

# Matrix Infrared Spectroscopic and Theoretical Studies on the Reactions of Late Lanthanoid Atoms with Nitrous Oxide in Excess Argon

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Reactions of laser-ablated late lanthanoid atoms (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) with N<sub>2</sub>O molecules in excess argon have been investigated using matrix-isolation infrared spectroscopy. Lanthanoid monoxide–dinitrogen complexes, OLn(N<sub>2</sub>) and OLnNN, are observed for Gd, Tb, Ho, and Er, and the OLnNN<sup>+</sup> cations are observed for Gd to Lu except for Yb. The new products are characterized on the basis of isotopic shifts, mixed isotopic splitting patterns, and CCl<sub>4</sub>-doping experiments. Density functional theory calculations have been performed on the new species, which support identification of the OLn(N<sub>2</sub>), OLnNN, and OLnNN<sup>+</sup> complexes from the matrix infrared spectra. Together with our earlier work involving early lanthanoid atoms, several trends are identified for the reactions of lanthanoid atoms with N<sub>2</sub>O molecules.

## Introduction

The chemistry of lanthanoid (Ln) atoms with small molecules (i.e., N<sub>2</sub>O, CO, N<sub>2</sub>, O<sub>2</sub>, NO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, etc.) has been the subject of considerable studies both in gas-phase and rare-gas matrixes as pointed out previously.<sup>1–9</sup> Taking the CO ligand as an example, matrix investigations have characterized several binary lanthanide metal carbonyls, Ln(CO)<sub>x</sub> (x = 1–6).<sup>3</sup> In particular, the lanthanide dimers react with CO to form a new series of the Ln<sub>2</sub>[η<sup>2</sup>(μ<sub>2</sub>-C, O)] complexes with asymmetrically bridging and side-on-bonded CO ligands, which exhibit unusually low C–O stretching frequencies and offer a structural configuration of the precursor to CO dissociation.<sup>3e–h</sup> The reactions of lanthanoid atoms with isoelectronic N<sub>2</sub> molecule produced a series of nitride and dinitrogen complexes, LnN, (LnN)<sub>2</sub>, Ln(N<sub>2</sub>), Ln(NN), and Ln(NN)<sub>2</sub>.<sup>4a</sup> Interestingly, the Gd<sub>2</sub> dimer reacts with N<sub>2</sub> in solid argon to form a homoleptic dinuclear dinitrogen complex [Gd<sub>2</sub>(μ-η<sup>2</sup>:η<sup>1</sup>-N<sub>2</sub>)] containing a drastically activated side-on and end-on bonded N<sub>2</sub> ligand.<sup>3</sup> This complex rearranges to a planar cyclic [Gd(μ-N)<sub>2</sub>Gd] isomer with a completely cleaved N–N bond and further dimerizes to form a unique cubic (Gd<sub>4</sub>N<sub>4</sub>) cluster.<sup>4b</sup>

Recent studies on the reactions of early lanthanoid atoms (La–Eu) with N<sub>2</sub>O in excess argon have identified a series of the metal monoxide–dinitrogen (OLn(N<sub>2</sub>)) and OLnNN<sup>+</sup> (Ln = La, Ce, Pr, Nd, and Sm) complexes.<sup>2b,c</sup> Here, we report a study of the reactions of late lanthanoid atoms (Gd–Lu) with N<sub>2</sub>O in excess argon. Infrared spectroscopy coupled with quantum chemical calculation provides evidence for the formation of the metal monoxide–dinitrogen complexes, OLn(N<sub>2</sub>) and OLnNN (Ln = Gd, Tb, Ho, and Er), and the OLnNN<sup>+</sup> (Ln = Gd–Lu except for Yb) cation complexes. The present results are compared with our previous study on the reactions of N<sub>2</sub>O with early lanthanoid atoms to explore the trends in the chemistry of lanthanoid atoms with N<sub>2</sub>O.

## Experimental and Theoretical Methods

Experiments for laser ablation and matrix-isolation infrared spectroscopy are similar to those previously reported.<sup>10</sup> In short,

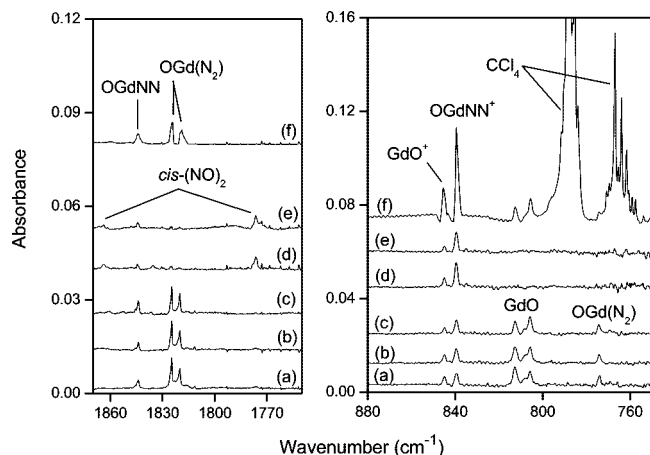
the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating late lanthanoid (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) (99.9%, Kojundo Chemical Laboratory Co.) targets. The laser-ablated lanthanoid atoms were codeposited with N<sub>2</sub>O in excess argon onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. Typically, 1–20 mJ/pulse laser power was used. N<sub>2</sub>O (99.5%, Taiyo Nippon Sanso Co.), <sup>15</sup>N<sub>2</sub>O (98%, Cambridge Isotopic Laboratories), and <sup>14</sup>N<sub>2</sub>O + <sup>15</sup>N<sub>2</sub>O mixtures were used in different experiments. In general, matrix samples were deposited for 30–60 min with a typical rate of 2–4 mmol per hour. After sample deposition, IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5 cm<sup>-1</sup> resolution using a liquid nitrogen cooled HgCdTe (MCT) detector for the spectral range of 5000–400 cm<sup>-1</sup>. Samples were annealed at different temperatures and subjected to broadband irradiation (λ > 250 nm) using a high-pressure mercury arc lamp (Ushio, 100 W).

Density functional theory (DFT) calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program.<sup>11</sup> All the present computations employed the BP86 density functional method.<sup>12</sup> The 6-311+G(d) basis set was used for the N and O atoms,<sup>13</sup> and the scalar-relativistic SDD pseudo-potential and basis set were used for the lanthanoid atoms.<sup>14</sup> Geometries were fully optimized and vibrational frequencies were calculated with analytical second derivatives. Earlier investigations have shown that such computational methods can provide reliable information for metal complexes, such as infrared frequencies, relative absorption intensities, and isotopic shifts.<sup>2,8</sup>

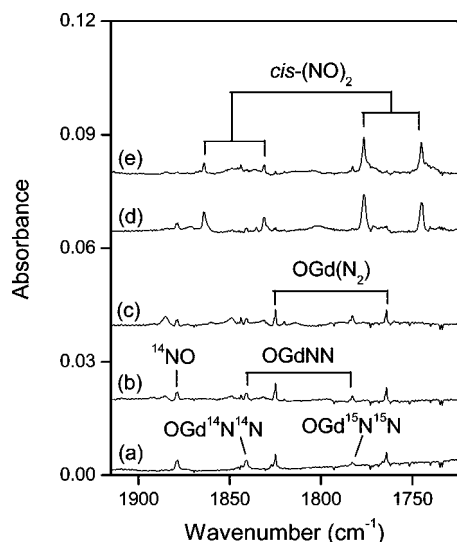
## Results and Discussion

Experiments have been done with different concentrations of N<sub>2</sub>O ranging from 0.02% to 2.0% in excess argon. Typical infrared spectra for the reactions of laser-ablated Gd atoms with N<sub>2</sub>O molecules in excess argon in the selected regions are illustrated in Figures 1 and 2. The spectra of the other lanthanoid atoms are shown as Supporting Information. The absorption bands in different isotopic experiments are listed in Table 1.

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**Figure 1.** Infrared spectra in the 1860–1770 and 880–760  $\text{cm}^{-1}$  regions from codeposition of laser-ablated Gd atoms with 0.4%  $\text{N}_2\text{O}$  in Ar at 4 K: (a) spectrum obtained from initial deposited sample for 1 h, (b) spectrum after annealing to 25 K, (c) spectrum after annealing to 30 K, (d) spectrum after 10 min of broadband irradiation, (e) spectrum after annealing to 35 K, and (f) spectrum obtained by depositing laser-ablated Gd atoms with 0.4%  $\text{N}_2\text{O}$  + 0.03%  $\text{CCl}_4$  in Ar at 4 K for 1 h and annealing to 30 K.



**Figure 2.** Infrared spectra in the 1900–1750  $\text{cm}^{-1}$  region from codeposition of laser-ablated Gd atoms with 0.2%  $^{14}\text{N}_2\text{O}$  + 0.2%  $^{15}\text{N}_2\text{O}$  in Ar at 4 K. For the meaning of a–e, see Figure 1

The stepwise annealing and irradiation behavior of the product absorptions is also shown in the figures and will be discussed below. Experiments have also been done with different concentrations of  $\text{CCl}_4$  serving as an electron scavenger.<sup>15</sup>

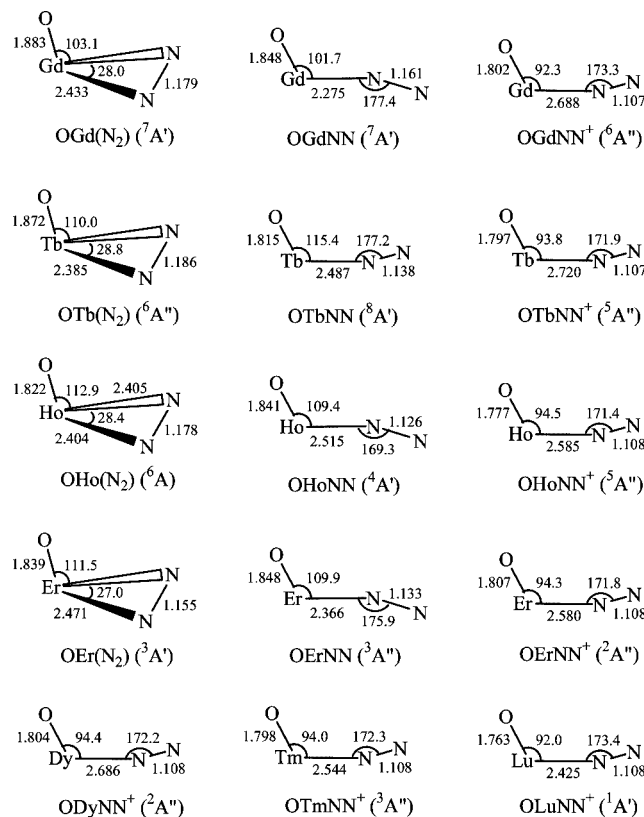
Quantum chemical calculations have been carried out for the possible isomers and electronic states of the species involved in the  $\text{Ln} + \text{N}_2\text{O}$  reactions. DFT calculations show that the optimized structures of the isomers for Gd to Lu are similar to those for Sc, Y, and La.<sup>2</sup> Herein, only the calculated results of the observed products are presented for discussion. Figure 3 shows the optimized structures of the products. The comparison of the observed and calculated IR frequencies and isotopic frequency ratios for the N–O and Ln–O stretching modes of the products are summarized in Table 2. The ground electronic states, point groups, vibrational frequencies, and intensities of the products are listed in Table 3. The comparison of the Ln–O stretching frequencies for the  $\text{LnO}$ ,  $\text{OLn}(\text{N}_2)$ ,  $\text{LnO}^+$ , and  $\text{OLnNN}^+$  complexes is given in Table 4. Natural electron

**TABLE 1: IR Absorptions (in  $\text{cm}^{-1}$ ) Observed from Codeposition of Laser-Ablated Late Lanthanoid Atoms (Gd–Lu) with  $\text{N}_2\text{O}$  in Excess Argon at 4 K**

$^{14}\text{N}_2\text{O}$	$^{15}\text{N}_2\text{O}$	$^{14}\text{N}_2\text{O} + ^{15}\text{N}_2\text{O}$	$^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$	assignment
1843.9	1782.7	1843.9, 1782.7	1.0343	OGdNN
1824.8	1764.0	1824.8, 1764.0	1.0345	OGd( $\text{N}_2$ )
839.5	839.5		1.0000	OGdNN <sup>+</sup>
774.4	774.4		1.0000	OGd( $\text{N}_2$ )
1838.8	1777.9	1838.8, 1777.9	1.0343	OTbNN
1818.7	1758.2	1818.7, 1758.2	1.0344	OTb( $\text{N}_2$ )
851.2	851.2		1.0000	OTbNN <sup>+</sup>
786.6	786.6		1.0000	OTb( $\text{N}_2$ )
855.9	855.9		1.0000	ODyNN <sup>+</sup>
1844.9	1783.5	1844.9, 1783.5	1.0344	OHoNN
1816.8	1756.3	1816.8, 1756.3	1.0344	OHo( $\text{N}_2$ )
855.1	855.1		1.0000	OHoNN <sup>+</sup>
790.6	790.6		1.0000	OHo( $\text{N}_2$ )
1849.2	1787.7	1849.2, 1787.7	1.0344	OErNN
1810.9	1750.6	1810.9, 1750.6	1.0344	OEr( $\text{N}_2$ )
855.8	855.8		1.0000	OErNN <sup>+</sup>
800.2	800.2		1.0000	OEr( $\text{N}_2$ )
859.0	859.0		1.0000	OTmNN <sup>+</sup>
862.1	862.1		1.0000	OLuNN <sup>+</sup>

configurations of lanthanoid atoms in the  $\text{OLn}(\text{N}_2)$  complexes are reported in Table 5.

**A.  $\text{OLn}(\text{N}_2)$  and  $\text{OLnNN}$  ( $\text{Ln} = \text{Gd, Tb, Ho, Er}$ ).** In the reaction of Gd atoms with  $\text{N}_2\text{O}$  in the argon matrix, two absorptions at 1824.8 and 774.4  $\text{cm}^{-1}$  appear together during sample deposition, change little after sample annealing, but decrease visibly upon broadband irradiation, and do not recover after further annealing to 35 K (Table 1 and Figure 1). The upper band at 1824.8  $\text{cm}^{-1}$  shifts to 1764.0  $\text{cm}^{-1}$  with  $^{15}\text{N}_2\text{O}$ , exhibiting an isotopic frequency ratio ( $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$ , 1.0345) characteristic of a N–N stretching vibration. The mixed  $^{14}\text{N}_2\text{O}$



**Figure 3.** Optimized structures (bond lengths in angstroms, bond angles in degrees) of the products.

**TABLE 2: Comparison of Observed and Calculated IR Frequencies (in  $\text{cm}^{-1}$ ) and Isotopic Frequency Ratios for the Products**

species	vibrational mode	observed		calculated	
		freq	$^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$	freq	$^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$
OGd(N <sub>2</sub> )	$\nu_{\text{N-N}}$	1824.8	1.0345	1837.5	1.0350
	$\nu_{\text{Gd-O}}$	774.4	1.0000	700.9	1.0000
OGdNN	$\nu_{\text{N-N}}$	1843.9	1.0343	1892.2	1.0350
OTb(N <sub>2</sub> )	$\nu_{\text{N-N}}$	1818.7	1.0344	1767.0	1.0350
	$\nu_{\text{Tb-O}}$	786.6	1.0000	639.5	1.0000
OTbNN	$\nu_{\text{N-N}}$	1838.8	1.0343	2051.2	1.0350
OHo(N <sub>2</sub> )	$\nu_{\text{N-N}}$	1816.8	1.0344	1841.5	1.0350
	$\nu_{\text{Ho-O}}$	790.6	1.0000	752.5	1.0000
OHoNN	$\nu_{\text{N-N}}$	1844.9	1.0344	2086.9	1.0350
OEr(N <sub>2</sub> )	$\nu_{\text{N-N}}$	1810.9	1.0344	1955.5	1.0350
	$\nu_{\text{Er-O}}$	800.2	1.0000	764.1	1.0000
OErNN	$\nu_{\text{N-N}}$	1849.2	1.0344	1908.0	1.0350
OGdNN <sup>+</sup>	$\nu_{\text{Gd-O}}$	839.5	1.0000	716.8	1.0000
OTbNN <sup>+</sup>	$\nu_{\text{Tb-O}}$	851.2	1.0000	728.7	1.0000
ODyNN <sup>+</sup>	$\nu_{\text{Dy-O}}$	855.9	1.0000	684.8	1.0000
OHoNN <sup>+</sup>	$\nu_{\text{Ho-O}}$	855.1	1.0000	818.2	1.0000
OErNN <sup>+</sup>	$\nu_{\text{Er-O}}$	855.8	1.0000	709.2	1.0000
OTmNN <sup>+</sup>	$\nu_{\text{Tm-O}}$	859.0	1.0000	730.1	1.0000
OLuNN <sup>+</sup>	$\nu_{\text{Lu-O}}$	862.1	1.0000	877.3	1.0000

+  $^{15}\text{N}_2\text{O}$  isotopic spectra (Figure 2) only provide the sum of pure isotopic bands, which indicates only one  $\text{N}_2$  unit is involved in the complex.<sup>16</sup> The  $774.4\text{ cm}^{-1}$  band, which is in the spectral range expected for the terminal Gd–O stretching mode,<sup>5b</sup> shows no nitrogen isotopic shift. The present spectra also show that the behavior with annealing and irradiation of another band at  $1843.9\text{ cm}^{-1}$  is similar to that of the absorption at  $1824.8\text{ cm}^{-1}$  (Figure 1). Furthermore, doping with  $\text{CCl}_4$  has no effect on these bands (Figure 1, trace f), suggesting that these products are neutral.<sup>15</sup>

BP86 calculations indicate that the OGd(N<sub>2</sub>) complex is the most stable isomer, followed by the OGdNN complex, which lies only 1.66 kcal/mol above OGd(N<sub>2</sub>) (Figure 3). The N–N stretching vibrational frequencies in the OGd(N<sub>2</sub>) and OGdNN complexes are calculated to be  $1837.5$  and  $1892.2\text{ cm}^{-1}$  (Table 3), respectively. The features of the IR spectra in the present matrix experiments are reminiscent of those of the side-bonded structure of OSc(N<sub>2</sub>) and end-on-bonded structure of OScNN, in which the corresponding N–N stretching vibrational frequencies appear at  $1817.2$  and  $1849.2\text{ cm}^{-1}$  in excess argon,<sup>2a</sup> respectively. Accordingly, the  $1824.8$  and  $774.4\text{ cm}^{-1}$  bands are assigned to the N–N and Gd–O stretching vibrations of the neutral OGd(N<sub>2</sub>) complex and the  $1843.9\text{ cm}^{-1}$  band to the corresponding vibration of the neutral OGdNN complex on the basis of the results of the isotopic substitution, the  $\text{N}_2\text{O}$  concentration change,  $\text{CCl}_4$ -doping experiments, and the comparison with theoretical predictions. The Gd–O stretching vibration of the neutral OGdNN complex is absent from the present experiment.

The Gd–O stretching vibration in OGd(N<sub>2</sub>) is predicted to be  $700.9\text{ cm}^{-1}$  (Table 3), which is  $73.5\text{ cm}^{-1}$  below the experimental value of  $774.4\text{ cm}^{-1}$ . Such large deviation for the Gd–O stretching vibrational frequency may be due to the inefficiency of the XC functional and/or the basis sets used here, posing a formidable theoretical challenge due to the large numbers of *f*-electrons and strong relativistic effects.<sup>17–20</sup> The intensity of the Gd–O stretching vibration in OGdNN is predicted to be about 1/3 that of the N–N stretching vibration, which is consistent with the absence of the Gd–O stretching vibration of the neutral OGdNN complex from the present experiment. As listed in Table 2, the calculated  $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$

isotopic frequency ratios for the N–N and Gd–O stretching vibrations are also in accord with the experimental values. These agreements between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts confirm the identifications of the OGd(N<sub>2</sub>) and OGdNN complexes from the matrix IR spectra.

In the reactions of  $\text{N}_2\text{O}$  with the other late lanthanoid atoms, the absorptions of the analogous OLn(N<sub>2</sub>) and OLnNN complexes have been observed for Tb, Ho, and Er (Table 1 and Figures S1–S9 in the Supporting Information) but not for Dy, Tm, Yb, and Lu. The N–N and Ln–O stretching vibrations of OLn(N<sub>2</sub>) appear at  $1818.7$  and  $786.6\text{ cm}^{-1}$  for Tb,  $1816.8$  and  $790.6\text{ cm}^{-1}$  for Ho, and  $1810.9$  and  $800.2\text{ cm}^{-1}$  for Er, respectively. The N–N stretching vibrations of OLnNN appear at  $1838.8\text{ cm}^{-1}$  for Tb,  $1844.9\text{ cm}^{-1}$  for Ho, and  $1849.2\text{ cm}^{-1}$  for Er, respectively. DFT calculations predict that the OLn(N<sub>2</sub>) (Ln = Tb, Ho, and Er) complexes have  $^6A''$ ,  $^6A$ , and  $^3A'$  ground states and the OLnNN (Ln = Tb, Ho, and Er) complexes have  $^8A'$ ,  $^4A'$ , and  $^3A''$  ground states (Figure 3), respectively. The calculated N–N and Ln–O stretching frequencies are consistent with the observed values (Tables 2 and 3). Furthermore, overall agreements between the experimental and calculated  $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$  isotopic frequency ratios have also been obtained for the N–N and Ln–O stretching frequencies of the OLn(N<sub>2</sub>) and OLnNN complexes (Table 2).

**B. OLnNN<sup>+</sup> (Ln = Gd, Tb, Dy, Ho, Er, Tm, Lu).** Taking the Gd +  $\text{N}_2\text{O}$  reaction as an example, the absorption at  $839.5\text{ cm}^{-1}$  appears during sample deposition, changes little after annealing, and increases markedly upon broadband irradiation at the expense of the neutral OGd(N<sub>2</sub>) and OGdNN complexes (Table 1 and Figure 1), indicating that this new species also has the GdN<sub>2</sub>O stoichiometry. The band at  $839.5\text{ cm}^{-1}$ , which is in the spectral range expected for the terminal Gd–O stretching mode,<sup>5b</sup> shows no nitrogen isotopic shift. Doping with  $\text{CCl}_4$  sharply increases this band (Figure 1, trace f), suggesting that the product is cationic.<sup>15</sup> Although the  $839.5\text{ cm}^{-1}$  band is only  $5.3\text{ cm}^{-1}$  red-shifted from the Gd–O stretching vibration of the GdO<sup>+</sup> cation ( $844.8\text{ cm}^{-1}$ ),<sup>5b</sup> the behavior of sample annealing and irradiation for the  $839.5\text{ cm}^{-1}$  band is different from that for the  $844.8\text{ cm}^{-1}$  band of the GdO<sup>+</sup> cation (Figure 1). By analogy with the OMNN<sup>+</sup> (M = Sc, Y, La, Ce, Pr, Nd, and Sm) spectra,<sup>2</sup> the  $839.5\text{ cm}^{-1}$  band is assigned to the Gd–O stretching mode of the OGdNN<sup>+</sup> cation.

The OGdNN<sup>+</sup> complex is predicted to have a  $^6A''$  ground-state with *C*<sub>v</sub> symmetry (Table 3 and Figure 3). The calculated Gd–O stretching mode is  $716.8\text{ cm}^{-1}$  (Table 2). The N–N stretching vibration is predicted to be  $2344.7\text{ cm}^{-1}$  (Table 3). With its small intensity (19 km/mol), it is not likely to be observed, which is consistent with the absence from the present experiments.

In the reactions of  $\text{N}_2\text{O}$  with the other late lanthanoid atoms, the absorptions of the analogous OLnNN<sup>+</sup> (Ln = Tb, Dy, Ho, Er, Tm, and Lu) complexes have been observed in the region of  $900$ – $800\text{ cm}^{-1}$  (Tb,  $851.2$ ; Dy,  $855.9$ ; Ho,  $855.1$ ; Er,  $855.8$ ; Tm,  $859.0$ ; Yb,  $840.1$ ; Lu,  $862.1\text{ cm}^{-1}$ ) (Table 1 and Figures S1–S9 in the Supporting Information) but not for Yb.

BP86 calculations predict the OLnNN<sup>+</sup> (Ln = Tb, Dy, Ho, Er, Tm, and Lu) complexes to have  $^5A''$ ,  $^4A'$ ,  $^5A''$ ,  $^2A''$ ,  $^3A''$ , and  $^1A'$  ground states with *C*<sub>v</sub> symmetry (Figure 3), respectively. Overall agreements between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts have been obtained for the Ln–O stretching vibrations (Tables 2 and 3), respectively. It is noted that the Ln–O and N–N distances in the OLnNN<sup>+</sup> (Ln = Gd, Tb, Ho,

**TABLE 3: Ground Electronic States, Point Groups, Vibrational Frequencies (in  $\text{cm}^{-1}$ ) and Intensities (km/mol) of the Products**

species	elec state	point group	frequency (intensity, mode)
OGd(N <sub>2</sub> )	<sup>7</sup> A'	C <sub>s</sub>	1837.5 (143, A'), 700.9 (125, A'), 305.4 (26, A'), 295.4 (12, A''), 158.4 (1, A''), 116.3 (10, A')
OGdNN	<sup>7</sup> A'	C <sub>s</sub>	1892.2 (378, A'), 677.2 (108, A'), 316.0 (14, A'), 229.2 (1, A'), 221.4 (27, A''), 94.2 (12, A')
OTb(N <sub>2</sub> )	<sup>6</sup> A''	C <sub>i</sub>	1767.0 (307, A'), 639.5 (71, A'), 294.5 (15, A''), 280.4 (4, A'), 161.4 (2, A''), 130.9 (16, A')
OTbNN	<sup>8</sup> A'	C <sub>s</sub>	2051.2 (672, A'), 784.3 (306, A'), 188.7 (1, A'), 156.2 (1, A'), 91.1 (3, A''), 68.1 (22, A')
OHo(N <sub>2</sub> )	<sup>6</sup> A	C <sub>i</sub>	1841.5 (205, A), 752.5 (153, A), 317.4 (22, A), 313.2 (20, A), 149.0 (16, A), 140.5 (7, A)
OHoNN	<sup>4</sup> A'	C <sub>s</sub>	2086.9 (2173, A'), 736.8 (247, A'), 198.7 (10, A'), 156.0 (6, A'), 110.8 (3, A''), 99.8 (45, A')
OEr(N <sub>2</sub> )	<sup>3</sup> A'	C <sub>s</sub>	1955.5 (416, A'), 764.1 (281, A'), 281.8 (3, A''), 248.9 (2, A'), 175.2 (0.3, A''), 133.6 (23, A')
OErNN	<sup>3</sup> A''	C <sub>s</sub>	1908.3 (7186, A'), 734.3 (197, A'), 222.8 (25, A'), 201.3 (78, A'), 139.5 (2, A''), 76.8 (7, A')
OGdNN <sup>+</sup>	<sup>6</sup> A''	C <sub>s</sub>	2344.7 (19, A'), 716.8 (64, A'), 189.2 (3, A'), 155.5 (1, A''), 151.8 (11, A'), 90.4 (12, A')
OTbNN <sup>+</sup>	<sup>5</sup> A''	C <sub>s</sub>	2345.8 (19, A'), 762.7 (65, A'), 181.6 (4, A'), 147.5 (16, A'), 139.4 (1, A''), 108.0 (8, A')
ODyNN <sup>+</sup>	<sup>4</sup> A'	C <sub>s</sub>	2342.6 (13, A'), 684.8 (46, A'), 193.1 (3, A'), 166.9 (1, A''), 151.3 (15, A'), 116.1 (6, A')
OHoNN <sup>+</sup>	<sup>5</sup> A''	C <sub>s</sub>	2341.2 (10, A'), 818.2 (100, A'), 211.0 (11, A'), 185.9 (12, A'), 171.9 (2, A''), 140.0 (7, A')
OErNN <sup>+</sup>	<sup>2</sup> A''	C <sub>s</sub>	2338.7 (7, A'), 709.2 (64, A'), 233.6 (11, A'), 190.4 (3, A'), 165.0 (2, A''), 160.0 (0.2, A')
OTmNN <sup>+</sup>	<sup>3</sup> A''	C <sub>s</sub>	2337.7 (7, A'), 730.1 (65, A'), 213.4 (3, A'), 176.5 (5, A'), 163.3 (2, A''), 79.4 (24, A')
OLuNN <sup>+</sup>	<sup>1</sup> A'	C <sub>s</sub>	2331.5 (5, A'), 877.3 (78, A'), 243.9 (7, A'), 206.7 (3, A'), 181.9 (1, A'), 91.6 (28, A')

**TABLE 4: Comparison of the Ln–O Stretching Frequencies (in  $\text{cm}^{-1}$ ) for the LnO, OLn(N<sub>2</sub>), LnO<sup>+</sup>, and OLnNN<sup>+</sup> Complexes**

Ln	LnO	ref	OLn(N <sub>2</sub> )	ref	LnO <sup>+</sup>	ref	OLnNN <sup>+</sup>	ref
La	796.7	5a	759.4	2b	838.2	5a	832.8	2b
Ce	808.3	5b	768.0	2c	849.4	5b	844.4	2c
Pr	816.9	5b	772.6	2c	857.4	5b	848.2	2c
Nd	825.1	5b	771.6	2c	878.4	5b	844.3	2c
Sm	807.4	5b	760.8	2c	840.0	5b	835.3	2c
Eu	667.8	5b			756.9	5b		
Gd	812.7	5b	774.4	this work	844.8	5b	839.5	this work
Tb	823.9	5c	786.6	this work	856.5	5c	851.2	this work
Dy	839.0	5c			888.6	5c	855.9	this work
Ho	838.1	5c	790.6	this work	887.9	5c	855.1	this work
Er	828.5	5c	800.2	this work	861.8	5c	855.8	this work
Tm	832.0	5c			864.2	5c	859.0	this work
Yb	660.0	5c			788.7	5c		
Lu	829.3	5c			864.9	5c	862.1	this work

**TABLE 5: Natural Electron Configurations of Lanthanoid Atoms in the OLn(N<sub>2</sub>) Complexes**

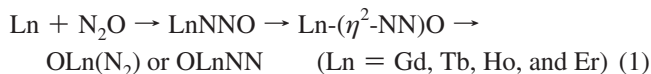
atom	natural electron configuration
La	[core] 6s(0.05) 4f(0.23) 5d(0.73) 6p(0.05) 5f(0.01) 6d(0.01)
Ce	[core] 6s(0.05) 4f(1.31) 5d(0.71) 6p(0.04) 5f(0.01) 6d(0.01)
Pr	[core] 6s(0.06) 4f(2.54) 5d(0.57) 6p(0.04) 5f(0.01)
Nd	[core] 6s(0.05) 4f(3.53) 5d(0.61) 6p(0.05)
Sm	[core] 6s(0.04) 4f(5.71) 5d(0.53) 6p(0.05)
Eu <sup>a</sup>	[core] 6s(0.05) 4f(6.79) 5d(0.48) 6p(0.06)
Gd	[core] 6s(0.47) 4f(7.07) 5d(0.54) 6p(0.03) 7s(0.03) 5f(0.01) 6d(0.01)
Tb	[core] 6s(0.70) 4f(7.91) 5d(0.48) 6p(0.02) 7s(0.02) 5f(0.01) 6d(0.01)
Dy <sup>a</sup>	[core] 6s(0.96) 4f(8.84) 5d(0.55) 6p(0.04) 7s(0.02) 5f(0.01)
Ho	[core] 6s(0.06) 4f(10.29) 5d(0.64) 6p(0.04) 5f(0.01)
Er	[core] 6s(0.06) 4f(11.51) 5d(0.52) 6p(0.05) 5f(0.01)
Tm <sup>a</sup>	[core] 6s(0.07) 4f(12.64) 5d(0.47) 6p(0.05)
Yb <sup>a</sup>	[core] 6s(0.07) 4f(13.51) 5d(0.40) 6p(0.03)
Lu <sup>a</sup>	[core] 6s(0.13) 5d(1.18) 6p(0.04) 5f(0.01) 6d(0.01)

<sup>a</sup>These OLn(N<sub>2</sub>) complexes are absent from the present matrix experiments.

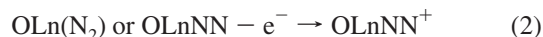
and Er) complexes are slightly shorter than those in the OLn(N<sub>2</sub>) and OLnNN complexes, whereas the Ln–N distances in the OLnNN<sup>+</sup> complexes are longer than those in the OLn(N<sub>2</sub>) and OLnNN complexes (Figure 3).

**C. Reaction Mechanism and Periodic Trend.** On the basis of the behavior of sample annealing and irradiation, together with the observed species and calculated stable isomers, a plausible reaction mechanism can be proposed as follows. Under the present experimental conditions, the OLn(N<sub>2</sub>) and OLnNN (Ln = Gd, Tb, Ho, and Er) complexes are the primary products during sample deposition (Figure 1 and Figures S1, S4, S6 in the Supporting Information), suggesting that the spontaneous insertion of laser-ablated Gd, Tb, Ho, and Er atoms into N<sub>2</sub>O

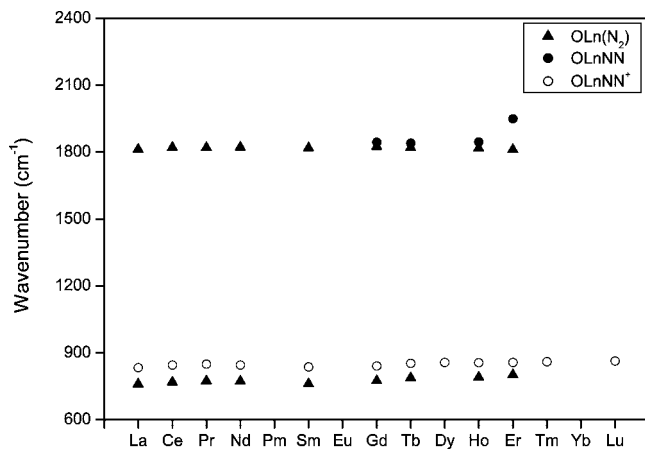
to form the OLn(N<sub>2</sub>) or OLnNN complexes is the dominant process (reaction 1). Recent studies on the Y and La systems indicated that the reactions start by binding the outer nitrogen atom of N<sub>2</sub>O with the metal atom to form a planar intermediate MNNO (M = Y and La) and then rearrange to form a side-bonded intermediate M-( $\eta^2$ -NN)O and the oxygen atom can further be transferred to form OM(N<sub>2</sub>).<sup>2b</sup> Similar isomerizations from LnNNO to OLn(N<sub>2</sub>) via Ln-( $\eta^2$ -NN)O for the Gd, Tb, Ho, and Er reactions have also been obtained and the details could be referred to the Y and La systems.<sup>2b</sup>



Recent investigations have shown that laser ablation of metal targets produces not only neutral metal atoms but also metal cations and electrons. Ionic metal complexes can also be formed in the reactions with small molecules.<sup>15</sup> In the present experiments, the OLnNN<sup>+</sup> (Ln = Gd, Tb, Ho, and Er) cation complexes appear during sample deposition and increase markedly upon broadband irradiation at the expense of the neutral OLn(N<sub>2</sub>) and OLnNN complexes (Figure 1 and Figures S1, S4, and S6 in the Supporting Information), suggesting that the OLnNN<sup>+</sup> cations may be generated by photoionization of the neutral OLnNN and OLn(N<sub>2</sub>) complexes via radiation in the ablation plume and/or broadband irradiation (reaction 2). It is noted that the OLnNN<sup>+</sup> (Ln = Dy, Tm, Yb, and Lu) cations are observed, whereas the corresponding neutral OLn(N<sub>2</sub>) and OLnNN complexes are absent (Figures S3, S8, and S9 in the Supporting Information). Moreover, the LnO<sup>+</sup> cations appear in the experiments.<sup>5</sup> Therefore, the reaction of the LnO<sup>+</sup> cations with N<sub>2</sub> may be responsible for the formation of the OLnNN<sup>+</sup> cations (reaction 3).



Together with our earlier work involving early lanthanoid atoms (La–Eu),<sup>2</sup> the neutral OLn(N<sub>2</sub>) complexes are observed for La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, and Er, and the neutral OLnNN complexes for Gd, Tb, Ho, and Er in the matrix experiments. The reactions of N<sub>2</sub>O with all of the lanthanoid atoms (except for radioactive Pm and for Eu and Yb) produce



**Figure 4.** Plot of the experimental N–N (upper dots) and Ln–O (lower dots) stretching frequencies (cm<sup>-1</sup>) in the OLn(N<sub>2</sub>), OLnNN, and OLnNN<sup>+</sup> complexes (Ln = lanthanoid atoms).

the OLnNN<sup>+</sup> cation complexes. However, no new product is observed in the reactions of N<sub>2</sub>O with Eu and Yb, which may be due to the stable electron configurations of Eu (4f<sup>7</sup>6s<sup>2</sup>) and Yb (4f<sup>14</sup>6s<sup>2</sup>) atoms. As illustrated in Figure 4, the N–N and Ln–O stretching frequencies of the neutral OLn(N<sub>2</sub>) complexes show small changes along the series. This trend holds true for the Ln–O stretching frequencies of the OLnNN<sup>+</sup> cation complexes.<sup>2</sup> Recent matrix investigations on the reactions of lanthanoid atoms with CO<sub>2</sub> molecules reveal that the early lanthanoid (La–Sm) oxocarbonyl complexes adopt the trans configurations, the europium and ytterbium ones adopt side-on-bonded modes (Eu-(η<sup>2</sup>-OC)O and Yb-(η<sup>2</sup>-OC)O), and the late lanthanoid (Gd–Lu) ones adopt the cis configurations, exhibiting intriguing structural and bonding trends in the interaction of lanthanoid atoms with CO<sub>2</sub>.<sup>9</sup> In contrast, the geometrical structures for the OLn(N<sub>2</sub>) and OLnNN<sup>+</sup> complexes are very similar. Unlike CO<sub>2</sub>, there is no such lanthanoid-ligand trend in the interaction of lanthanoid atoms with N<sub>2</sub>O. The present study on the reactions of lanthanoid atoms with N<sub>2</sub>O exhibits the difference in chemistry between the semifilled-f-orbital Eu/full-filled-f-orbital Yb and the other lanthanoid elements.

It is noted that the neutral LnO molecules are the major products in the reactions of N<sub>2</sub>O with lanthanoid atoms in the gas phase.<sup>1</sup> However, it has been found from the matrix experiments (in the condensed phase) that the yields of the OLn(N<sub>2</sub>) molecules are larger than those of the neutral LnO molecules. This suggests the reactivity of gas-phase lanthanoids toward N<sub>2</sub>O is quite different from that of condensed phase lanthanoids. It can be found from Table 4 that the Ln–O stretching frequencies of OLn(N<sub>2</sub>) are ca. 40 cm<sup>-1</sup> red-shift from those of LnO and the Ln–O stretching frequencies of OLnNN<sup>+</sup> are ca. 5 cm<sup>-1</sup> red-shift from those of LnO<sup>+</sup>. This suggests that the interaction between LnO and NN in OLn(N<sub>2</sub>) is stronger than that in OLnNN<sup>+</sup>, which is consistent with the calculated intensities of these stretching vibrations (Table 3).

As listed in Table 5, there are some electrons in the 5d and 6p orbitals of Ln atoms in the OLn(N<sub>2</sub>) complexes, which are similar to the lanthanoid oxocarbonyl complexes. This implies that the formation of OLn(N<sub>2</sub>) involves the promotion of 6s and 4f electrons into the metal valence shell. The NBO analyses further reveal that the OLn(N<sub>2</sub>) complexes have significant bonding interactions between the 2p orbitals of O and N atoms and the 5d orbitals of Ln atoms. The OEu(N<sub>2</sub>), ODy(N<sub>2</sub>), OYb(N<sub>2</sub>), and OLu(N<sub>2</sub>) complexes are absent from the present

experimental conditions and hopefully observed in the future experiments with the development of experimental technique.

## Conclusions

Reactions of late lanthanoid (Gd–Lu) atoms with N<sub>2</sub>O molecules in excess argon have been investigated using matrix-isolation infrared spectroscopy. The OLn(N<sub>2</sub>), OLnNN (Ln = Gd, Tb, Ho, and Er), and OLnNN<sup>+</sup> (Ln = Gd, Tb, Dy, Ho, Er, Tm, and Lu) complexes have been observed and characterized in an argon matrix on the basis of the isotopic substitution, the N<sub>2</sub>O concentration change, and CCl<sub>4</sub>-doping experiments, whereas no such species is apparent with Yb. Density functional theory calculations have been performed on the products. The agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts supports identification of these new species from the matrix infrared spectra. Together with our earlier work involving early lanthanoid atoms (La–Eu), it has been found that the N–N and Ln–O stretching frequencies of the neutral OLn(N<sub>2</sub>) complexes show small changes along the lanthanoid series. This trend holds true for the Ln–O stretching frequencies of the OLnNN<sup>+</sup> cation complexes. The present study exhibits the difference in chemistry between the semifilled-f-orbital Eu/full-filled-f-orbital Yb and the other lanthanoid elements.

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**Supporting Information Available:** The infrared spectra of the Tb, Dy, Ho, Er, Tm, Yb, and Lu reactions. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Campbell, M. L. *J. Chem. Phys.* **1999**, *111*, 562 (Ln + N<sub>2</sub>O, in the gas phase).
- (2) (a) Zhou, M. F.; Wang, G. J.; Zhao, Y. Y.; Chen, M. H.; Ding, C. *F. J. Phys. Chem. A* **2005**, *109*, 5079 (Sc + N<sub>2</sub>O, in matrix). (b) Jiang, L.; Xu, Q. *J. Phys. Chem. A* **2008**, *112*, 6289 (Y, La + N<sub>2</sub>O, in matrix). (c) Jiang, L.; Xu, Q. *J. Phys. Chem. A* **2008**, *112*, 8690 (Ce, Pr, Nd, Sm, Eu + N<sub>2</sub>O, in matrix).
- (3) (a) Slater, J. L.; Sheline, R. K.; Lin, K. C.; Weltner, W., Jr. *J. Chem. Phys.* **1971**, *55*, 5129. (b) Slater, J. L.; DeVore, T. C.; Calder, V. *Inorg. Chem.* **1973**, *12*, 1918. (c) Slater, J. L.; DeVore, T. C.; Calder, V. *Inorg. Chem.* **1974**, *13*, 1808. (d) Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed.* **1975**, *14*, 309. (e) Xu, Q.; Jiang, L.; Zou, R. Q. *Chem. Eur. J.* **2006**, *12*, 3226. (f) Zhou, M. F.; Jin, X.; Li, J. *J. Phys. Chem. A* **2006**, *110*, 10206. (g) Jin, X.; Jiang, L.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2006**, *110*, 12585. (h) Jiang, L.; Jin, X.; Zhou, M. F.; Xu, Q. *J. Phys. Chem. A* **2008**, *112*, 3627 (Ln + CO, in matrix).
- (4) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1998**, *102*, 10238. (a) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 1311 (Ln + N<sub>2</sub>, in matrix). (b) Zhou, M. F.; Jin, X.; Gong, Y.; Li, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2911 (Gd + N<sub>2</sub>, in matrix).
- (5) (a) Andrews, L.; Zhou, M. F.; Chertihin, G. V.; Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **1999**, *103*, 6525 (Y, La + O<sub>2</sub>, in matrix). (b) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 3171 (Ce, Pr, Nd, Sm, Eu, Gd + O<sub>2</sub>, in matrix). (c) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 6972 (Tb, Dy, Ho, Er, Tm, Yb, Lu + O<sub>2</sub>, in matrix).
- (6) Willson, S. P.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **2000**, *104*, 3446 (Ln + NO, in matrix).
- (7) Willson, S. P.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1640 (Ln + H<sub>2</sub>, in matrix).
- (8) (a) Xu, J.; Zhou, M. F. *J. Phys. Chem. A* **2006**, *110*, 10575. (b) Xu, J.; Jin, X.; Zhou, M. F. *J. Phys. Chem. A* **2007**, *111*, 7105 (Ln + H<sub>2</sub>O, in matrix).

- (9) Jiang, L.; Zhang, X. B.; Han, S.; Xu, Q. *Inorg. Chem.* **2008**, *47*, 4826 (Ln + CO<sub>2</sub>, in matrix).
- (10) (a) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697. (b) Zhou, M. F.; Tsumori, N.; Andrews, L.; Xu, Q. *J. Phys. Chem. A* **2003**, *107*, 2458. (c) Jiang, L.; Xu, Q. *J. Chem. Phys.* **2005**, *122*, 034505. (d) Jiang, L.; Teng, Y. L.; Xu, Q. *J. Phys. Chem. A* **2006**, *110*, 7092.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc., Pittsburgh, PA, 2003.
- (12) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (13) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- (14) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
- (15) Zhou, M. F.; Andrews, L.; Bauschlicher, C. W., Jr. *Chem. Rev.* **2001**, *101*, 1931, and references therein.
- (16) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2496.
- (17) See, for example, Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719. Seth, M.; Dolg, M.; Fulde, P.; Schwerdtfeger, P. *J. Am. Chem. Soc.* **1995**, *117*, 6597. Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1997**, *119*, 9021.
- (18) Adamo, C.; Maldivi, P. *J. Phys. Chem. A* **1998**, *102*, 6812. Dolg, M.; Liu, W.; Kalvoda, S. *Int. J. Quantum Chem.* **2000**, *76*, 359. Maron, L.; Eisenstein, O. *J. Phys. Chem. A* **2000**, *104*, 7140.
- (19) Gibson, J. K. *J. Phys. Chem. A* **2003**, *107*, 7891.
- (20) de Almeida, K. J.; Cesar, A. *Organometallics* **2006**, *25*, 3407.

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