

Observation of Dinitrogen Adsorption by Rhodium Oxide Clusters

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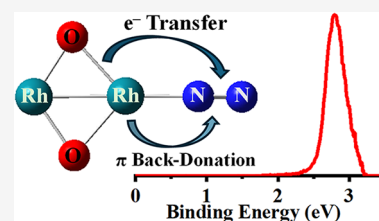


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ABSTRACT: Nitrogen fixation is a challenging target in chemistry. N_2 adsorption on transition metal sites has been identified as a prerequisite for activating the stable $N\equiv N$ triple bond in industrial and biological processes. The structural and bonding properties of the $Rh_2O_2(N_2)_n^-$ ($n = 1-2$) complexes have been investigated via mass-selected photoelectron velocity-map imaging spectroscopy combined with quantum chemical calculations. The experimental and theoretical results indicate that the N_2 molecules in the $Rh_2O_2(N_2)_n^-$ ($n = 1-2$) complexes possess the end-on bonding motifs. Adsorption and activation of dinitrogen are facilitated by charge transfer from Rh and O to N_2 . The importance of π back-donation from the 4d orbital of the Rh atom to the antibonding π orbitals of N_2 for dinitrogen activation is discussed in detail; these results identify $Rh_2O_2(N_2)_n^-$ ($n = 1-2$) as a key adsorbed species in the initial stage of dinitrogen activation by rhodium oxide clusters.



1. INTRODUCTION

N_2 serves as the primary nitrogen source for most pharmaceuticals, dyes, food treatment chemicals, etc.^{1,2} N_2 activation and transformation have various applications in industrial production and chemical research; however, these processes face rigorous challenges.³ Despite the extreme abundance of N_2 in the atmosphere, living organisms generally cannot use N_2 directly but instead acquire nitrogen through ammonia or nitrate.⁴⁻⁶ The primary reason for this phenomenon is that the $N\equiv N$ triple bond has a high bond energy of ~ 941 kJ mol⁻¹, which makes cleavage and hydrogenation difficult.⁷⁻⁹ Currently, the Haber–Bosch process dominates the commercial production of NH_3 via N_2 reduction using H_2 . However, this process suffers from energy-intensive consumption and simultaneously generates remarkable byproduct emissions (such as carbon dioxide), which may lead to some undesired global environmental changes.¹⁰⁻¹³ Industrial catalysts and natural nitrogenase use transition metal centers to catalyze the nitrogen conversion process.¹⁴⁻¹⁶ N_2 adsorption on transition metal centers is regarded as the initial and crucial step for the subsequent complicated dinitrogen reduction.^{17,18} However, in the condensed-phase system, the experimental conditions are readily disturbed by the external environment.¹⁹ Isolated gaseous metal clusters can provide an ideal model for studying chemical reaction processes and the associated mechanisms.²⁰⁻²³

Previous studies have shown that most of the products from the reactions between nitrogen and metal compounds are initialized via chemical adsorption, resulting in either undissociated or cleavage of $N\equiv N$ bonds.²⁴⁻³² The undissociated adsorption of N_2 is important to investigate the original N_2 activation process. For the adsorption of N_2 on $Co_3D_n^-$ ($n = 0-4$) complexes, H atoms adjust the energies of

Co 3d orbitals, thereby activating $Co_3D_n^-$ ($n = 2-4$) to react with N_2 . In contrast, $Co_3D_n^-$ ($n = 0-1$) complexes are inert to N_2 because of their higher negative charges and more 4s components on Co. More specifically, the original study also pointed to changes in electron detachment energies and orbital symmetry as contributing factors, indicating that multiple electronic effects govern N_2 adsorption on cobalt deuteride clusters.³⁰ In the congeneric reaction between $Rh_3D_n^-$ ($n = 0-3$) and N_2 , σ donation is more important than π back-donation during the adsorption process.³² The reactivity of the tantalum carbide cluster with N_2 has also been studied, demonstrating that only TaC_4^- absorbs N_2 and TaC_{1-3}^- does not react with N_2 . This reactivity is determined by the presence of frontier orbitals with proper symmetry.²⁹ Similar to CO, N_2 can form highly coordinated structures with metal ions via end-on configurations. For instance, infrared photodissociation spectroscopic and theoretical studies identified the eight-coordinate $M(N_2)_8^+$ ($M = Y, La, \text{ and } Ce$) complexes.²⁸

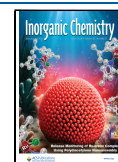
However, most gas-phase studies focus on bare metal clusters, metal-hydride, and metal carbides. Metal oxides are central to many heterogeneous catalysts (e.g., iron oxide promoters in Haber–Bosch), yet the intrinsic ability of a well-defined metal oxide cluster to bind and activate N_2 has not been systematically explored. In particular, the role of π back-donation from metal d orbitals to N_2 π^* orbitals has not been directly probed for an isolated oxide cluster. Herein, we

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generate $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes via laser vaporization and characterize them with mass-selected photoelectron spectra and quantum chemical calculations. This study aims to elucidate the structure and electronic structure of Rh_2O_2^- clusters after nitrogen adsorption, with a focus on the role of π back-donation.

2. EXPERIMENTAL AND THEORETICAL METHODS

Experiments were conducted by using a self-made laser vaporization source and a dual-channel time-of-flight mass spectrometer. The details of the device have been described elsewhere,³³ and only a brief description is provided below. The $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes were generated via pulsed laser vaporization of a rhodium catalyst in a supersonic stream of helium gas. The typical carrier gas stagnation pressure was approximately 2–5 atm. The $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) anionic clusters were quickly cooled and expanded in a laser ablation chamber. The clusters were further picked by using a mass spectrometer (Wiley-McLaren), introduced into the photodetachment region, and then made to interact with laser beams of 355 nm (3.496 eV). The produced photoelectrons were collected by a velocity-map imaging photoelectron spectrometer coupled with a charge-coupled device camera at a 10 Hz repetition rate. Each raw image was obtained from 10,000 to 50,000 laser shots. The raw imaging stands for the projection of the photoelectron density in the 3D laboratory frame on the 2D imaging detector. The original 3D distribution was reconstructed using the Basis Set Expansion (BASEX) inverse Abel transform method, and the photoelectron spectrum (PES) and photoelectron angular distribution (PAD) were obtained by integrating one central slice of the 3D distribution. The photoelectron spectra were calibrated by using the known spectrum of Au^- .³⁴ The energy resolution was >5%, corresponding to 50 meV at an electron kinetic energy of 1 eV.

To elucidate the electronic and geometrical structures of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$), theoretical calculations were performed by using the Gaussian 09 program.³⁵ The structures were optimized by using density functional theory with the B3LYP function, along with the basis set of aug-cc-pVTZ for the O and N atoms and aug-cc-pVTZ-PP for the Rh atoms.^{36–38} All plausible spin states and structures were considered. Harmonic frequency analysis was performed to ensure that the obtained structures were real minima on the potential energy surfaces. Theoretically, the vertical detachment energy (VDE) was calculated as the difference between the neutral and anionic species based on the optimized anion geometries, whereas the adiabatic detachment energy (ADE) was calculated as the difference between the neutral and anionic species based on their optimized structures. The structure of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) clusters was analyzed by using Wiberg bond orders and natural population analysis (NPA). These calculations were performed by using the NBO version 3.1 program within the Gaussian 09 package.³⁹ The energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV)⁴⁰ was performed to investigate the nature of bonding interactions at the B3LYP/TZ2P level of theory using the ADF program.^{41,42}

3. RESULTS AND ANALYSIS

3.1. Photoelectron Spectroscopy

The laser ablation-generated cluster anions (Rh_2O_2^-) were cooled to react with N_2 , yielding the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) products that were mass-selected and characterized using photoelectron velocity-map imaging spectroscopy with 355 nm photons. The corresponding photoelectron spectra of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) recorded at 355 nm are shown in Figure 1. The reconstructed images (purple background) denote the central slice of the three-dimensional (3D) laboratory frame photoelectron distribution from its two-dimensional (2D) projection. The ground-state transition of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) is observed in the 355 nm spectra,

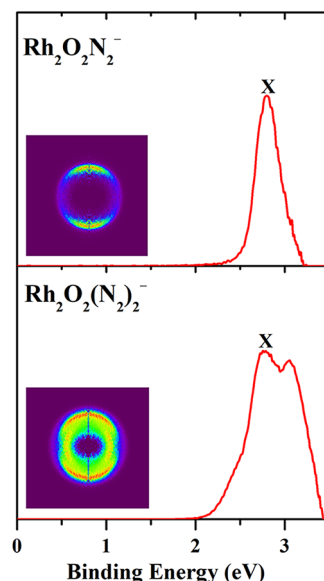


Figure 1. Photoelectron spectra of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) at 355 nm (3.496 eV). Photoelectron images after inverse Abel transformation are embedded in the photoelectron spectra.

where the first dominant main peak in each spectrum corresponds to the ground-state VDE of each species. The photoelectron spectroscopy of isolated Rh_2O_2^- clusters has been reported in previous studies, yielding experimentally VDE and ADE values of 2.51 ± 0.06 eV and 2.40 ± 0.08 eV, respectively.⁴³ Upon the introduction of nitrogen, the VDE values exhibit varying degrees of increase. As shown in Figure 1 and listed in Table 1, the VDE values of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ for $n = 1$

Table 1. Comparison of Experimental VDE and ADE Values to B3LYP Calculated Ones of the Three Lowest-Lying Isomers for $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$)

cluster	isomer	relative energy (eV)	VDE (eV)		ADE (eV)	
			expt. ^a	calc.	expt. ^a	calc.
$\text{Rh}_2\text{O}_2\text{N}_2^-$	1A	0.00	2.80(3)	2.85	2.53(5)	2.68
	1B	0.20		3.60		3.47
	1C	0.34		3.86		3.57
$\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$	2A	0.00	2.77(4)	2.71	2.37(6)	2.54
	2B	0.02		3.07		2.75
	2C	0.42		3.17		2.92

^aNumbers in parentheses represent the uncertainty of the last digit.

and 2 are 2.80 ± 0.03 eV and 2.77 ± 0.04 eV, respectively. Because the photoelectron spectra lack resolved vibrational structure, the ADE cannot be measured directly; instead, it is estimated by drawing a straight line at the rising edge of the main band and then adding the instrumental resolution to the intersection with the binding energy axis.⁴⁴ Consequently, the ADE values of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) were estimated to be 2.53 ± 0.05 and 2.37 ± 0.06 eV, respectively.

3.2. Comparison between Experimental and Theoretical Results

To assign the observed spectral features and identify the geometric and electronic structures of the low-lying isomers, quantum chemical calculations were performed for

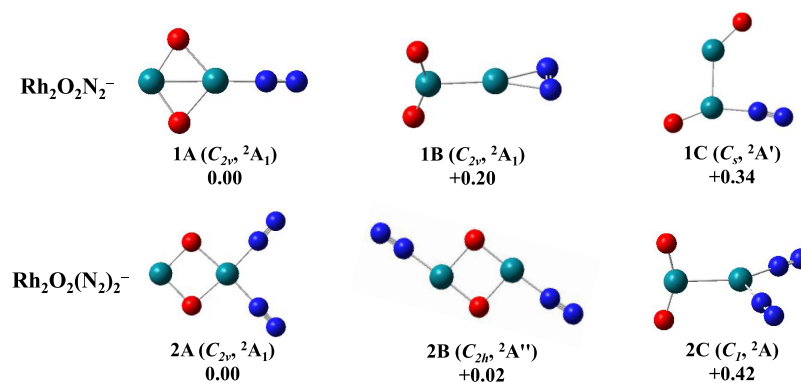


Figure 2. Ground-state structures and selected low-lying isomers of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) anions calculated at the B3LYP/aug-cc-PVTZ-PP (Rh)/aug-cc-PVTZ (O, N) level. Relative energies are given in eV.

$\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) at the B3LYP/aug-cc-PVTZ-PP (Rh)/aug-cc-PVTZ (O, N) level. The three lowest-lying structures are shown in Figure 2. Other higher-energy isomers ($n\text{D}-n\text{I}$) are shown in Figures S1 and S2, which lie too high in energy to be probed in the experiment.

3.2.1. $\text{Rh}_2\text{O}_2\text{N}_2^-$. The most stable isomer (labeled 1A) features a diamond-shaped Rh_2O_2 core with N_2 attached to one Rh atom in a termination mode. Isomer 1A is in a $^2\text{A}_1$ ground state and has a C_{2v} symmetry. The calculated VDE and ADE values of 1A are 2.85 and 2.68 eV, respectively, which are consistent with the experimental VDE and ADE values (2.80 ± 0.03 and 2.53 ± 0.05 eV). The 1B isomer energetically lies 0.20 eV higher than 1A; 1B also has a C_{2v} structure with a $^2\text{A}_1$ electronic state. The 1B isomer includes two O atoms bonded to one Rh atom, and N_2 is bonded to the other Rh atom in a side-on mode. The calculated VDE and ADE values of 1B are 3.60 and 3.47 eV, respectively, which are significantly higher than the experimental values. The 1C isomer is 0.34 eV higher than isomer 1A; 1C is in a $^2\text{A}'$ ground state and has a C_s symmetry. The two O atoms are each bonded to two Rh atoms, and the N_2 molecule is bonded to one Rh atom. The calculated VDE and ADE values of 1C (3.86 and 3.57 eV, respectively) are much higher than the experimental values. As shown in Figure 3, the calculated spectrum of 1A agrees well with the experimental spectrum. Consequently, 1A is assigned to the $\text{Rh}_2\text{O}_2(\text{N}_2)^-$ complex.

3.2.2. $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$. The most stable $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$ structure (labeled as 2A, Figure 2) is in a $^2\text{A}_1$ ground state and has a C_{2v} symmetry. The two N_2 molecules are end-on coordinated with the same Rh atom, which is an evolution from the 1A isomer. The calculated VDE and ADE values of 2A are 2.71 and 2.54 eV (Table 1), respectively, which agree well with the corresponding experimental values (2.77 ± 0.04 and 2.37 ± 0.06 eV). The 2B isomer is 0.02 eV higher than 2A, which has a C_{2h} structure with a $^2\text{A}''$ electronic state. Unlike 2A, each N_2 molecule is coordinated to a different Rh atom on opposite sides. The calculated VDE and ADE values of 2B are 3.07 and 2.75 eV, respectively, which differ from the experimental values. The 2C isomer has a C_1 symmetry and an electronic state of ^2A ; it lies 0.42 eV higher than the 2A isomer. The calculated VDE and ADE values of 2C (3.17 and 2.92 eV) also significantly deviate from the experimental values. Based on the simulated spectra in Figure 3, only 2A yields agreement with the experimental spectrum. Therefore, the 2A isomer should contribute to the experimental spectrum, whereas the presence of 2B and 2C can be ruled out.

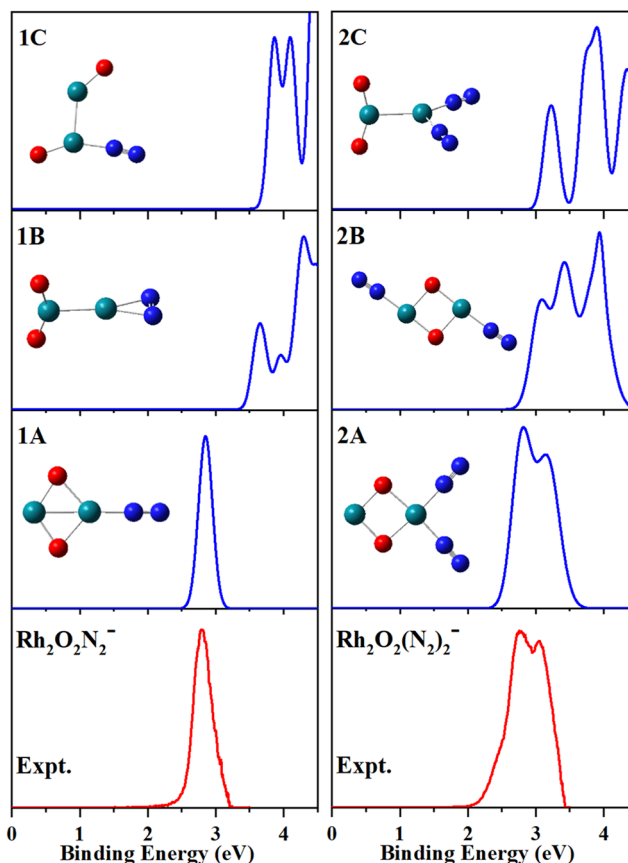


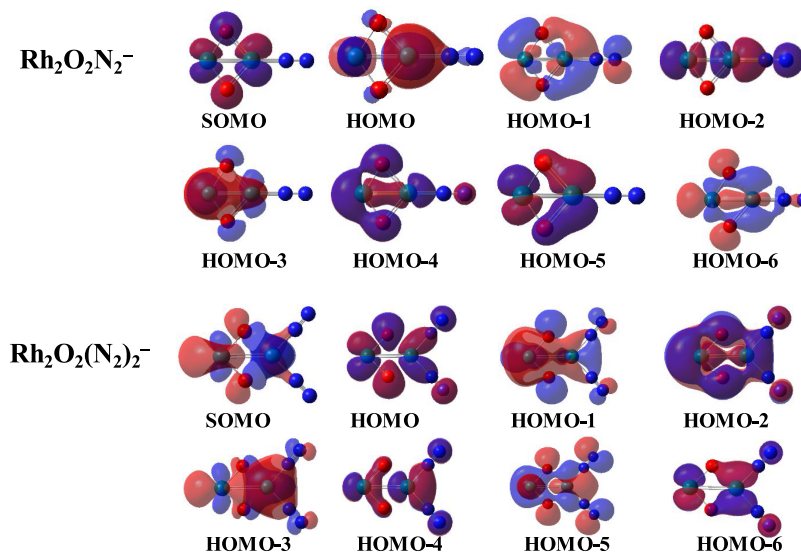
Figure 3. Comparison of experimental 355 nm photoelectron spectra (bottom rows) of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) to the simulated spectra of the three lowest-energy isomers (top rows).

4. DISCUSSION

The consistency between the theoretical and experimental results enables the establishment of the structural features of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$). The bond lengths of the N–N bonds in these clusters are listed in Table 2. After the adsorption of the N_2 molecule on Rh_2O_2^- , the elongation of the N–N bond (from 1.095 Å in free N_2 to 1.123 Å in 1A and 1.111 Å in 2A) and the decrease in Wiberg bond order (from 3.000 to 2.574/2.699) directly reflect bond weakening along the reaction coordinate of N_2 adsorption, and these changes are consistent with the degree of π back-donation observed in the molecular orbitals. This result reveals that Rh_2O_2^- contributes to

Table 2. Rh–Rh/N–N Bond Lengths, N–N Wiberg Bond Orders, and Natural Population Analysis (NPA) of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) Species Calculated at the B3LYP Level

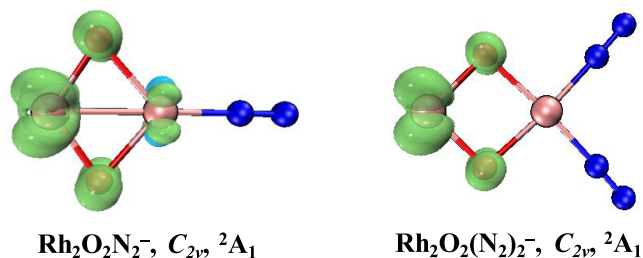
species	Rh–Rh bond length	N–N bond length	N–N Wiberg bond order	NPA charges		
				Rh	O	N
$\text{Rh}_2\text{O}_2\text{N}_2^-$	2.368	1.123	2.574	0.731	−1.531	−0.200
$\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$	2.804	1.111	2.699	0.705	−1.658	−0.047

**Figure 4.** Molecular orbital pictures of the most stable isomers for $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) calculated at the B3LYP/aug-cc-PVTZ-PP (Rh)/aug-cc-PVTZ (O, N) level of theory.

dinitrogen activation. To visualize the charge changes among these clusters, NPA analyses were performed (Table 2). Based on the overall trends, the N_2 unit charge exhibits a negative tendency, indicating that Rh_2O_2^- transfers charges to N_2 , thereby promoting nitrogen activation. From $n = 1$ to $n = 2$, the positive charge on the Rh atoms decreases slightly (from 0.731 to 0.705), the negative charge on O atoms increases (from −1.531 to −1.658), and the negative charge on N becomes less negative (from −0.200 to −0.047). Based on the bond order and length analyses, the adsorption of the second N_2 molecule weakens the interaction between Rh atoms and N_2 , thereby reducing the degree of activation.

To study the mechanism of nitrogen adsorption and activation, molecular orbital analysis was performed for the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes. Figure 4 illustrates the frontier orbital images of the most stable isomers. Tables S1 and S2 present the orbital composition analyses of these isomers using the natural atomic orbital method for different elements. For $\text{Rh}_2\text{O}_2\text{N}_2^-$, the highest occupied molecular orbitals HOMO−1 and HOMO−2 are π back-donations from the Rh 4d orbital to the π antibonding orbitals of N_2 , contributing 13% and 12% to the back-donation interactions based on the percentage of N, respectively. Other orbitals possess negligible Rh_2O_2^- – N_2 interactions. For $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$, HOMO, HOMO−1, HOMO−2, HOMO−4, and HOMO−6 can also be regarded as π back-donations from the 4d orbital in the Rh atom to the antibonding π orbitals of N_2 , and the percentages of N in these orbitals are 4%, 11%, 8%, and 10%, respectively. These results indicate that π back-donations dominate the interactions between Rh_2O_2^- and N_2 , which also conform to charge transfer from Rh/O to N. PAD analysis is correlated to molecular orbital characteristics.^{45,46} The

anisotropy parameters (β) values of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) are 1.40 and 0.73, respectively. The ground-state transition for $\text{Rh}_2\text{O}_2\text{N}_2^-$ is nearly parallel. For $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$, the symmetric coordination alters the symmetry of the ground-state ionization orbitals, leading to hybridization involving more orbitals, reduced anisotropy, and a significantly altered SOMO electron cloud. Furthermore, the π back-donation is stronger in $\text{Rh}_2\text{O}_2\text{N}_2^-$ than that in $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$ because the former has a higher percentage of N molecules in π back-donation orbitals, which is consistent with the longer N–N bonds and smaller N–N orders for $\text{Rh}_2\text{O}_2\text{N}_2^-$. In addition, the higher 5s electron occupation in the Rh atom on the right side of 2A (0.41) than that in 1A (0.37) can also result in stronger repulsions between Rh_2O_2^- and N_2 . The calculated N_2 dissociation energies of 1A and 2A are 1.55 and 0.98 eV, respectively, which also coincides with the aforementioned results. Subsequently, we performed spin density analysis (Figure 5). With the addition of nitrogen, the number of unpaired electrons on the Rh atom on the right

**Figure 5.** Isosurface map of electron spin density distributions for $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) calculated at the B3LYP/aug-cc-PVTZ-PP (Rh)/aug-cc-PVTZ (O, N) level of theory.

side gradually decreases, approaching zero as n increases from 1 to 2. This result could be attributed to the more 4d orbitals of active Rh participating in π back-donation bonds from $n = 1$ to $n = 2$. Thus, the bonding mechanism of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) clusters provides a molecular insight into the activation of nitrogen by a single nuclear metal oxide cluster.

The nature of the interactions in $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes was analyzed by the energy decomposition analysis-natural orbitals for chemical valence (EDA-NOCV) method, which provides a quantitative estimation of the contributions from the fragment MOs to the bonding interactions. The interaction energy (ΔE_{int}) between the Rh_2O_2^- and N_2 fragments is decomposed into Pauli repulsive orbital interaction (ΔE_{Pauli}), electrostatic interaction (ΔE_{elstat}), and orbital interaction ($\Delta E_{\text{orbital}}$). The numerical results of EDA-NOCV analyses of $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes are given in Table 3. The EDA-NOCV results indicate that there is

Table 3. EDA-NOCV Results of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) Complexes at the B3LYP/TZ2P Level of Theory^a

energy term	$\text{Rh}_2\text{O}_2^- + \text{N}_2$	$\text{Rh}_2\text{O}_2^- + 2\text{N}_2$
ΔE_{int}^b	−173.4	−282.8
ΔE_{Pauli}	536.4	907.8
$\Delta E_{\text{elstat}}^c$	−351.4 (49.5%)	−593.1 (49.8%)
$\Delta E_{\text{orbital}}^c$	−358.4 (50.5%)	−597.6 (50.2%)
$\Delta E_{\text{orbital}(1)}^d$	−28.4 (7.9%)	−60.2 (10.1%)
$\Delta E_{\text{orbital}(2)}^d$	−27.5 (7.7%)	−32.6 (5.5%)
$\Delta E_{\text{orbital}(3)}^d$	−20.0 (2.2%)	−27.6 (4.6%)
$\Delta E_{\text{orbital}(4)}^d$	−8.0 (2.2%)	−11.4 (1.9%)
$\Delta E_{\text{orbital}(\text{rest})}^d$	−274.6 (76.6%)	−465.7 (77.9%)

^aEnergy values are given in kcal/mol. ^b $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orbital}}$, where ΔE_{int} , ΔE_{Pauli} , ΔE_{elstat} , and $\Delta E_{\text{orbital}}$ is the interaction energy, Pauli repulsive orbital interaction energy, electrostatic interaction energy, and orbital interaction energy, respectively. ^cThe values in parentheses show the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orbital}}$. ^d $\Delta E_{\text{orbital}(n)}$ ($n = 1-4$) denotes the n th orbital interaction energy in the order of charge eigenvalues. The values in the parentheses show the percentage contribution to the total orbital interaction $\Delta E_{\text{orbital}}$.

an attractive interaction between the two fragments and that electrostatic and orbital interactions account for nearly equal proportions ($\sim 50\%$). Deep insight into the composition of $\Delta E_{\text{orbital}}$ is given by several individual orbital terms $\Delta E_{\text{orbital}(n)}$ ($n = 1-4$) and $\Delta E_{\text{orbital}(\text{rest})}$, which is identified by the relevant deformation density ($\Delta\rho$) (Figures S3 and S4). For $\text{Rh}_2\text{O}_2\text{N}_2^-$, the contributions V_1 and V_2 come from $\text{Rh}_2\text{O}_2^- \rightarrow \text{N}_2$ π -back-donation, and $\Delta E_{\text{orbital}(1)}$ and $\Delta E_{\text{orbital}(2)}$ account for about 7.9% and 7.7%, respectively, where $\Delta E_{\text{orbital}(4)}$ represents a weaker σ -type donor–acceptor channel along the Rh–N–N axis. For $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$, V_2 and V_3 correspond to dominant π -back-donation interactions involving the Rh_2O_2^- core and the coordinated N_2 ligands, and $\Delta E_{\text{orbital}(2)}$ and $\Delta E_{\text{orbital}(3)}$ account for about 5.5% and 4.6%, which indicates that the π -back-donation effect in $\text{Rh}_2\text{O}_2(\text{N}_2)_2^-$ is relatively weak, which is consistent with the previous orbital and bond analysis results.

5. CONCLUSIONS

A laser vaporization supersonic cluster source was used to generate the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) clusters, which were characterized by mass-selected time-of-flight photoelectron velocity-map imaging spectroscopy. Theoretical calculations

were performed to elucidate their geometric and electronic structures. The results revealed that the most stable isomers of the $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) clusters have the N_2 -end-on-bonded structures. Chemical bonding analyses show that the adsorption and activation of dinitrogen is facilitated by the charge transfer from Rh and O to N_2 . We note that bond cleavage or catalytic turnover was not observed; however, the identification of stable end-on N_2 adducts and the quantification of charge transfer and orbital interactions provide a foundation for understanding the initial adsorption step in more complex systems. In addition, the importance of the π back-donation of the 4d orbital of Rh to the antibonding π orbitals of N_2 for dinitrogen activation is emphasized. This gas-phase study reveals the detailed bonding mechanism by which a rhodium oxide cluster activates N_2 through π back-donation, offering molecular-level insights that may inform the design of heterogeneous catalysts for nitrogen activation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.6c01444>.

Optimized structures, plots of the deformation densities in the orbitals, and orbital composition analysis for $\text{Rh}_2\text{O}_2(\text{N}_2)_n^-$ ($n = 1-2$) complexes. (PDF)

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Notes

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