Facile Dinitrogen and Dioxygen Cleavage by a Uranium(III) Complex: Cooperativity Between the Non-Innocent Ligand and the Uranium Center

Penglong Wang, Iskander Douair, Yue Zhao, Shuao Wang, Jun Zhu, Laurent Maron,* and Congqing Zhu*

Dedicated to the 100th anniversary of the School of Chemistry and Chemical Engineering, Nanjing University

Abstract: Activation of dinitrogen (N₂, 78%) and dioxygen (O₂, 21%) has fascinated chemists and biochemists for decades. The industrial conversion of N₂ into ammonia requires extremely high temperatures and pressures. Herein we report the first example of N₂ and O₂ cleavage by a uranium complex, [Ni(CH₃CH₂NPPr₂)₂][TMEDA], under ambient conditions without an external reducing agent. The N₂ triple bond breaking implies a U₃⁺–O₂ anion. The hydrolysis of the N₂ reduction product allows the formation of ammonia or nitrogen-containing organic compounds. The interaction between U₃⁺ and O₂ in this molecule allows an eight-electron reduction of two O₂ molecules. This study establishes that the combination of uranium and a low-valent nonmetal is a promising strategy to achieve a full N₂ and O₂ cleavage under ambient conditions, which may aid the design of new systems for small molecules activation.

Introduction

The activation and cleavage of dinitrogen (N₂) remains a challenge due to its inert N≡N triple bond.[1–5] Since the first N₂ complex of a transition metal was reported in 1965,[6] chemists endeavor to explore molecular systems which can be utilized for fixation and activation of N₂ under mild conditions.[7–14] In the past few decades, a series of significant advances in the N₂ fixation and activation have been demonstrated by transition metal complexes[15–30] as well as by organoboron species.[31–35] In addition, molecular uranium systems also exhibit attractive ability for N₂ binding, reduction, and activation.[36–40] For instance, Mazzanti and co-workers reported that the multimetallic diuranium(III) complex [K₆[U(OSi(OBu)₃)]₅(μ-E) (E = N, O) is capable of activating N₂ to N₂⁺ via a four-electron reduction process.[43,44] Arnold and co-workers found that the four-electron reduction of N₂ was also achieved by the thorium or uranium dinuclear metallacycles, M₆(mTP)₄ (mTP = [2-(OC₃H₃–Bu₂,Me-4)-C₆H₄]–C₆H₄,1,3) [46]; M = U, Th) in the presence of a strong reductant (KC₆). However, recently we reported an example of N₂ cleavage by a heterometallic uranium-rhodium cluster with KC₆.[47] Moreover, the six-electron reduction of N₂ by a molecular uranium system without an external reducing agent has not been reported.

On the other hand, the binding and activation of O₂ is important for metabolism and synthetic oxidative catalysis.[48–51] It is understood that the metal-oxygen species from the activation of O₂ is the key intermediates in enzymatic reactions.[52] Thus, a number of high-valent bis(μ-oxo) bimetallic complexes have been synthesized by cleavage of O₂ in biomimetic studies.[49,50] Here we report the first example of N₂ and O₂ cleavage under ambient temperature and pressure by a uranium complex via a metal-ligand cooperative strategy.

Results and Discussion

The diuranium(III) complex, [Ni(CH₃CH₂NPPr₂)₂][TMEDA] (2), was prepared by the reduction of the previously reported uranium(IV) complex [N(CH₃CH₂NPPr₂)₄][UCl] (1) with potassium-graphite (KC₆) in the presence of tetramethylthelenediamine (TMEDA) under argon (Scheme 1). Complex 2 was isolated as a dark purple solid in a 38% yield after recrystallization from hexane at −40°C and was fully characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), elemental analysis, and single-crystal X-ray diffraction.[54] The solid-state molecular structure of complex 2 features two U₃⁺ which are bridged by a TMEDA molecule (Figure 1).
The assignment of the oxidation state of $^+$III to the uranium ions was confirmed by the variable-temperature magnetic moment measured with a superconducting quantum interference device (SQUID). The magnetic moment of complex 2 at 5K is 1.4 $\mu_B$ (per U), which gradually increases to 3.2 $\mu_B$ (per U) at 300 K (Figure S1). The measured magnetic moment at 300 K is lower than the theoretical value (3.6 $\mu_B$) for free $^+$III ion. However, the magnitude of $\mu_{eff}$ and temperature dependence of complex 2 are comparable to those of the other $^+$III complexes. Under argon, complex 2 appears to be stable both in solution and in the solid-state, while exposure of a solution of 2 in benzene to one atmosphere of $N_2$ at room temperature overnight resulted in a color change from dark purple to brown. A crystalline complex, $[\text{N}(\text{CH}_2\text{CH}_2\text{NPPr}_2)\text{Cl}(\text{CH}_2\text{CH}_2\text{NPPr}_2)\text{U}](3)$, was isolated from this reaction in 45% yield and determined to be the product of a six-electron reduction of 2 (Scheme 1). Complex 3 shows two resonances in the $^3P$ NMR spectrum at $+404.1$ and $-471.1$ ppm, suggesting two inequivalent phosphine environments in solution. The $^1H$ NMR spectrum of complex 3 exhibits 15 paramagnetic resonances in a range from $+141.44$ to $-31.48$ ppm. The HRMS for complex 3 shows a molecular ion peak at 1525.7787, which corresponds to a dinuclear form in solution. Complex 3 exhibits an intense absorption peak at 288 nm in THF solution, which may be assigned to charge-transfer bands (Figure S8). In the NIR region, several weak absorptions ($\varepsilon < 100 M^{-1} \text{cm}^{-1}$) at 955, 1016, 1075, 1118, 1460, and 1515 nm were observed (Figure S9), which may be attributed to $f-f$ transitions expected for $^+$IV species. Complex 2 was demonstrated to be the first uranium complex capable of spontaneous $N_2$ cleavage in the absence of other reducing reagents such as KC$_8$, Na/Hg, or Mg.

Complex 3 can be prepared independently by the reduction of complex 1 with KC$_8$ under $N_2$ at 1 atm and RT. In this case, crystalline complex 3 was isolated in 37% yield after recrystallization from benzene, and exhibits spectroscopic features identical to those obtained from the reaction of $N_2$ with the TMEDA-bridged diuranium(III) complex (2). Ligand induced $N_2$ cleavage was already reported for group 4 metals. However, in these systems, an in situ reduction of the metal complexes under a $N_2$ atmosphere was needed and no intermediates were isolated. The formation of complex 3 from 1 or 2 is the first example of phosphine ligand induced $N_2$ cleavage with $f$-block elements. The reaction between uranium(III) complex $[\text{U}(N_3\text{N})]$ ($N_3\text{N} = \text{N}(\text{CH}_2\text{CH}_2\text{NSi}(\text{Bu})\text{Me}_2)$) with $N_2$ was reported by Scott and co-workers in 1998, which led to the formation of the first example of $N_2$ cleavage with an actinide element, $[(\text{U}(N_3\text{N}))_2(\mu^2-\text{N}^2\text{N}))]$.$^{[30]}$ The $N-N$ bond distance in this species is 1.109(7) Å, which is identical with that found in free $N_2$ (1.0975 Å). This result further supports for the importance of the phosphine ligand in $N_2$ cleavage in complex 2.
An X-ray diffraction analysis of complex 3 (Figure 2) shows a centrosymmetric structure in the solid state, which is consistent with its $^1$H and $^3$P NMR spectra in solution. The most salient structural feature of 3 is the diamond-shaped geometry of the U$_2$N$_2$ core that is formed from the N$_2$ cleavage. The bond length of U1-N5 (2.460(3) Å) is longer than that of the U1-N5' (2.241(3) Å), possibly due to the steric reason. The P3-N5 distance (1.593(3) Å) is slightly shorter than that of N3-P3 (1.617(3) Å). In addition, the U1–U1' separation in complex 3 (3.775(3) Å) is longer than the sum of the covalent single bond radii for U (3.40 Å), which suggests that there is no significant U-U interaction. Notably, the long N5-N5' distance (2.807(4) Å) corresponds to the complete cleavage of N$_2$ via a six-electron reduction. The magnetic moment of complex 3 declines slowly from 4.2 µB (per U) at 300 K to 3.2 µB at 50 K, and then drops sharply to 1.1 µB at 5 K with a trend to zero (Figure S2). These values and the temperature dependence are consistent with the reported U$^{IV}$ complexes.

Of the six electrons needed for the full N$_2$ reduction, two are derived from the one-electron oxidation of the two U$^{III}$ atoms. The four extra electrons come from the transformation of the two phosphine ligands into phosphinimides in this process (formal two electrons oxidation per phosphine). Thus, the formal oxidation state for the uranium ion in complex 3 is + IV and for the phosphorus in phosphinimide is + V. This results seems to indicate that cooperativity between the presence of U$^{IV}$ and P$^{III}$ centers is responsible for the six-electron reduction of N$_2$ by complex 2.

The possibility of generating ammonia (NH$_3$) or nitrogen-containing organic compounds from this N$_2$ activation product was investigated. Rather than using dihydrogen or acid as sources of hydrogen for NH$_3$ production, the use of water as an alternative was considered. Treatment of a THF solution of 3 with 8 equivalents of degassed H$_2$O gave an organic species [N(CH$_2$CH$_2$NPP$_2$)$_2$](CH$_2$CH$_2$NPNP$_2$N) (L-NH) in 55% yield and an insoluble green precipitate (Scheme 1). The structure of L-NH was confirmed by NMR spectroscopy and HRMS. Compound L-NH can further react with excess H$_2$O to give ammonia via a similar process of Staudinger reaction.$^{[60]}$ Ammonia could also be obtained directly by the addition of an excess of H$_2$O to a THF solution of complex 3. Ammonia production was clearly identified by $^1$H NMR of the formation of NH$_4$Cl after treating the solution with an excess of ethereal HCl (Figure S19). Noted that no NH$_4$Cl was observed when a solution of ethereal HCl was added to a solution of either complex 3 or L-NH directly. Attempts to identify the possible products in these reactions were unsuccessful. Nevertheless, the nitrogen fixation and hydrolysis to organic species and ammonia have been accomplished under mild conditions through a well-defined U$^{III}$ complex and H$_2$O.

In order to further confirm that the two additional nitrogen atoms in complex 3 arise from the N$_2$ cleavage, the isotopically labelled species 3-$^{15}$N was synthesized in a similar manner to that used for 3 by the reaction of complex 2 with $^{15}$N$_2$ (98% isotopic purity) at RT. The IR spectra for 3 and 3-$^{15}$N were recorded on solid samples (KBr pellet), which exhibit isotope-sensitive bands in the range of 600–900 cm$^{-1}$ (Figure S10). Purified 3-$^{15}$N reacts with 8 equivalents of H$_2$O to form L-$^{15}$NH, which was confirmed by HRMS (Figure S21), showing a molecular ion signal at 511.3978 (510.3979 for L-$^{14}$NH). In addition, $^{13}$NH$_2$ was formed by the reactions of 3-$^{15}$N or L-$^{15}$NH with excess H$_2$O and was identified by the characteristic doublet signal of its conjugated acid ($^{15}$NH$_2$Cl) in the $^1$H NMR spectrum (Figure S20). These labeling studies confirm that the source of the nitrogen atoms in the phosphinimide units of 3 is N$_2$.

The formation of complex 3 was thus investigated by density functional theory (DFT) calculations at the B3PW91 level. The formation of a monomeric U$^{III}$ complex from complex 2 is endothermic by 20.0 kcal mol$^{-1}$. The uranium ions in complex 2 are being oxidized upon N$_2$ coordination, leading to the formation of a U$^{IV}$ complex A (Figure 3). Complex A may be regarded as a “key intermediate” in small molecule reduction by low valent f elements.$^{[51,52]}$ In complex A, the N–N bond has been extended to 1.23 Å (vs. 1.0975 Å in free N$_2$) in line with the reduction of N$_2$ and the formation of complex A is endothermic by 6.8 kcal mol$^{-1}$. From complex A, the full reduction of N$_2$ occurs at the transition state (TS1) with a kinetically accessible barrier of 23.1 kcal mol$^{-1}$ from A (29.9 kcal mol$^{-1}$ from complex 2). The lone pairs of electrons of the two phosphorus (one on each uranium unit) simultaneously attack the two nitrogen atoms in a trans fashion, one above and one below the U$_2$N$_2$ plane. Therefore, the two lone pairs of the phosphorus are attacking the π* orbital of the N$_2^2-$ moiety of complex A as evidenced by the depiction of the HOMO of TS1 (Figure S22) as well as the HOMO (phosphorus lone pairs) and LUMO (π* orbital of the N$_2^2-$) of intermediate A (Figure S23).

At TS1, the N–N bond is not yet fully broken (1.30 Å) which is consistent with the attack of only the π system of N$_2^2-$ and the P–N bonds are not yet formed (2.18 and 2.20 Å). The two nitrogen atoms are bonded to the two uranium centers in a symmetrical way (U–N distances of 2.34–2.35 Å and 2.41 Å). Following the intrinsic reaction coordinate, the system evolves to the formation of complex 3, which is exothermic by 35.5 kcal mol$^{-1}$ with respect to the reactants. The geometry of complex 3 compares well with the experimentally observed...
geometry as the N–N bond distance is 2.80 Å, in line with a full disruption of the N₂ triple bond.

Dioxygen is an abundant and environmentally benign oxidant. High-valent bis(μ-oxo) bimetallic species have been proposed as one of the important intermediates in O₂ activation. However, most of the reported examples of O₂ activation have been focused on transition metals and the controlled cleavage of O₂ by a molecular U^{III} complex has not been reported[63–66]. The addition of one atmosphere of O₂ gas to a solution of 2 in THF at ambient temperature resulted in the formation of dinuclear bis(μ-oxo) complex [N(CH₂CH₂NP_iPr₂)₂(CH₂CH₂NP_iPr₂O)]U₂(μ-O)₂ (4) (Scheme 1), which can be isolated in 43% yield after recrystallization from THF. The dark-red complex 4 shows broad absorption into the visible region below 600 nm (Figure S8). Generally, U^{V} complexes with a 5f⁶ configuration exhibit less complicated electronic absorption spectra than U^{IV} species with a 5f⁶ configuration in the NIR region. Compared with U^{IV} complex 3, complex 4 shows less absorption peaks in the range of 900 to 1600 nm (Figure S9), which may be suggested the presence of U^{V} in complex 4. NMR characterization of complex 4 was hampered by its poor solubility even in [D₆]DMSO and accordingly, single-crystal X-ray diffraction were used to verify its structure. The solid-state structure of complex 4 is centrosymmetric with the presence of two uranium centers and four oxygens (Figure 4). The distances of U₁–U₁ (3.417(6) Å) in complex 4 is shorter than that in complex 3 (3.775(3) Å), which compares well with the U⋯U distance of 3.4222(3) Å in the species of [[((Me₆ArO)₄tacn)U³⁺(μ-O)₄] reported by Meyer and coworkers[66]. Complex 4 has a slightly distorted [U(μ-O₂)₂U] core with two U–O distances of 2.030(6) Å (U₁-O₂) and 2.193(5) Å (U₁'-O₂). The angles of U₁-O₂-U₁ and O₂-U₁-O₂ were determined to be 107.98° and 72.02°, respectively. The two other oxygens are clearly bonded to the phosphorus (P₁-O₁ and P₁'-O₁' distances of 1.432(6) Å) with a structure reminiscent of that of complex 3. These data are therefore consistent with the eight-electron reduction of two molecules of O₂ by complex 2. This reduction is possible because of the cooperative effect between U^{III} and P^{III} which was already...

Figure 3. Computed enthalpy profile (in kcal mol⁻¹) for the formation of complex 3 by full reduction of N₂.

Figure 4. Solid-state structure of 4. Thermal ellipsoids are set at 35% probability. Hydrogen atoms and isopropyl moieties in PPr₂ are omitted for clarity. Selected interatomic distances [Å] and angles [°]: U₁–N₁ 2.420(6), U₁–N₂ 2.720(6), U₁–N₃ 2.332(6), U₁–N₄ 2.307(6), U₁–O₂ 2.030(6), U₁–O₂' 2.193(5), U₁–O₁' 2.275(6), N₁–P₁ 1.657(6), N₁–P₁ 1.657(6), P₁–O₁ 1.432(6), U₁–U₁' 3.417(6); U₁–O₂–U₁' 107.98, O₂–U₁–O₂' 72.02.⁵₆
observed in the reduction of N₂. However, since the formal oxidation state of uranium ions in complex 4 is + V, the implication is that the uranium centers act as a two electrons reductant, which is rather rare.[67] Although the bis(μ-oxo) bridged dinuclear uranium species was previously reported,[66] the formation of complex 4 with [U(μ-O₂)₂] moiety represents the first example of controlled O₂ cleavage by a U⁵⁺ complex under ambient conditions.

The temperature-dependent SQUID magnetization data for complex 4 were very similar to the high-valent dinuclear bis(μ-oxo) complex [[[(µ⁶-O₂)₂(tacn)]U⁵⁺]₂(µ-Ο₂)] reported by Meyer and co-workers.[66] The magnetic moment of 4 at 300 K is 2.3 μₜ per U (Figure S5), which is comparable to those of the other U⁵⁺ complexes.[66] With decreasing temperatures, the magnetic moments of 4 persistently decline to 0.4 μₜ per U at 5 K, which suggests that the antiferromagnetic coupling was present in 4. This antiferromagnetic coupling was probably due to the orbital overlap between the U ions via the bridging O-atoms. The χ versus T plot of 4 exhibits an antiferromagnetic coupling with a Néel temperature of approximately 44 K (Figure S6), which is close to that observed for the complex [[[(µ⁶-O₂)₂(tacn)]U⁵⁺]₂(µ-Ο₂)] (70 K) reported by Meyer and co-workers.[66] In addition, the χT versus T plot of complex 4 was also similar to Meyer’s species (Figure S7).

The formation of complex 4 was also investigated computationally (Figure 5). The direct oxidation of the phosphine by O₂ without uranium involvement was first considered and found not to be kinetically competitive (Figure S24). The reaction begins with the oxidation of uranium ions in complex 2 upon O₂ coordination, yielding the stable “key intermediate” C (−99.9 kcal mol⁻¹). Such a high stabilization has been found in the reaction of divalent samarium with O₂.[69] In this intermediate (C), the O₂ molecule has been doubly reduced, as evidenced by the O–O bond distance of 1.51 Å (1.20 Å in free O₂), so that the two uranium centers are oxidized to the + IV state. The O–O bond is thus broken with a low barrier (13.9 kcal mol⁻¹) in the TS₂, which is similar to the TS₁ found for the N–N bond breaking as it involves the two phosphorus atoms. Geometrically, the TS₂ appears to be symmetrical with the two P-O distances of 2.15 Å (vs. 2.18/2.20 Å for P–N bonds in TS₁). The O–O bond is already broken (2.57 Å). Quirks surprisingly, the U–O distances are not equivalent for the two oxygen atoms as one interacts strongly with one uranium atom (U–O distance of 2.06 Å and to a lower extend with the second one, U–O distance of 2.30 Å). For the second oxygen atom, the U–O distances are 2.24 and 2.50 Å, indicating a weaker interaction.

These geometrical features are explained by analyzing the frontier orbitals in the TS₂ (Figure S25). The HOMO of TS₂ is similar to the HOMO of TS₁ with the exception that only one phosphorus lone pair attacks one oxygen atom of O₂. The second phosphorus lone pair is involved in the HOMO-1 where there is an important contribution from f orbitals of the uranium centers (one of the uranium contributions is more important). The communication between the phosphorus lone pair and the uranium is ensured by the p orbitals of the two oxygen atoms. Indeed, the O–O bond breaking of complex C is formally a two-electron reduction process, while it is a four-electron reduction process for the N–N bond breaking in TS₁. Thus, the O₂⁺ two-electron reduction is ensured by one phosphorus lone pair as highlighted in the HOMO, and the lone pair of the second phosphorus induces

---

**Figure 5.** Computed enthalpy profile (in kcal mol⁻¹) for the formation of complex 4 by full reduction of two molecules of O₂.
a two-electron reduction of the uranium centers, as can be derived from the HOMO-1.

The reduction of the uranium centers is further confirmed following the intrinsic reaction coordinates from TS2. This yields intermediate D, whose formation is strongly exothermic (33.2 kcal mol⁻¹ from C and 133.1 kcal mol⁻¹ from complex 2). In intermediate D, unpaired spin density analysis indicates that the oxidation state of the two uranium center is + III. Interestingly, the presence of U(III) centers in intermediate D makes it prone to further substrate reduction. Complex D can then react with another O₂ molecule in a four-electron reduction process to yield complex 4 in a highly exothermic process (−148.6 kcal mol⁻¹ from intermediate D). In this reaction, each U(III) center acts as a two-electron reductant, which is quite unusual but has been reported by Liddle and co-workers.[9] The driving force of the second reduction is the formation of very strong U=O bonds. Interestingly, the putative reduction of O₂ by complex 3, bearing two U(IV) centers, is predicted to be highly favorable by 90.1 kcal mol⁻¹, forming B with two U(IV) centers (Figure 3). Experimentally, the reaction of complex 3 with 1 atm O₂ was found to occur, but no single-crystals suitable for X-ray crystallographic analysis were obtained. Spectroscopic data however are consistent with the formation of a diamagnetic U(IV) complex.

Conclusion

The first full reductions of N₂ and O₂ were accomplished under ambient temperature and pressure by a well-defined U(III) complex. The electrons required for the reduction were stored in a dimeric U(III)-P(III) species, in which two U(III) and two P(III) atoms allow a facile six-electron reduction of N₂ and an eight-electron reduction of two molecules of O₂. The interaction between T(III) and P(III) has been demonstrated to play an important role in the reduction of N₂ and O₂. This work represents an important step in increasing our understanding of the fundamental reactions of N₂ and O₂ activations. We envisage that the metal-ligand cooperativity shown in this study could be extended to other metals and low-valent main group elements (such as B, C, and P etc.), and thereby contribute to a rational design of new molecular systems for the activation of small molecules.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Grant Nos. 21772088 and 91961116), the Fundamental Research Funds for the Central Universities (14380216), the Young Elite Scientist Sponsorship Program of China Association of Science and Technology, the program of Jiangsu Specially-Appointed Professor, and Shuangchuan Talent Plan of Jiangsu Province. LM is member of the Institut Universitaire de France. Humboldt Foundation and Chinese Academy of Science are acknowledged for support. CalMip is also gratefully acknowledged for a generous grant of computing time.

Conflict of interest

The authors declare no conflict of interest.

Keywords: DFT calculations · dinitrogen cleavage · dioxygen · phosphorus · uranium


[54] Deposition Numbers 1983713 (for 2), 1983714 (for 3), and 1983716 (for 4) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.


Manuscript received: September 7, 2020
Accepted manuscript online: September 15, 2020
Version of record online: October 26, 2020