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Remarkable Dinitrogen Activation and Cleavage by the Gd Dimer: From Dinitrogen Complexes to Ring and Cage Nitrides**

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Dinitrogen activation and its chemical transformations are one of the most challenging subjects in chemistry. Coordination of N_2 to transition-metal or f-element metal complexes is often an effective strategy for activation because it weakens the σ and/or π bonds of N_2 through side-on or end-on coordination. Many dinitrogen complexes exhibit subsequent reactivity at the N_2 unit that can lead to its further activation, complete N–N bond cleavage, and functionalization.[1–3] Reactions of metal atoms and small clusters with dinitrogen serve as ideal models for fundamental understanding of the multifaceted mechanisms of dinitrogen activation by d- and f-metal complexes and surfaces.

Previous investigations have demonstrated N–N bond cleavage by some transition-metal atoms and dimers.[4,5] Herein we report a joint matrix-isolation infrared-spectroscopic and theoretical study of the reaction of Gd_2 with N_2, which proceeds by the initial formation of an unprecedented dinuclear lanthanide dinitrogen complex with a simultaneously side-on and end-on bonded N_2 ligand. The complex isomerizes to a planar cyclic $[Gd(\mu\text{-}N)_2Gd]$ structure with a completely cleaved N–N bond. This complex can further dimerize to form a unique cubic $[Gd_4N_4]$ cluster, a fundamental building block for ferromagnetic GdN nanoparticles and crystals. We have shown that the formation of the $[Gd_4N_4]$ block from cyclic $[Gd(\mu\text{-}N)_2Gd]$ is exothermic and barrierless, thus indicating that the self-assembly formation of $[Gd_4N_4]$ and possibly $(GdN)_x$ nanoparticles from elemental Gd and N_2 is thermodynamically and kinetically feasible.

The above-mentioned species were prepared by codeposition of laser-evaporated Gd atoms and clusters with N_2/Ar mixtures onto a CsI window at 6 K as previously described.[6] Infrared spectra were recorded on a Bruker IFS 66-V spectrometer at 0.5 cm^{-1} resolution using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. With relatively high N_2 concentration (0.5%) and low laser energy (< 5 mJ/pulse), the $[Gd(N_2)]$ and high-coordinate dinitrogen complexes, which have been previously identified,[7] were produced. The IR spectra in the selected regions with lower N_2 concentration (0.05%) and higher laser energy (10 mJ/pulse) are shown in Figure 1, with the product absorptions listed in Table 1. Weak new absorptions at 1117.3, 1103.3, 688.5, and 558.3 cm^{-1} appeared on sample annealing (30–40 K). When taking the spectra after annealing the matrix sample, it was found that the band intensities of the

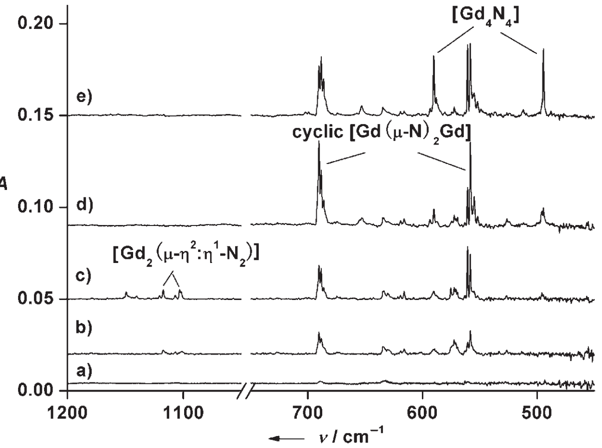

Figure 1. Infrared spectra in the 1200–1050 and 750–450 cm^{-1} regions from codeposition of laser-evaporated Gd with 0.05% N_2 in argon: a) 1 h of sample deposition at 6 K; b) after annealing to 30 K; c) after annealing to 40 K; d) after 15 min irradiation with $\lambda > 700$ nm; e) after 15 min irradiation with $\lambda > 300$ nm.

Table 1: Observed and calculated vibrational frequencies and isotopic frequency ratios for $[Gd_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-}N_2)]$ (**1**), cyclic $[Gd(\mu\text{-}N)_2Gd]$ (**2**), and cubic $[Gd_4N_4]$ (**3**).

Exptl		Calcd			Assignment
ν [cm^{-1}]	$^{14}N/^{15}N$	ν [cm^{-1}]	$^{14}N/^{15}N$		
1117.3	1.0334	1211	1.0349	**1**	a′ (N–N stretch)
1103.3	1.0337			**1**	site
688.5	1.0318	696	1.0320	**2**	B_{3u}
558.3	1.0316	540	1.0320	**2**	B_{2u}
590.1	1.0320	585	1.0325	**3**	T_2
494.4	1.0322	477	1.0330	**3**	T_2

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absorptions at 1117.3 and 1103.3 cm^{-1} decrease, whereas the band intensities of the absorptions at 688.5 and 558.3 cm^{-1} increase with increasing sample scan times. This finding suggests that the red irradiation from the IR spectrometer induces a transformation of the absorptions at 1117.3 and 1103.3 cm^{-1} to the absorptions at 688.5 and 558.3 cm^{-1}. The absorptions at 1117.3 and 1103.3 cm^{-1} dissipated upon subsequent irradiation ($\lambda = 700$–1000 nm), during which the absorptions at 688.5 and 558.3 cm^{-1} markedly increased. After the absorptions at 1117.3 and 1103.3 cm^{-1} were bleached, the intensities of the absorptions at 688.5 and 558.3 cm^{-1} stayed unchanged with increasing sample scan times. Continued irradiation ($\lambda = 300$–580 nm) decreased the absorptions at 688.5 and 558.3 cm^{-1} and produced two new absorptions at 590.1 and 494.4 cm^{-1}.

Isotopic substitutions ($^{15}N_2$, $^{14}N_2 + {}^{15}N_2$, and $^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$) were employed for product identification based on isotopic shifts and absorption splitting. The absorptions at 1117.3 and 1103.3 cm^{-1} exhibit $^{14}N/^{15}N$ isotopic frequency ratios that are characteristic of the N–N stretching vibrations. The mixed $^{14}N_2 + {}^{15}N_2$ and $^{14}N_2 + {}^{14}N^{15}N + {}^{15}N_2$ spectra (Figure S1 in the Supporting Information) indicate that only one N_2 unit with two slightly inequivalent N atoms is involved in the mode. These absorptions were only observed in the experiments with high laser energy and low N_2 concentrations, which indicates that the new product involves more than one Gd atom. The unusually low N–N stretching frequency implies that N_2 is involved in side-on bonding. The observed conversion of the species with absorptions at 1117.3 and 1103.3 cm^{-1} into cyclic [Gd(μ-N)$_2$Gd] (see below) suggests that the product is a structural isomer of cyclic [Gd(μ-N)$_2$Gd]. Accordingly, we assign the bands at 1117.3 and 1103.3 cm^{-1} to the N–N stretching mode of a side-on bonded [Gd_2N_2] complex (**1**) at different trapping sites.

To validate the experimental assignment and to investigate the formation mechanism of the complexes, we performed scalar-relativistic density functional theory (DFT) calculations on various possible structures of the intermediates, transition states, and products.[8] Calculations on the [Gd_2N_2] complex predict a rare structure with side-on and end-on coordination of the N_2 ligand (**1**; Figure 2), similar to some recently identified dinuclear transition-metal and lanthanide-metal carbonyl complexes.[9] The side-on and end-on bonded dinitrogen structural motif has been previously reported, most recently on dinuclear tantalum complexes.[10] The N–N stretching frequencies of these dinuclear complexes were determined to be around 1150 cm^{-1},[11] similar to that reported here. The [GdGdNN] and [Gd_2(μ-NN)] isomers with terminal and bridging N_2 ligands were also calculated, but they are 55.6 and 34.9 kcal mol^{-1} higher in energy than **1**. Complex **1** has a $^{15}A'$ ground state with a planar structure and a calculated N–N bond length of 1.293 Å, which is intermediate between those of azobenzene (PhN=NPh, 1.255 Å) and hydrazine (H_2N–NH_2, 1.460 Å).[1c] The frequency and IR absorption intensity of the N–N stretching mode of **1** are predicted to be 1211 cm^{-1} and 299.8 km mol^{-1} with the calculated $^{14}N/^{15}N$ frequency ratio in agreement with the observed value. Our assignment of **1** is further supported by calculations on other dinitrogen complexes of Gd_x ($x > 2$) clusters. The N–N stretching frequencies (with IR intensities in parenthesis) of [Gd_3N_2] and [Gd_4N_2] are predicted to be 977 cm^{-1} (41.5 km mol^{-1}) and 951 cm^{-1} (2.0 km mol^{-1}), respectively. These absorptions are too weak in intensity and too low in frequency to match the observed absorption, particularly when considering the matrix effects on frequency.

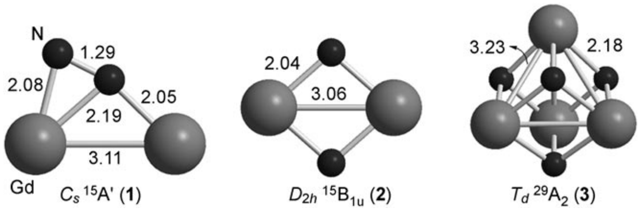

Figure 2. Optimized structures (bond lengths in Å) of **1**, **2**, and **3**.

The absorptions at 688.5 and 558.3 cm^{-1} correspond to the absorptions reported at 688.3 and 558.2 cm^{-1} that were previously assigned to the in-plane B_{2u} and B_{3u} stretching modes of cyclic [Gd(μ-N)$_2$Gd] (**2**).[7] The present experimental observations confirm the assignment. This molecule is predicted to have a $^{15}B_{1u}$ ground state with an $(f^7)(f^7)(b_{1u})^2(a_{1g})^2(b_{3u})^2(b_{3g})^2(b_{1g})^2(b_{2u})^2$ electron configuration, for which the b_{1u} and b_{3g} orbitals are δ- and π-bonding orbitals (Figure S3 in the Supporting Information) and the others are σ-bonding orbitals. The molecule can be viewed as having four Gd–N σ bonds and two delocalized three-center two-electron (3c–2e; d–p–d) π bonds, thus rendering partial double-bond character for each Gd–N bond. The N···N separation in the ground state is calculated to be 2.704 Å, thus indicating no direct bonding interaction between the two N atoms.

The absorptions at 590.1 and 494.4 cm^{-1} exhibit Gd–N stretching frequency ratios (Table 1). In the experiments with an equimolar mixture of $^{14}N_2$ and $^{15}N_2$, a triplet with approximately 5:2:5 relative intensities is clearly resolved, while a quintet with three weak intermediates is produced for the low-frequency mode in the experiments with a 1:2:1 mixture of $^{14}N_2/^{14}N^{15}N/^{15}N_2$ (Figure S2 of the Supporting Information). These spectral features indicate that the band at 494.4 cm^{-1} is due to a triply degenerate Gd–N stretching mode of a tetrahedral molecule with four equivalent N atoms, which arise from two equivalent N_2 molecules.[12] The absorptions at 590.1 and 494.4 cm^{-1} are produced only under $\lambda > 300$ nm irradiation at the expense of **2** and are therefore assigned to a cubic [Gd_4N_4] cluster (**3**), a dimer formed by fusing the π bonds of two cyclic [Gd(μ-N)$_2$Gd] complexes. Our calculations predict that [Gd_4N_4] has a $^{29}A_2$ ground state with T_d symmetry. The calculated frequencies, isotopic ratios (Table 1), and mixed isotopic splitting patterns strongly support the assignment.

The experimental and theoretical results clearly demonstrate that the Gd dimer reacts with dinitrogen in an argon matrix to form the unique side-on and end-on bonded complex **1**. This association reaction is predicted to be exothermic by 55 kcal mol^{-1} from the ground states of Gd_2 ($^{19}\Sigma_g^-$)[13] and N_2 ($^1\Sigma_g^+$). The unusually low N–N stretching frequency of **1** indicates that the simultaneously side-on and end-on coordination of N_2 to Gd_2 has drastically weakened the N–N bond, thus making it susceptible to dissociation. This situation is reminiscent of dissociative nitrogen adsorption with a similar coordination mode on an Fe(111) surface, whereby the side-on bound N_2 molecule is the immediate precursor to its dissociation on the Fe(111) surface and such adsorption is the rate-determining step in ammonia synthesis with Fe catalysts.[14]

Under near-infrared light irradiation, **1** rearranges to **2**. The absorptions of **2** also increase on annealing cycles, owing to the red irradiation from the IR spectrometer, which can induce isomerization. There is no bonding interaction between the two N atoms in **2**, that is, the robust N–N triple bond is completely cleaved. This N–N bond-dissociation reaction (**1**→**2**) is exothermic by 44 kcal mol^{-1}, and proceeds via a nonplanar bridge-bonded C_{2v} intermediate which lies 11 kcal mol^{-1} lower in energy than **1**. The reaction path is summarized in Figure 3. The bridge-bonded C_{2v} intermediate is not observed, presumably owing to the low barrier to the more stable cyclic $[\text{Gd}(\mu\text{-N})_2\text{Gd}]$ isomer. Although the formation of **1** from Gd_2 and N_2 is initially exothermic by 55 kcal mol^{-1}, which significantly surmounts the energy barrier for the N–N bond-breaking reaction, the $[\text{Gd}_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-N}_2)]$ complex can be stabilized since the matrix environment effectively removes its internal thermal energy.

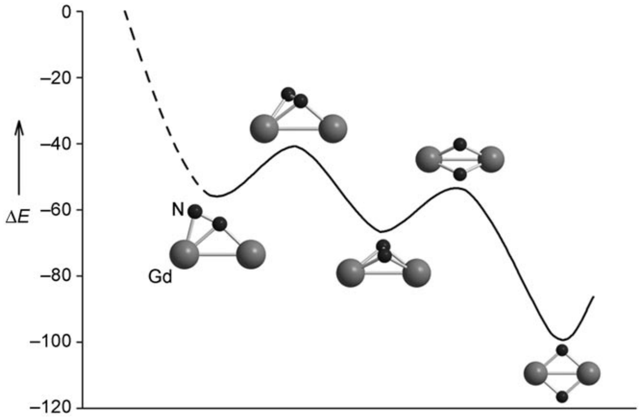

Figure 3. Reaction paths and structures of the transition states and products. The energies were calculated with the PW91 functional in kcal mol^{-1}. The dashed line indicates the computationally unexplored spin-crossing area.

The cyclic $[\text{Gd}(\mu\text{-N})_2\text{Gd}]$ molecule dimerizes to form the cubic $[\text{Gd}_4\text{N}_4]$ cluster under UV light irradiation. This dimerization reaction is predicted to be barrierless and exothermic by 168 kcal mol^{-1} in the gas phase. In a solid-argon matrix, however, energy is required to "liberate" the cyclic $[\text{Gd}(\mu\text{-N})_2\text{Gd}]$ molecules from the matrix to form the $[\text{Gd}_4\text{N}_4]$ oligomer. Because of the availability of lone pairs of electrons on the N atoms and empty d orbitals on Gd atoms, the cubic $[\text{Gd}_4\text{N}_4]$ cluster with tetrahedral symmetry is a perfect building block for $(\text{GdN})_x$ nanoparticles and for the bulk GdN crystal, which has a NaCl-type rocksalt structure[15] and has potential applications in magnetic semiconductors and spintronics materials.[16] The present investigation clearly demonstrates the dinitrogen activation processes from the initially formed dinitrogen complex **1** to the N–N bond-cleaved $[(\text{GdN})_2]$ ring **2** and to the $[(\text{GdN})_4]$ cage oligomer **3**, which are potential important intermediates for the formation and fabrication of nanoparticles and crystals of gadolinium nitrides.

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