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Stable Geometry and Rotation of the Dinitrogen Ligand in a Nickel Complex, $Ni(O_2)(N_2)$

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This paper describes the stable geometry and the rotation of a N_2 ligand in $Ni(O_2)(N_2)$. Ab initio MO calculations give reasonable results for the bonding between Ni and the dinitrogen ligand. However, it is necessary to include the correlation effect in order to express the bonding nature between Ni and the dioxygen ligand. It is ascertained that the end-on structure of the dinitrogen ligand is more advantageous than the side-on geometry.

Introduction

Dinitrogen complexes are typical compounds with a small molecule as a ligand. Attention so far has been focused not only on the nauture of bonding between a metal and a dinitrogen ligand but also on reduction of the coordinated nitrogen molecule to NH_3 or N_2H_4.[1] In relation to the former property were discussed stable conformations of the dinitrogen ligand, i.e., why the dinitrogen ligand prefers an end-on coordination to a side-on structure. It is more profitable to use a side-on complex as a reactant for reduction of the dinitrogen ligand because the nitrogen molecule in the side-on complex is considered to be more activated than that in the end-on one. In fact, Robinson et al. discussed the side-on form in their works of a nitrogenase model.[2] On the other hand, isomerization between the two geometrical isomers was observed in $Ru(NH_3)_5(N_2)^{2+}$ by Armor and Taube.[3] They estimated an activation enthalpy for the N_2 rotation to be 21 kcal/mol. It is, therefore, very interesting to investigate the mechanism of isomerization from the end-on to the side-on coordination.

Ozin and Klotzbücher[4] found Ni complexes $Ni(O_2)(N_2)_n$ (n = 1 and 2). These complexes have the unique feature that they have both dinitrogen and dioxygen ligands within the molecule. The preferred geometries of these complexes were analyzed in detail by use of IR measurements. They proposed a complex geometry such that the dioxygen ligand was coordinated to Ni in a side-on manner while the dinitrogen ones were coordinated in an end-on manner.

From the theoretical viewpoint, a mechanism of isomerization of the dinitrogen ligand has not yet been investigated by use of ab initio molecular orbital (MO) calculations. It is because dinitrogen complexes are in general too large to study by nonempirical and energy gradient methods. However, the rotation of the dinitrogen ligand is very interesting and suggestive in relation to both the M–N bonding nature and the reduction of the dinitrogen ligand. On the other hand, the complex found by Ozin et al. is small enough to permit these kinds of approaches. Moreover, the geometry of the complex was well investigated. In this paper, the stable geometry of a complex $Ni(O_2)(N_2)$, is studied by use of ab initio MO calculations. The bonding nature between Ni and N atoms are also investigated with the energy decomposition technique of Kitaura and Morokuma.[6]

Method of Calculation

LCAO–MO–SCF calculations were carried out with the GAUSSIAN-80[7] program. The vibrational analysis and the energy decomposition were performed by use of HONDOG and IMSPAC.[8] All geometries were optimized with the energy gradient method. A Gaussian basis set (12s6p4d) by Roos et al.[9] was contracted to [5s2p1d] and p, d orbitals of 1G[10] were added to the basis set. 3-21G basis sets internal to the program were used for ligand atoms.

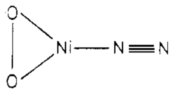
Table I. Optimized Bond Lengths (Å) in the Three Geometrical Isomers of $Ni(O_2)(N_2)$

	Ni-N	Ni-O	N-N	O-O
1	1.821	2.546	1.083	1.241
2	1.974	2.581	1.113	1.242
3	2.407	2.021	1.111	1.243

A singlet state was adopted as the ground state of the Ni complex, because complexes with the side-on dioxygen ligand are, in general, diamagnetic. On the other hand, an oxygen molecule has a triplet state as the most stable spin multiplicity. It is necessary to discuss the stable spin multiplicity of the complex when the dioxygen ligand is weakly bound to the central metal. However, our attention is focused on the rotation of the dinitrogen ligand. Therefore, MO calculations have been performed for the complex assumed to have a lower spin state.

Results and Discussion

Stable Geometry. Three geometrical isomers with a C_{2v} symmetry are considered for $Ni(O_2)(N_2)$ as shown in **1**–**3**. **1** has dioxygen and dinitrogen ligands bonded in a side-on and an end-on fashion, respectively, while **3** has a conformation opposite to that of **1**. Both ligands are coordinated to Ni in a side-on manner in **2**. Geometries optimized for the isomers are summarized in Table I. Total energies of **1**–**3** are calculated to be −1760.8203, −1760.7937, and −1760.7885 au, respectively. Therefore, the N_2 end-on geometry is the most stable of the three structures.[11] This geometry is consistent



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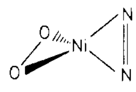

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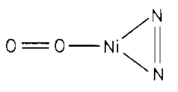

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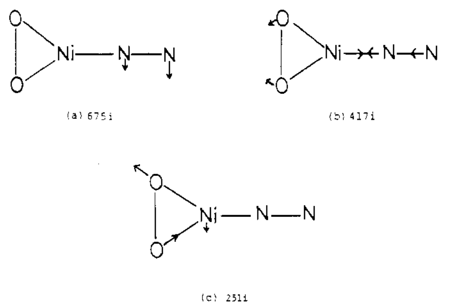

(a) 675i (b) 417i (c) 251i

Figure 1. Vibrational modes with imaginary frequencies calculated for the end-on structure.

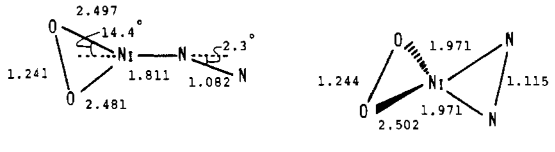

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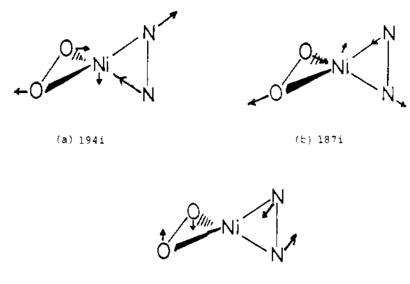
Figure 2. Optimized geometries of end-on and side-on structures that lowered their symmetries.



(a) 194i (b) 187i (c) 74i

Figure 3. Vibrational modes with imaginary frequencies calculated for the side-on structure.

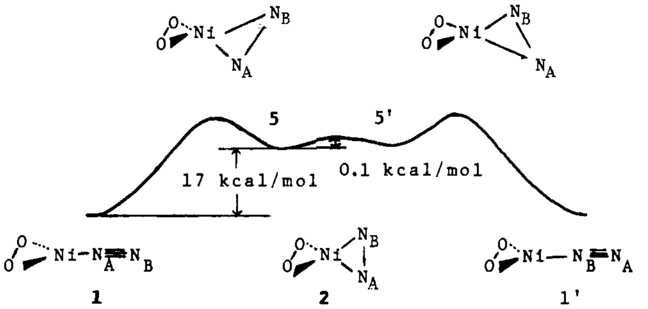


Figure 4. Schematic representation of the reaction path for isomerization of the dinitrogen ligand.

with that proposed by Ozin et al.[4]

In order to assign IR absorpton bands observed, vibrational analysis is performed for the end-on complex. The second derivatives of the potential energy are obtained by the numerical differentiation of the analytically calculated energy gradient. Three imaginary frequencies are obtained for the complex with the C_{2v} geometry as illustrated in Figure 1. These displacement vectors require the end-on complex to have C_s rather than C_{2v} symmetry, so that a complex with the C_s symmetry, **4**, is optimized. Total energy of **4** is −1760.8203 au, which is the same as that of **1**. The optimum geometry of **4** is almost unchanged from that of **1**: i.e., the difference between bond lengths in these complexes are all within ~0.05 Å as illustrated in Figure 2. Therefore, the vibrational frequencies of O–O and N–N bonds in **4** are not so largely different from those calculated for **1**. The N–N and O–O (ν_{NN} and ν_{OO}) frequencies calculated are 2597 (2207) and 1589 (1531) cm^{-1}, respectively. Values in parentheses are reduced frequencies of calculated values.[12] Observed values of ν_{NN} and ν_{OO} are 2243 and 997 cm^{-1}, respectively. The frequency of the N–N stretching mode is similar to that obtained from the MO calculations. On the other hand, that of the O–O bond is overestimated even though reduced. It seems to be very difficult to express the bonding between the Ni and dioxygen ligand in the complex. This is probably attributed to the fact that the complex has triplet or excited singlet states near the ground state or a triplet state in the ground state because of having an oxygen molecule loosely bound to Ni. It is necessary to include the correlation effect in order to describe the property more precisely.

Mechanism of the N_2 Rotation. It is necessary to find a transition state of the N_2 rotation in order to analyze the mechanism in detail. The side-on geometry is one of the candidates for the transition state for rotation of the dinitrogen ligand. Therefore, the vibrational frequencies are calculated for the optimum geometry of **2**. It gives real as well as three imaginary frequencies. It is well-known that only one imaginary frequency exists at a transition state, so that the structure is neither an equilibrium geometry nor a transition state. The imaginary modes are illustrated in Figure 3. Figure 3c shows the mode that causes the rotation of the dihedral angle between NiOO and NiNN planes. The modes of Figure 3a, b lead to an asymmetric coordination of dinitrogen and dioxygen ligands in the *xz* and *yz* planes, respectively. There are two possibilities for the results of the vibrational analysis. One is that the equilibrium geometry can be obtained in terms of lowering the symmetry from C_{2v} to C_1. The other is that this structure is a transition state for the rotation of the dinitrogen or dioxygen ligands although other parameters must be optimized along the imaginary vibrational modes. In order to ascertain these possibilities the complex having symmetric dioxygen and asymmetric dinitrogen ligands, **5**, is studied and the optimum geometry is represented in Figure 2. The figure shows that all the bond lengths and angles do not change very much; i.e., increment and decrement of lengths and angles are within ~0.05 Å or 5°. Therefore, it is considered that there is a stable complex with nearly the same geometry as that of the side-on isomer although the symmetry is lowered. Moreover, there also exists a transition state where the complex has a more asymmetric dinitrogen coordinating to the central metal. The total energy of **5** is calculated to be −1760.7938 au. The energy difference between **2** and **5** is only 0.0001 au (0.1 kcal/mol). The result is expected in terms of the small imaginary frequency of mode b of the geometry. Therefore, it will be possible to investigate the N_2 rotation of the complex with the C_s symmetry throughout the reaction. A schematic representation of the N_2 rotation is illustrated in Figure 4 together with the energy relation obtained. More than 17 kcal/mol of energy is required for changing the coordination geometry from **1** to **5**.[13] Along the path of the reaction, the transition state has a more slanting dinitrogen ligand than that in **5**. As the energy difference between **2** and **5** is very small (0.1 kcal/mol), the interconversion between **5** and **5′** through

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(11) As discussed later, both **1** and **2** have imaginary frequencies. To discuss the stable geometry of the Ni complex, it is necessary to optimize this with C_1 or C_s symmetry. However, the lowering effect of the symmetry is ascertained not to be important to the total energy. Thus, it is possible to compare the relative stability of the three isomers with C_{2v} symmetry.

(12) It is well accepted that the experimental frequencies would be obtained by reduction of 10–15% from the calculated ones: Pulay, P. "Modern Theoretical Chemistry"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4.

(13) We tried to find a transition state of the N_2 rotation by use of GAUSSIAN-80 program. However, it could not be obtained. This result suggests that the geometries of **4** and the transition state are very close to each other. Therefore, the activation energy would not be so largely different from the energy differences between **1** and **4**.

Table II. Results of Energy Decomposition for $Ni(O_2)(N_2)$ with End-On and Side-On Geometries (kcal/mol)

	end-on	side-on		end-on	side-on
ES	−56.0	−41.7	BCTPLX	−26.5	−28.3
EX	72.1	73.4	MIX	0.6	−8.2
FCTPLX	−24.5	−14.9	ΔE_T	−34.3	−19.7

2 is very easy. The rotational barrier from side-on to end-on coordination of the N_2 ligand is small while the energy required for the opposite direction is large. Therefore, even if the complex with dioxygen and dinitrogen ligands coordinating in the side-on manner forms, it will rapidly return to the most stable structure that has the end-on dinitrogen and side-on dioxygen ligands. Ozin et al. could not find the IR spectra indicating the N_2 side-on geometry. This experimental evidence is consistent with the present calculation results.

Nature of Bonding between Ni and N Atoms. As mentioned above, the complex with the end-on N_2 ligand is more stable than that with the side-on one. This result is consistent with the trend observed in many dinitrogen complexes. Therefore, it is very interesting to discuss this property in these geometrical isomers. To analyze the bonding nature of the Ni–N bond, the interaction energy[14] between $Ni(O_2)$ and N_2 fragments, ΔE_T, is decomposed to several types of energies such as ΔE_{ES}, ΔE_{EX}, ΔE_{FCTPLX}, ΔE_{BCTPLX}, and ΔE_{MIX} by use of the energy decomposition technique of Kitaura and Morokuma.[6] The first two terms represent energies of electrostatic (ES) interaction and exchange (EX) repulsion. ΔE_{FCTPLX} and ΔE_{BCTPLX} are coupling terms of charge-transfer (CT) and polarization (PL) interactions.[15] They are defined as donative and back-donative interactions, respectively. The last term is a coupling energy of all above components. Results are listed in Table II. The interaction energies for end-on and side-on complexes are calculated to be −34.3 and −19.7 kcal/mol, respectively. The sums of total energies of the two fragments are −1760.7656 and 1760.7634 au, respectively. As the difference of these energies is very small, the relative stability of the geometrical isomers is determined by the magnitude of the interaction energies. The absolute value of ΔE_{ES} of **1** is larger by 14.3 kcal/mol than that of **2**. Moreover, that of ΔE_{FCTPLX}, which is the contribution of the σ donation, is large in **1** in comparison with that in **2**. Therefore, the relative values of these contributions indicate that the end-on coordination is preferred to the side-on structure.

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(14) The interaction energy is defined as the difference between the total energy of $Ni(O_2)(N_2)$ and the sum of those for the two fragments $Ni(O_2)$ and N_2.

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Inequivalent Clusters and Energy Transfer in Trinuclear Chromium(III) Acetate

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Below 211 K the structure of hydrated chromium acetate, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl\cdot 6H_2O$, consists of equal numbers of two inequivalent trimers, a and b. Dehydration produces domains of an anhydrous phase characterized by species c and d, each consisting of a family of inhomogeneous members. Selectively excited emission and excitation spectra, as well as fluorescence-lifetime measurements, show evidence for energy transfer d → c and a → b. The mechanism is identified as a pure electronic resonant energy transfer $({}^7/{}_2{}^*)_a({}^5/{}_2)_b \rightsquigarrow ({}^7/{}_2)_a({}^7/{}_2{}^*)_b$ ($\Delta S_a = 0$; $\Delta S_b = +1$). Energy transfer between higher lying excited states is quenched by a faster intracluster radiationless relaxation.

1. Introduction

The electronic structure, in particular the order of the ground electronic levels, of basic chromium(III) acetate, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl\cdot 6H_2O$, has stimulated considerable interest.[1-6] It is now established that at low temperatures the structure of the hydrated chloride salt consists of equal numbers of two inequivalent trimeric clusters, labeled a and b.[3,6] Recently, Morita and Kato[4] have reported new emission lines, here labeled c and d, in addition to those associated with clusters a and b. Their assignment of c and d to stressed clusters was not supported by our preliminary spectroscopic measurements, and the first objective of the present work was the characterization of the origin of the lower lying energy levels of species c and d.

From studies of excitation spectra we obtained evidence for energy transfer from a to b and from c to d. Energy transfer between the lowest lying excited states $S_a{}^* = {}^7/{}_2$ and $S_b{}^* = {}^7/{}_2$ was also noted by Morita and Kato.[4] Independently, Schenk and Guedel[6] examined this problem in more detail and proposed a phonon-assisted energy-transfer mechanism involving intercluster exchange. Estimates of the latter were low ($J_{ab} < 0.1$ cm^{-1}), which led to criticism of a recent reanalysis of the thermal and magnetic properties of the hydrated chloride salt.[5] In this connection it is important to emphasize that spectroscopic techniques are far more sensitive than "direct" X-ray structure methods for the detection of inequivalent molecules. For example, the X-ray analysis of $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5\cdot H_2O$ showed only one dimeric species,[7] whereas spectroscopic measurements gave clear

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