on their oxophilicity and low-reduction potentials.⁵ In light of both long-standing and recent evidence that uranium can be an efficient catalyst for important small molecule reactions, such as N₂, CO₂, and H₂O reduction,^{6–12} the potential complementary reactivity of uranium with NO may offer unique solutions for NO reduction. However, the investigation of low-valent early actinide reductive disproportionation of NO has been limited by the lack of appropriate coordination chemistry to isolate the reaction products and to identify the relevant redox chemistry of the actinides with NO.

While Bursten *et al.* predicted the stability of a N-bound uranium nitrosyl,⁵ Evans and coworkers only recently reported the isolation of a uranium NO complex, namely [(C₅Me₄H)₃U(NO)], featuring a formal (η¹-NO)^{1–} unit with significant interaction between the NO π* and the uranium 5f_π orbitals.¹³ In f-element chemistry, NO gas acts predominantly as an oxygen atom transfer reagent, yielding bridging μ-oxo complexes.^{6,14,15} The mechanism of formation of the μ-oxo and the fate of the NO's nitrogen are unknown. Cloke *et al.* demonstrated the formation of isocyanate from the U^{III} reduction of an equimolar mixture of CO and NO. DFT calculations suggested the attack of CO onto a η²:η² bound NO; however, from the direct reaction of NO with U^{III} molecular complexes no products could be identified.^{16,17}

In order to directly interrogate U^{III} reactivity with NO and to determine the fate of nitrogen in the reaction, a bulky tris-aryloxyde complex was developed to enforce monometallic reactivity and the formation of mononuclear reaction products. Herein, we report the synthesis of [U^{III}(OAr^{Ad,Ad,Me})₃] (1) and its reactivity with NO. The bulky, monodentate aryloxyde ligand Ar^{Ad,Ad,Me}ArOK was chosen to protect the reactive, low-coordinate U^{III} center, and still be flexible enough to form a cavity for binding and activating NO. The coupling of NO to form N₂O and H₂O is a key step in enzymatic systems, such as bacterial nitric oxide reductase (NOR) enzymes and is dependent on exogenous acid (H⁺).^{2,18,19} Complex 1 is the first example of an f-element complex to show reductive NO coupling to form N₂O, and it is not dependent on the addition of H⁺.

The *ortho*-disubstituted *para*-cresol, Ar^{Ad,Ad,Me}ArOH (Ar^{Ad,Ad,Me} = O-C₆H₂-2,6-Ad-4-Me), is synthesized following a procedure from Kawaguchi *et al.*²⁰ This rigid ligand provides larger steric bulk compared to the sterically encumbered, yet flexible monodentate aryloxyde ligand (Ar*O)[–] (with Ar* = 2,6-Ph₂CH-C₆H₂-4-Me).²¹ The corresponding deprotonated salt, Ar^{Ad,Ad,Me}ArOK, is prepared in 94% yield by addition of KN(SiMe₃)₂ to the phenol in DME suspension. In order to synthesize complex 1 three equivalents of Ar^{Ad,Ad,Me}ArOK are added to freshly prepared UI₃(dioxane)_{1.5}.²² After workup, compound 1 can be isolated as a red powder in 84% yield.

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[†] This paper is dedicated to Professor Helmut Hartung on the occasion of his 80th birthday.

[‡] Electronic supplementary information (ESI) available: Synthetic and crystallographic details, NMR spectroscopic, magnetic, computational details, and GC/MS data are included. CCDC 1477612 and 1477613. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc06095a

An X-ray diffraction study on single crystals of **1**·1.445 *n*-hexane·0.555 C₆H₆, grown from slow diffusion of *n*-hexane into a benzene solution of **1** at room temperature, reveals that the uranium center lies close to the plane defined by three oxygen atoms of the aryloxo ligand (ESI,† Fig. S23). Therefore, the geometry can be described as a distorted trigonal plane with the uranium center shifted out of plane (oop) by 0.343 Å. This unusual displacement for a three coordinate U^{III} ion is rather small in comparison to other complexes with monodentate aryloxo ligands, such as [U^{III}(ODtbp)₃] (with (ODtbp)[−] = O-C₆H₃-2,6-*t*Bu), where the U ion is shifted 0.81 Å out of the plane of the three phenolate oxygens.²³ However, this steric enforcement of a near trigonal planar geometry is similar to that observed in [U^{III}(N(SiMe₂*t*Bu)₂)₃], where the uranium center lies almost perfectly in the plane of the ligating nitrogen atoms (*U*_{oop} = 0.008(2) Å).²⁴

Characterization by ¹H NMR shows seven characteristic, temperature-independent resonances (ESI,† Fig. S3). The UV/vis/NIR spectrum shows two bands with $\epsilon \approx 13\,000\text{ M}^{-1}\text{ cm}^{-1}$ at 250 and 278 nm, and one absorption at 513 nm with an extinction coefficient of $1413\text{ M}^{-1}\text{ cm}^{-1}$ (ESI,† Fig. S19 and S20). The spectrum agrees well with that observed for [U^{III}(ODtbp)₃].²³ To further validate the U^{III} oxidation state, SQUID magnetization measurements were conducted (ESI,† Fig. S15). The complex exhibits an effective magnetic moment of $\mu_{\text{eff}} = 2.96\ \mu_{\text{B}}$ at 300 K, which is in the range of other trivalent uranium complexes with monodentate aryloxides, such as [U^{III}(ODtbp)₃] with $3.3\ \mu_{\text{B}}$ and [U^{III}(OAr*)₃] with $2.53\ \mu_{\text{B}}$.^{21,23,25} It is also in good agreement with other aryloxo complexes from the Meyer group, namely [((^{*t*}Bu,^{*t*}BuArO)₃tacn)U^{III}] (with ((^{*t*}Bu,^{*t*}BuArO)₃tacn)^{3−} = trianion of 1,4,7-tris-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane) and [((^{*t*}Bu,^{*t*}BuArO)₃N)U^{III}] (with ((^{*t*}Bu,^{*t*}BuArO)₃N)^{3−} = trianion of tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)amine) with values of $2.92\ \mu_{\text{B}}$ and $3.0\ \mu_{\text{B}}$, respectively.^{25–27} Upon cooling to 2 K, the magnetic moment decreases to $1.97\ \mu_{\text{B}}$, and is in range with the aforementioned U^{III} complexes [((^{*t*}Bu,^{*t*}BuArO)₃tacn)U^{III}] with $1.77\ \mu_{\text{B}}$ and [((^{*t*}Bu,^{*t*}BuArO)₃N)U^{III}] with $1.6\ \mu_{\text{B}}$. Low-temperature EPR data of trivalent **1**, recorded at 8 K in toluene, show an asymmetric signal with g_{eff} values at 3.20, 2.73, and 1.42 (ESI,† Fig. S18). Calculations with the relation $4\mu_{\text{eff}}^2 = (g_1^2 + g_2^2 + g_3^2)$ result in a value of $\mu_{\text{eff}} = 2.22\ \mu_{\text{B}}$, which is in good agreement with the experimentally determined magnetic moment of $\mu_{\text{eff}} = 2.13\ \mu_{\text{B}}$ at 8 K.²⁸

In the solid-state, deep-red trivalent **1** reacts with excess gaseous nitric oxide on contact to form the dark brown terminal oxo species [(^{Ad,Ad,Me}ArO)₃U^V(O)] (**2**) as the only product in quantitative yield (Scheme 1). The exclusive formation of nitrous oxide was confirmed by GC-MS measurements (ESI,† Fig. S7–S10). The formation of N₂ was not observed when excess nitric oxide was used. This observation suggests that reduction of NO is substantially faster than N₂O reduction. In contrast, the solid-state reaction of **1** with N₂O does not lead to complete and clean conversion (ESI,† Fig. S6). In benzene solution, complex **2** can be isolated by treatment of **1** with either excess NO (1 atm) in 73% yield, or with excess N₂O (1 atm) in 75% yield. The reaction of **1** with N₂O is similar to the one observed for the monomeric

Scheme 1 Reactivity of **1** with NO/N₂O yielding **2** (left) and the molecular structures of **1** and **2** in the solid state (right).

aryloxo complex, [(Ar*O)₃U^{III}(thf)], from which the terminal oxo complex [(Ar*O)₃U^V(O)(thf)] can be isolated.²¹

The molecular structure of **2**, obtained from a single crystal grown from slow diffusion of *n*-hexane into a benzene solution of **2**, confirms that **2** is a monometallic U^V terminal oxo complex with a trigonal pyramidal coordination geometry (ESI,† Fig. S24). The uranium center is shifted 0.237 Å out of the plane defined by the oxygen atoms of the aryloxo ligands. The U–O bond length of the terminal oxo moiety is determined to be 1.8175(17) Å; and thus, is in line with other terminal U^V oxo complexes reported in the literature.^{21,29,30} In UV/vis/NIR spectra, only a single band can be observed in the UV region at 278 nm ($\epsilon = 10\,500\text{ M}^{-1}\text{ cm}^{-1}$). Only a few distinct absorption bands typical for the oxidation state of +V for uranium appear to arise from f–f transitions in the near infrared region from 900 to 2200 nm (ESI,† Fig. S21 and S22). The extinction coefficients vary from 20 to $70\text{ M}^{-1}\text{ cm}^{-1}$.

SQUID magnetization data provides additional evidence for the U(V) oxidation state (ESI,† Fig. S16). At 300 K, **2** exhibits an effective magnetic moment of $\mu_{\text{eff}} = 2.31\ \mu_{\text{B}}$, which is significantly higher than μ_{eff} values reported for the terminal oxo complexes [(Ar*O)₃U^V(O)(thf)] and [((Me₃Si)₂N)₃U^V(O)], with values of 1.96 and $1.59\ \mu_{\text{B}}$, respectively. The low-temperature magnetic moment of $0.88\ \mu_{\text{B}}$ at 2 K is in better agreement compared to $0.86\ \mu_{\text{B}}$ for [(Ar*O)₃U^V(O)(thf)] (at 2 K) as well as $0.94\ \mu_{\text{B}}$ for [((Me₃Si)₂N)₃U^V(O)] (at 4 K).^{21,29} Pentavalent **2** is EPR active, producing an axial EPR spectrum with $g_{\text{eff}} = 2.25$ and 0.71 (ESI,† Fig. S17). Once again, the calculated $\mu_{\text{eff}} = 1.23\ \mu_{\text{B}}$ matches well with its experimentally determined low temperature moment of $\mu_{\text{eff}} = 1.24\ \mu_{\text{B}}$, obtained at 12 K in toluene solution.

The steric protection afforded by the bulky, monodentate aryloxo enforces the production of a single, monometallic product in the oxidation of U^{III} by NO. As stated before, examples for clean reactivity with NO are rare for f-element complexes and the fate of the nitrogen atom is often not reported. Similarly, after completion of the reaction from **1** to **2** under NO, the nitrogen also cannot be traced to a solid product, as confirmed by elemental analysis. However, GC-MS analysis of the head-space of the reaction mixture confirmed the formation of N₂O.

Scheme 2 Feasible transition states for the reaction of **1** with nitric oxide.

This observation and the absence of uranium nitride products suggest that a bimetallic NO cleavage reaction, as observed by Cummins and coworkers, was not operative.³¹

The rapid reaction with NO and exclusive formation of N₂O in the absence of added H⁺ suggested three possible mechanisms. As shown in Scheme 2 (pathway 1), N₂O can be formed *via* an intermediate bimetallic *trans*-hyponitrite to give **2** and N₂O. Even though it is a reoccurring theme in transition metal chemistry,^{19,32–34} such a possible bimetallic intermediate is unlikely based on the absence of reactivity of complex **1** with CO, which is likely due to the steric constraints of the bulky ligand architecture. This absence of reactivity with CO is in contrast to the reactivity of less sterically encumbered U^{III} complexes with CO,^{23,35–37} which form bridging ynediolate complexes, analogous to the proposed *trans*-hyponitrite intermediate in pathway 1. No reactivity of **1** with CO is observed; even under elevated temperatures up to 80 °C and five days reaction time.

Alternatively, two pathways to form **2** are possible, involving the monometallic reductive disproportionation of NO (Scheme 2). After an initial NO binding event, coupling with a second equivalent of NO can result in either a κ^2 -*cis*-hyponitrite intermediate (pathway 2), as has been demonstrated for early metal reduction of NO to N₂O,³⁸ or a *trans*-hyponitrite intermediate (pathway 3), similar to azide to imide conversion mechanisms observed for group 5 metals.^{39–41} Decomposition of either one of these intermediates would result in the formation of **2** and N₂O.

Due to the rapid reaction and the fleeting nature of intermediates, DFT calculations were undertaken on the full system (no modeling of the adamantyl substituents) to establish a reaction profile (Fig. 1). This binding event is coupled with a redox event with electron transfer from uranium to nitrosyl.

Fig. 1 DFT(B3PW91) computed reaction profile.

Indeed, the two O- and N-bonded coordination modes are found to be stable minima, with the latter being only 11.5 kcal mol^{−1} more stable than the former. This result is in accord with the calculations of Bursten *et al.* and the isolation of a uranium nitrosyl complex by Evans and coworkers.^{5,13} While in our case these nitrosyl intermediates are too fleeting to observe directly, it is informative to note that both the O- and N-bound nitrosyls are bent with a U–N–O and U–O–N angle of 160.9° and 165.6°, respectively.

However, from the N-bonded adduct, no plausible reaction pathway describing our experimental results was found. This observation indicates that this complex is likely only a resting state for the reaction. From there, it is possible to access the O-bonded adduct *via* an η^2 -NO isomerization transition state. Starting from the O-bonded adduct, a radical coupling with another molecule of NO readily occurs (estimated barrier of 0.7 kcal mol^{−1}), yielding a very stable mononuclear hyponitrite complex with a U^{IV} center. This complex exhibits an η^1 -*trans*-hyponitrite rather than a κ^2 -*cis*-coordination (that was not located as a minimum on the potential energy surface (PES)) and the spin density at the uranium center is consistent with a U^{IV} rather than a U^V (two unpaired electrons located at the uranium center in a quartet spin state; depiction of spin density plot in the ESI,† Fig. S25). From this hyponitrite complex, a transition state for the N₂O release could be located with a low activation barrier of 16.1 kcal mol^{−1}. The analysis of the spin density indicates that the uranium center is already oxidized at the transition state (U^V) (the transition state was located on the doublet spin state PES, which is in line with an oxidized uranium center as indicated by the presence of one unpaired spin at the uranium center). This step is thus a single electron transfer (SET) from the uranium center as it induces oxidation from oxidation state +IV to +V. DFT methods have proven their ability to properly describe SET reactions involving lanthanide and uranium centers.⁴² Finally, this transition state connects the hyponitrite intermediate with the final oxo complex, which

is strongly stabilized with respect to both complex **1** and the hyponitrite species.

In summary, we have prepared the sterically encumbered tris-aryloxide U^{III} complex [U^{III}(OAr^{Ad,Ad,Me})₃] (**1**) and demonstrated that its reaction with NO leads to the formation of [(^{Ad,Ad,Me}ArO)₃U^V(O)] (**2**) and N₂O. DFT calculations suggest that the transformation proceeds through a monometallic η¹-transhyponitrite intermediate, formed through the coupling of exogenous NO with a thermally accessible O-bound nitrosyl ligand. This mechanism is unique to uranium. These results also indicate that, due to the strong reduction potential and oxophilicity of U^{III}, reaction mechanisms for the reduction of NO can diverge dramatically from those typically observed for first row transition metals. With the renewed interest in uranium small molecule catalysis,¹¹ the results on divergent mechanistic pathways accessible to uranium suggest that catalytic reactivity, complementary to transition metal catalysis, can be developed. Finally, considering the similarities between uranium and some transition metal ions, such as iron, with regard to the reducing strength of the low oxidation states and the oxophilicity of the high-valent ion, the presented disproportionation pathway might also be relevant for low-valent transition metal systems, where steric constraint can prevent bimolecular reactions.

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Notes and references

§ Direct measurement of reaction rates is not possible given the extremely fast rates in solution and solid-state. Based on previous attempts to measure NO and N₂O reduction by low-valent early metals (see ref. 38) the rates of these reactions are mass transport limited.

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