Theoretical Study of $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ Complexes

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Ab initio molecular orbital theory and density functional theory have been applied to study the isoelectronic-liganded NiL_2 ($L = N_4^{2-}$, $C_4H_4^{2-}$, and $C_2O_2^{2-}$) sandwich complexes at the MP2/6-31G*, B3LYP/6-31G*, B3LYP/6-311+G*, and BHLYP/6-311+G(3df,3pd) levels of theory. The stable structure for $Ni(N_4)_2$ is a staggered conformer with D_{4d} symmetry. The dissociation barriers for one N_2 elimination and two N_2 eliminations for $Ni(N_4)_2$ are 37.1 and 84.9 kcal/mol, respectively, at the B3LYP/6-31G* level of theory, which suggest that $Ni(N_4)_2$ is kinetically stable enough to resist dissociation. The calculated reaction energies for the dissociation of $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ at the B3LYP/6-31G* level of theory suggest that both $Ni(N_4)_2$ and $Ni(C_2O_2)_2$ are high-energy species; however, $Ni(C_4H_4)_2$ is not.

1. Introduction

In the past decades, pure nitrogen clusters have been noticed by the idea that pure nitrogen molecules may be used as possible candidates for environmentally friendly high-energy density materials (HEDMs).[1−6] However, more and more hypothetical stable structures of pure nitrogen clusters have recently been questioned about their possibilities of being used as HEDMs because of their kinetic instabilities.[7−11] Therefore, other stable forms of polynitrogens were explored. Wilson et al.[12] quantitatively showed how four- and six-membered nitrogen rings could be stabilized by coordinating covalent bonds to oxygen. Gagliardi and Pyykö predicted the structure and stability of ScN_7.[13] Subsequently, they reported N_5MN_7 (M = Ti, Zr, Hf, and Th), N_5ScN_7, and N_5VN_7 with a total charge of 0, −1, and +1, respectively.[14] The dissociation barriers, 20 kcal/mol for ScN_7 and 21.5 kcal/mol for N_5ThN_7, indicate that both of these two species have the chance of existing. Straka[15] theoretically suggested the possibility of stabilizing the N_6 species as a planar hexagonal ring in MN_6 (M = Ti, Zr, Hf, and Th) systems. $Fe(N_5)_2$ was reported by Lein et al.[16] to have a strong metal−ligand interaction. This iron bispentazole is an energy-rich compound, lying 226.8 kcal/mol higher in energy than its most stable dissociation products of an iron atom and five N_2 molecules. Analogous to the reported $Fe(N_5)_2$, in which the N_5^- is a planar aromatic ring, the N_4^{2-} planar ring might be stabilized as a π-system ligand by the interaction between a ligand and a transition metal atom. Previous research on N_4^{2-} has been reported.[15,17] The N_4^{2-} was predicted to be a D_{4h}-symmetric planar-square anion. Moreover, in the neutral CaN_4[15] and bipyramidal Li_2N_4,[17] N_4^{2-} remains planar. On the basis of the previous studies,[1−21] structure and thermodynamic and kinetic stability of a hypothetical $Ni(\eta^4\text{-}N_4)_2$ sandwich complex were investigated in the present paper. Because $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$ are isoelectronic with $Ni(N_4)_2$, it is also interesting to see their thermodynamic stabilities and compare the bonding nature between them. Therefore, the geometries, energies, harmonic vibrational frequencies, and the nature of bonding of the isoelectronic-liganded complexes $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$ were also investigated in the present study.

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2. Methods

Geometries and harmonic vibrational frequencies of all complexes were calculated using density functional theory (DFT) and second-order perturbation theory (MP2) methods at the B3LYP/6-31G*, B3LYP/6-311+G*, BHLYP/6-311+G(3df,3pd), and MP2/6-31G* levels of theory, where B3LYP is a DFT method using Becke's three-parameter nonlocal functional[22] along with the Lee−Yang−Parr nonlocal correlation functional (LYP)[23] and BHLYP is a "half-and-half" HF/DFT hybrid exchange functional (BH)[24] with the LYP[23] model for correlation. The MP2 method uses the frozen core approximation.[25] The 6-31G* is a standard split-valence double-ζ polarization basis set,[26] and 6-311+G* is a split-valence triple-ζ plus polarization basis set augmented with diffuse functions.[27] Natural bond orbital[28−31] (NBO) analysis was carried out at the B3LYP/6-31G* level of theory based on the optimized geometries at the same level of theory. Minimum-energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez−Schlegel second-order algorithm.[32] Throughout this paper, bond lengths are provided in angströms, bond angles in degrees, total energies in hartrees, and relative energies and zero-point vibrational energies, unless otherwise stated, in kcal/mol. All calculations were performed with the Gaussian 98 program package.[33]

3. Results and Discussion

The molecular structures, along with their optimized geometrical parameters, for $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ are illustrated in Figures 1, 2, and 3, respectively. Figure 4 shows the molecular structures for the transition states and dissociation products, along with their optimized geometrical parameters. The qualitative frontier molecular orbital correlation diagrams for the interactions between the ligand and Ni^{4+} for $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ are shown in Figures 5−7, respectively. The total energies, zero-point vibrational energies (ZPE), and number of imaginary vibrational frequencies are listed in Table 1. The relative energies with ZPE corrections are given in Table 2. Table 3 shows the dissociation energies of the homolytic bond cleavage. Harmonic vibrational frequencies and IR intensities for $Ni(N_4)_2$ (D_{4d}), $Ni(C_4H_4)_2$ (D_{4d}), and $Ni(C_2O_2)_2$ (D_{2d}) are shown in Table 4.

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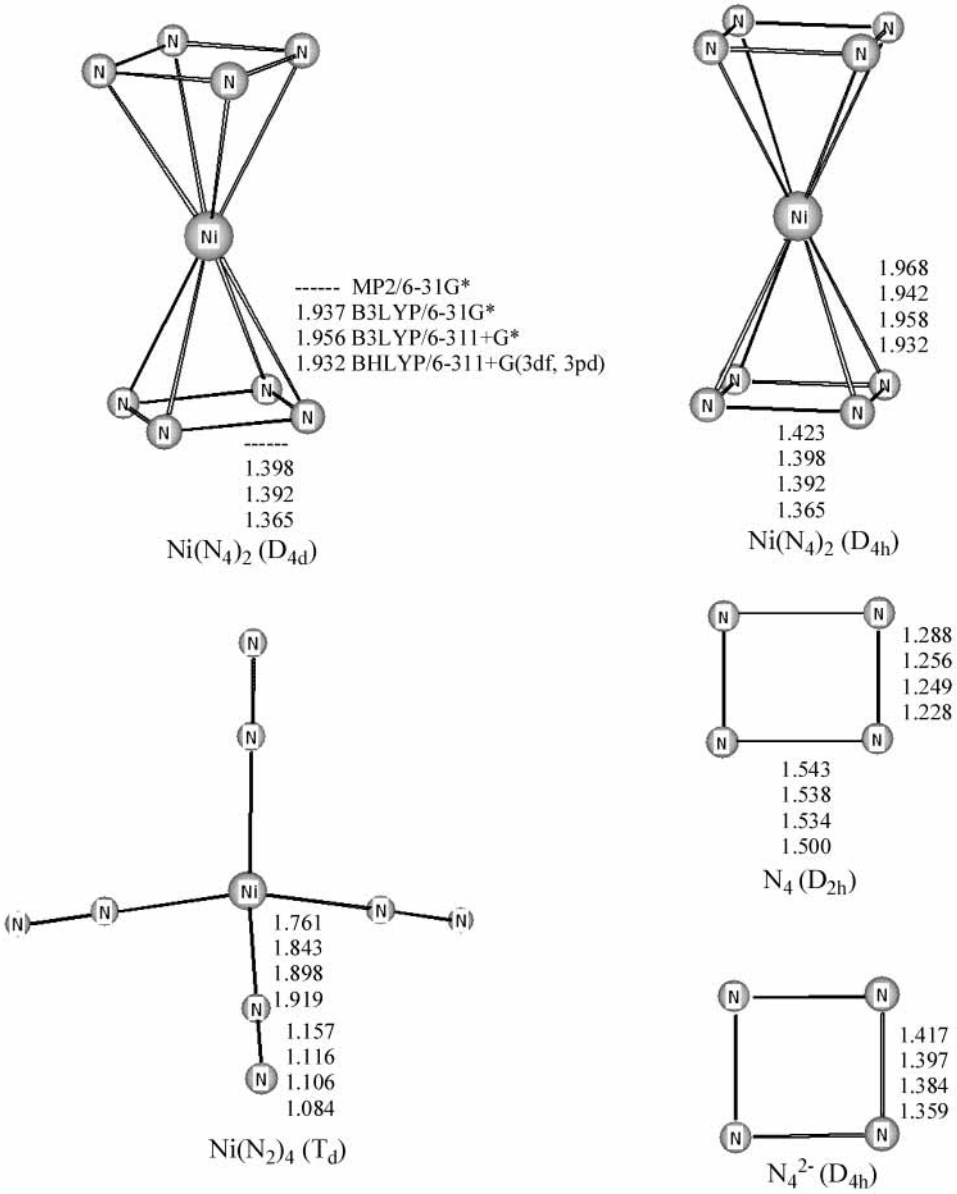

Figure 1. Optimized molecular structures, along with their geometrical parameters, for $Ni(N_4)_2$ (D_{4d}), $Ni(N_4)_2$ (D_{4h}), $Ni(N_2)_4$ (T_d), N_4 (D_{2h}), and N_4^{2-} (D_{4h}).

The calculations predict that the stable structure of $Ni(N_4)_2$ is a staggered conformer with D_{4d} symmetry, rather than an eclipsed one with D_{4h} symmetry. For the two conformers, the latter is a transition state with one small imaginary vibrational frequency, being only 0.6 kcal/mol less stable than the former at the B3LYP/6-31G* level of theory. When larger basis sets 6-311+G* (at the B3LYP level of theory) and 6-311+G(3df,-3pd) (at the BHLYP level of theory) were used, the energy difference between the staggered and eclipsed conformers of $Ni(N_4)_2$ becomes extremely slight (as listed in Table 2), which suggests that there is probably no internal barrier for the rotation of the two N_4^{2-} ligands about the C_4 axis. In our calculations, we have attempted to optimize the D_{4d}-symmetric structure at the MP2/6-31G* level of theory; however, we failed in finding it. From Table 2, we can see that the differences of the relative energies obtained at the above three different levels of theory are also slight. As shown in Figure 1, the bond length of N−N in $Ni(N_4)_2$ (the following discussions focus on the conformation of D_{4d} symmetry, unless otherwise stated) is 1.398 (B3LYP/6-31G*), 1.392 (B3LYP/6-311+G*), and 1.365 Å (BHLYP/6-311+G(3df,3pd)), which is close to the bond length of N_4^{2-} (D_{4h}) (1.397, 1.384, and 1.359 Å at the above three levels of theory, respectively). The bond-length equalization, which is the sign of aromaticity for hydrocarbons,[34] has also been observed in $Ni(N_4)_2$. Moreover, according to NBO analysis, the calculated Wiberg bond indices (WBI) for all N−N bonds in $Ni(N_4)_2$ are 1.2, indicating delocalization. The bond length of Ni−N in $Ni(N_4)_2$ is 1.937 (B3LYP/6-31G*), 1.956 (B3LYP/6-311+G*), and 1.932 Å (BHLYP/6-311+G(3df,3pd)). The covalent radius value for nitrogen is 0.70[35] or 0.75 Å,[36] while that for nickel is 1.21 Å.[36] It is clear that the calculated Ni−N bond length in $Ni(N_4)_2$ lies between the two sums of the covalent radii of nickel and nitrogen (1.91 and 1.96 Å). At the B3LYP/6-31G* level of theory, Mulliken charge analysis shows that all positive charges lie on the nickel (about +0.64) while all negative charges populate on the nitrogens (about −0.08 per N atom). Moreover, the WBIs for all Ni−N bonds are about 0.4. According to the calculation results listed above, it seems that the metal−ligand bonds are possibly partly ionic and partly covalent.

Thermodynamically speaking, $Ni(N_4)_2$ is a local minimum on its potential energy surface. To assess its stability further,

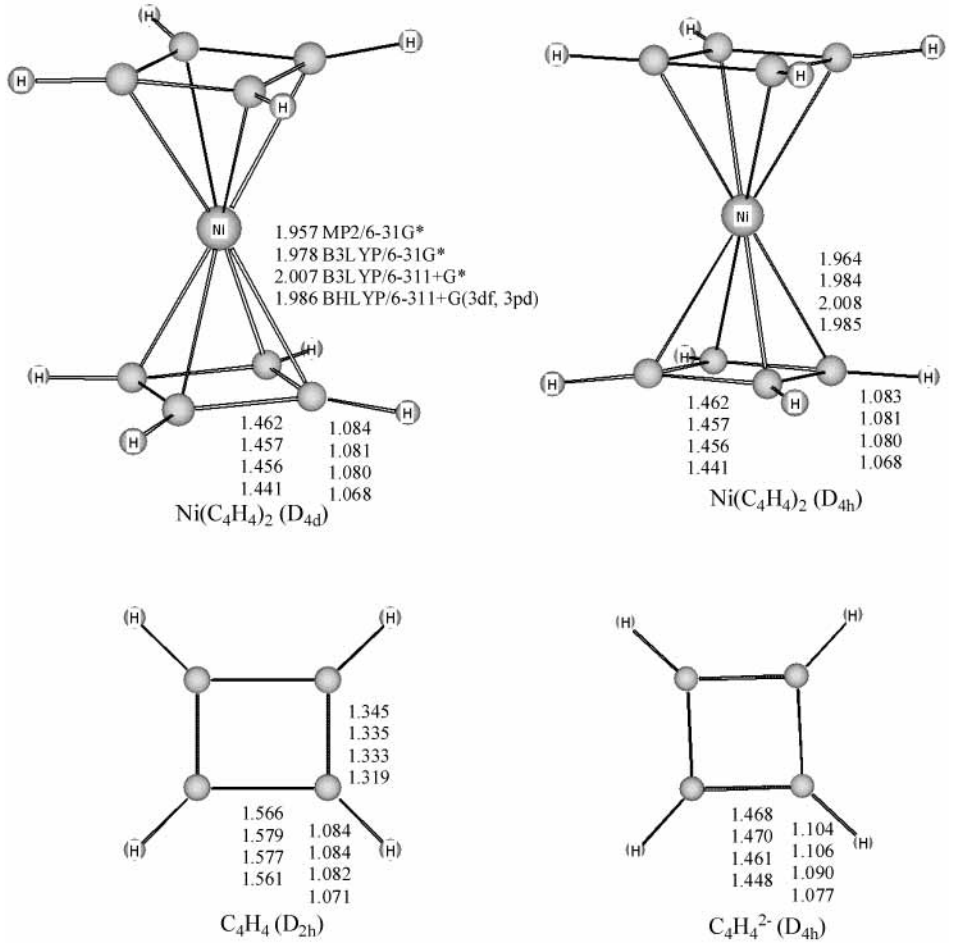

Figure 2. Optimized molecular structures, along with their geometrical parameters, for $Ni(C_4H_4)_2$ (D_{4d}), $Ni(C_4H_4)_2$ (D_{4h}), C_4H_4 (D_{2h}), and $C_4H_4^{2-}$ (D_{4h}).

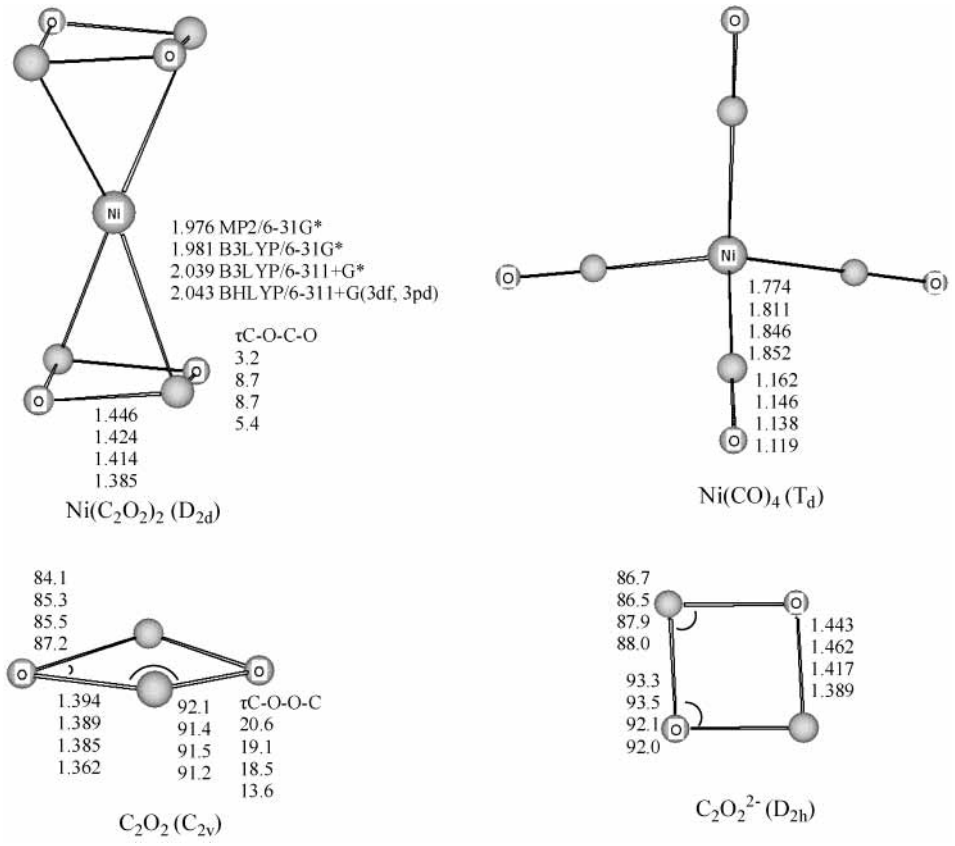

Figure 3. Optimized molecular structures, along with their geometrical parameters, for $Ni(C_2O_2)_2$ (D_{2d}), $Ni(CO)_4$ (T_d), C_2O_2 (C_{2v}), and $C_2O_2^{2-}$ (D_{2h}).

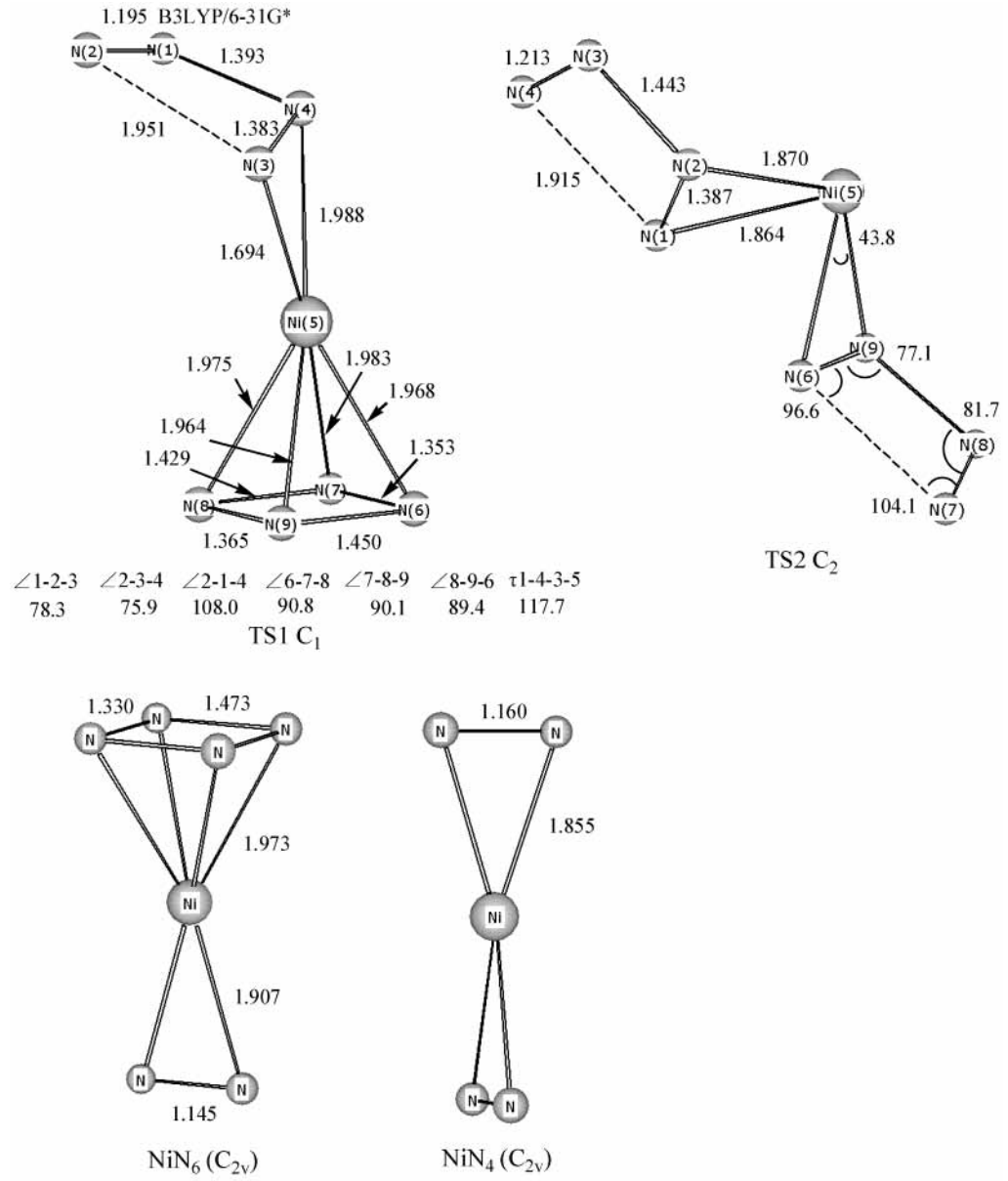

Figure 4. Optimized molecular structures, along with their geometrical parameters, for the transition states (TS1 and TS2) and dissociation products (NiN_6 (C_{2v}) and NiN_4 (C_{2v})).

the dissociation reactions were investigated at the B3LYP/6-31G* level of theory. As shown in Figure 4, two transition states (TS1, TS2) were found on the potential energy surface. TS1 corresponds to one N_2 elimination and TS2 corresponds to two N_2 eliminations, lying 37.1 and 84.9 kcal/mol above $Ni(N_4)_2$, respectively, at the B3LYP/6-31G* level of theory with ZPE corrections. Such high dissociation barriers may be attributed to its strong ligand ↔ metal interaction. The high dissociation barriers suggest that $Ni(N_4)_2$ should be stable enough to resist decomposition. The IRC calculation confirms that TS1 is connected to $Ni(N_4)_2$ on the reactant side and to NiN_6 (C_{2v}) and N_2 on the product side. Moreover, the IRC path suggests that there is a ring slippage, which brings the hapticity from η^4 to η^2 before the N_2 molecule starts to pull out. On the other hand, starting from TS2, the IRC leads to NiN_4 (C_{2v}) and two N_2 molecules. From the results presented here, it can be inferred that the elimination of N_2 molecules is a stepwise process. In addition, concerning possible interactions with the environment, such as other ligands (e.g., H^-, OH^-, and OR^-), we looked into the energy levels of the frontier orbitals of $Ni(N_4)_2$ at the B3LYP/6-31G* level of theory. The energy levels of the frontier orbitals are −8.94 and −4.62 eV for the HOMO and LUMO of $Ni(N_4)_2$, respectively. For a comparison, the energy levels of the frontier orbitals of $Ni(C_4H_4)_2$ (HOMO, −5.23 eV; LUMO, −0.64 eV) and $Ni(C_2O_2)_2$ (HOMO, −7.71 eV; LUMO, −3.81 eV) were also examined at the same level of theory. The large HOMO−LUMO gaps for these three complexes suggest that they all may be thermodynamically stable. The lower LUMO for $Ni(N_4)_2$ suggests that it would be chemically more reactive as a Lewis acid than $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$. Therefore $Ni(N_4)_2$ may be more prone to act as an electrophile than $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$ in chemical reactions.

To compare the stabilities of $Ni(N_4)_2$ with the recently predicted ScN_7, ThN_6, N_5ThN_7, and $Fe(N_5)_2$, we investigated the energy release of $Ni(N_4)_2$ at the B3LYP/6-31G* level of theory, considering a Ni atom and four N_2 molecules as possible final dissociation products. The predicted ScN_7 lies about 36 kcal/mol per N_2 unit higher in energy above a Sc atom and $^7/_2N_2$.[13] For ThN_6, it lies about 24 kcal/mol per N_2 unit above the energy of a Th atom and $3N_2$.[15] The energy of N_5ThN_7 lies

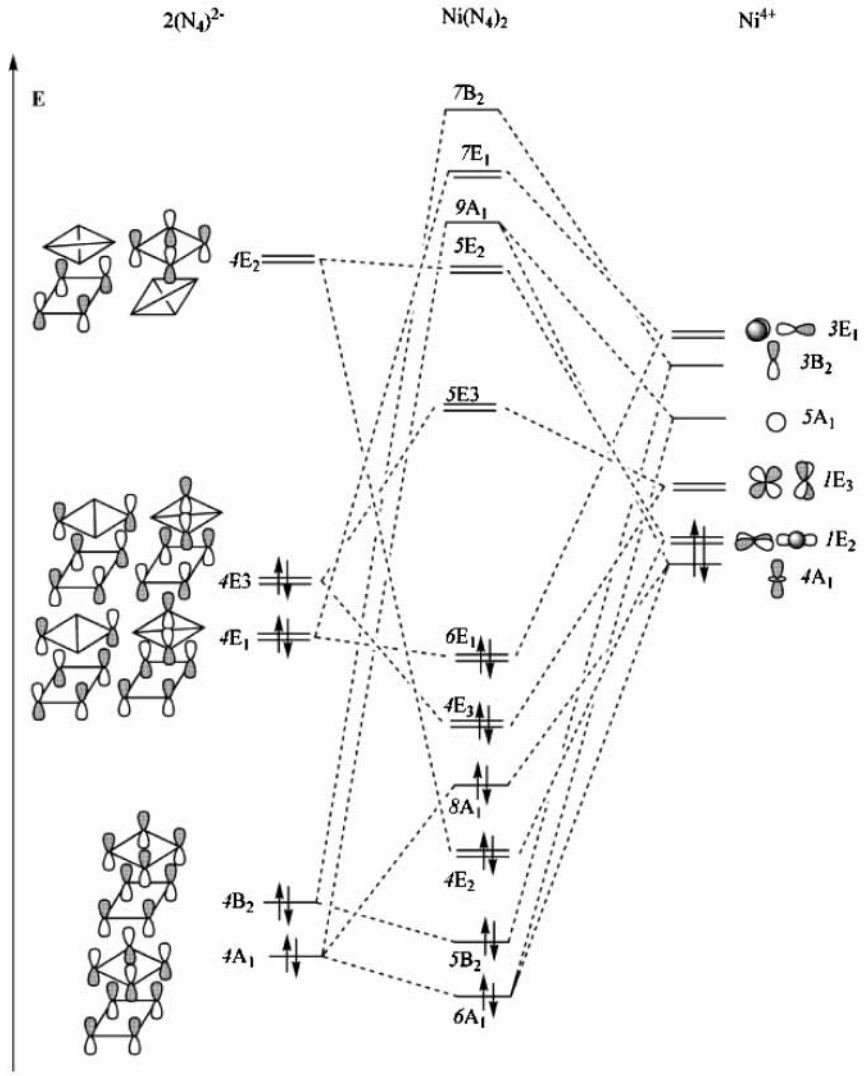

Figure 5. A qualitative frontier molecular orbital correlation diagram for $Ni(N_4)_2$ (D_{4d}).

22 kcal/mol per N_2 unit higher than that of a Th atom and six N_2 molecules.[14] The calculated reaction energy for the decay of $Fe(N_5)_2$ into the most stable products of an Fe atom and five N_2 molecules was predicted to be 45 kcal/mol per N_2 unit.[16] The present calculation on the dissociation of $Ni(N_4)_2$ into a Ni atom and $4N_2$ is 52.5 kcal/mol per N_2 unit including ZPE correction (as shown in Table 3). It seems that $Ni(N_4)_2$ is energetically substantially higher than the predicted ScN_7, ThN_6, N_5ThN_7, and $Fe(N_5)_2$. If $Ni(N_4)_2$ could be prepared, it would be an effective HEDM.

From the results presented in Tables 1 and 2, it is noted that the theoretically predicted geometries (minimum or saddle point) and relative energies are dependent upon the methods and basis sets employed, which have also been pointed out by other authors.[9,37] It should be mentioned that electron correlation plays an important role in these Ni complexes. Moreover, larger basis sets produce more accurate descriptions of electrons that are very important for these complexes containing metal−ligand interaction. Considering that the MP2 method is usually liable in overestimating the electron correlation effect and both 6-311+G* and 6-311+G(3df,3pd) involve diffuse functions, our view at present is that the results obtained at the B3LYP/6-311+G* and BHLYP/6-311+G(3df,3pd) levels of theory are preferable to those obtained at the MP2/6-31G* and B3LYP/6-31G* levels of theory. However, for $Ni(C_4H_4)_2$ with D_{4d} symmetry, the B3LYP/6-311+G* level of theory predicts it to be a minimum while the BHLYP/6-311+G(3df,3pd) predicts it to be a transition state. We then optimized the geometries of the staggered and eclipsed conformers of $Ni(C_4H_4)_2$ and performed frequency analyses at the B3LYP/6-311+G(3df,3pd) level of theory. The calculated result suggests that the eclipsed conformer is a local minimum while the staggered one is a transition state. That B3LYP and BHLYP methods give the identical result with the same 6-311+G(3df,3pd) basis set suggests the importance of the inclusion of the f-function in the present calculation.

In $Ni(C_4H_4)_2$ (the following discussions focus on the conformation of D_{4h} symmetry, until otherwise stated), all bond lengths of C−C bonds are equal, being close to those of $C_4H_4^{2-}$ (D_{4h}). NBO analysis shows that the WBIs for all C−C bonds in $Ni(C_2H_4)_2$ are 1.2, which suggests that there exists strong electronic delocalization in the vicinity of the two C_4 ring planes. The covalent radius value for carbon is 0.77 Å.[36] The bond length of Ni−C in $Ni(C_4H_4)_2$ is close to the sum of the covalent radii of nickel and carbon (1.98 Å). In $Ni(C_4H_4)_2$, it should be mentioned that all H atoms tip slightly out of the C_4 ring plane, bending away from the nickel atom by a small degree. At the B3LYP/6-31G* level of theory, Mulliken charge analysis shows that all positive charges lie on the nickel (about +0.23), all

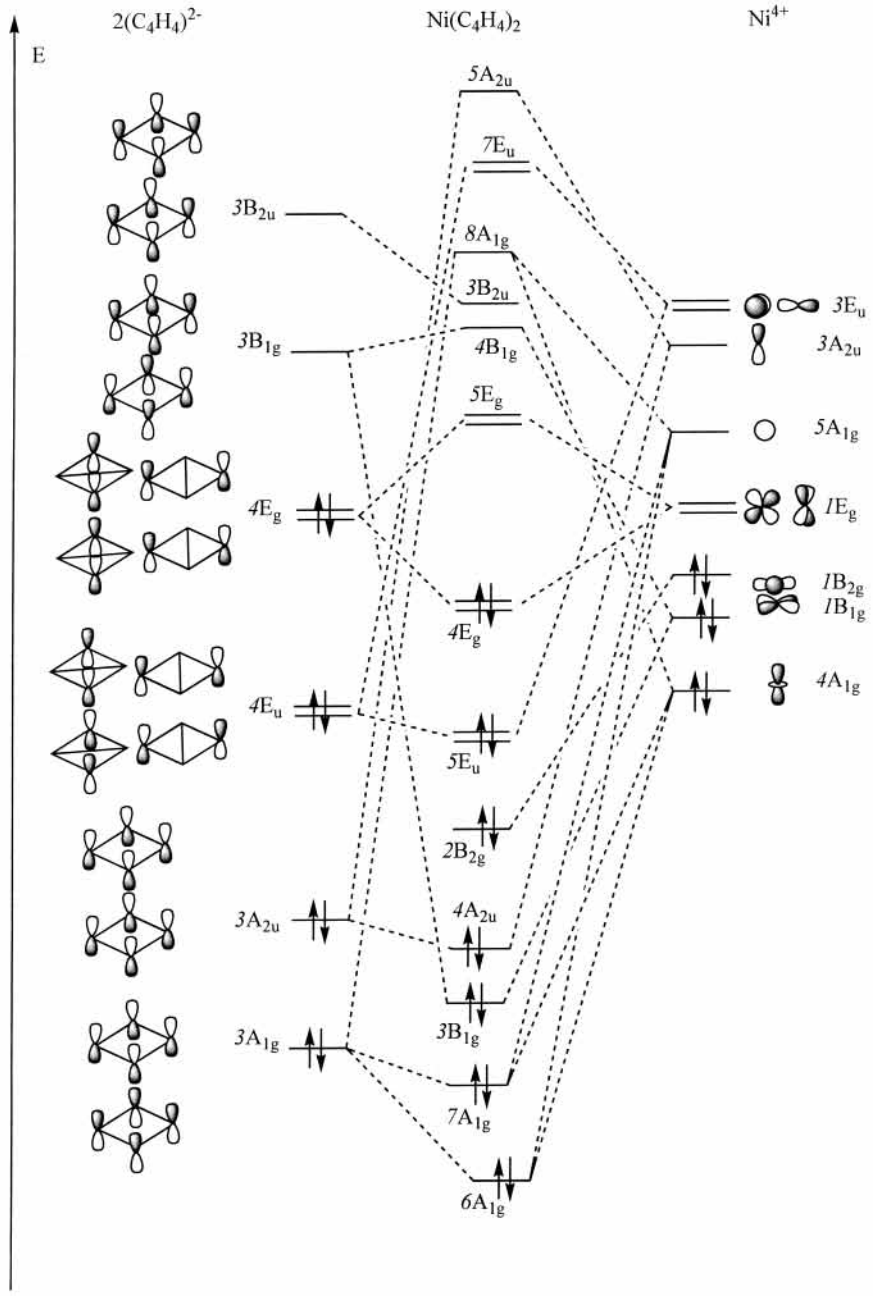

Figure 6. A qualitative frontier molecular orbital correlation diagram for $Ni(C_4H_4)_2$ (D_{4h}).

negative charges populate on the carbons (about −0.03), while no net charges lie on the hydrogens.

$Ni(C_2O_2)_2$, isoelectron with $Ni(N_4)_2$ and $Ni(C_4H_4)_2$, is an isomer of the known nickel carbonyl $Ni(CO)_4$ (T_d). The bond length of C−O in the $Ni(C_2O_2)_2$ is close to that of $C_2O_2^{2-}$ (D_{2h}). The bond length of Ni−C is close to the sum of the covalent radii of the nickel and carbon atoms (1.98 Å). To assess the reliability of our computation, we also optimized the structure of the known $Ni(CO)_4$. For $Ni(CO)_4$ (T_d), our calculated Ni−C bond length is 1.774 (MP2/6-31G*), 1.811 (B3LYP/6-31G*), 1.846 (B3LYP/6-311+G*), and 1.852 Å (BHLYP/6-311+G-(3df,3pd)), while the C−O bond length is 1.162, 1.146, 1.138, and 1.119 Å at the above four levels of theory, respectively. The available experimental bond lengths of Ni−C and C−O in $Ni(CO)_4$ are 1.838 and 1.141 Å, respectively.[38] Our calculated bond lengths at the B3LYP/6-311+G* level of theory are in good agreement with the experimental values. Note that the ligand in $Ni(C_2O_2)_2$ is not a planar ring with a small dihedral angle.

In addition, we also investigated $Ni(N_2)_4$, an isomer of $Ni(N_4)_2$ with four end-on bonded N_2 ligands. The bond length of Ni−N is close to the sum of the covalent radii of nickel and nitrogen atoms (1.91 and 1.96 Å). The bond length of N−N is longer than the experimental triple-bond length of N_2 (1.098 Å).[39] NBO analysis shows that the WBIs for all N−N bonds in $Ni(N_2)_4$ are 2.7, while those for all Ni−N bonds are 0.4. According to Mulliken charge analysis, positive charges lie mainly on the nickel (about +0.41) and partly on the neighboring nitrogens (about +0.03 per N atom), while all negative charges populate on the terminal nitrogens (about −0.13 per N atom).

To estimate the strength of the interactions between the transition metal Ni and the ligands L (L = N_4^{2-}, $C_4H_4^{2-}$, $C_2O_2^{2-}$, N_2, and CO), we performed the calculations on their

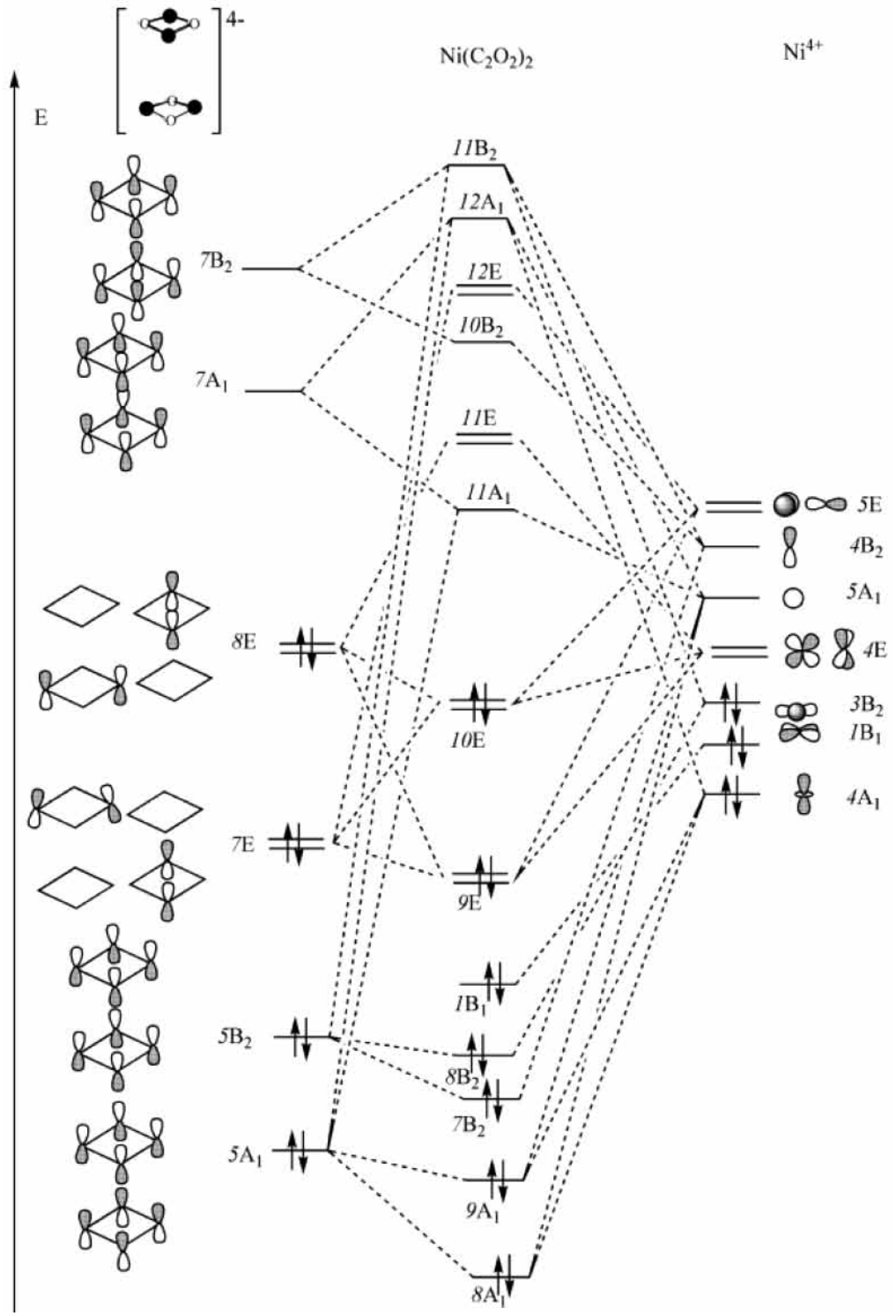

Figure 7. A qualitative frontier molecular orbital correlation diagram for $Ni(C_2O_2)_2$ (D_{2d}).

dissociation energies of the homolytic bond cleavage at the B3LYP/6-31G* level of theory. The results obtained are listed in Table 3. The average dissociation energies of the homolytic bond cleavage for $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ are 71.2, 81.5, and 42.4 kcal/mol, respectively, after ZPE correction. It is obvious that the bond energy ordering is $Ni(C_4H_4)_2 > Ni(N_4)_2 > Ni(C_2O_2)_2$. This energy trend might be attributed to the following two facts: (1) The N_4^{2-} and $C_2O_2^{2-}$ rings both have large lone-pair repulsion, which comes from the N and O atoms, respectively. (2) The ligand $C_2O_2^{2-}$ in $Ni(C_2O_2)_2$ is not a planar ring, which may affect the strength of interaction between the ligand and metal. According to the average dissociation energies of the homolytic bond cleavage for $Ni(N_2)_4$ and $Ni(CO)_4$, we may come to a conclusion that the strength of the interaction between the metal and ligand in $Ni(N_2)_4$ (19.1 kcal/mol) is weaker than that in $Ni(CO)_4$ (37.4 kcal/mol). The available experimental value for the homolytic bond cleavage energy for $Ni(CO)_4$ is 140[40] or 144 kcal/mol,[41,42] while our calculation result is 149.7 kcal/mol after ZPE correction, which agrees well with the experimental value. It can be seen from Table 3 that the $Ni(C_2O_2)_2$ is also high in energy, being 36 kcal/mol per CO unit higher with respect to its most stable dissociation products, a Ni atom and four CO molecules. As shown in Table 3, the dissociation of $Ni(C_4H_4)_2$ into a nickel

TABLE 1: Total Energies [au], Zero-Point Energies [kcal/mol],[a] and Number of Imaginary Vibrational Frequencies[b] of the Complexes Calculated at the MP2/6-31G*, B3LYP/6-31G*, B3LYP/6-311+G*, and BHLYP/6-311+G(3df,3pd) Levels of Theory and of the Transition States Calculated at the B3LYP/6-31G* Level of Theory

complexes	MP2/6-31G*	B3LYP/6-31G*	B3LYP/6-311+G*	BHLYP/6-311+G(3df,3pd)	B3LYP/6-311+G(3df,3pd)[c]
$Ni(N_4)_2$ (D_{4d})		−1945.83111 (21.3) (0)	−1946.07009 (20.9) (0)	−1945.67353 (22.8) (0)	
$Ni(N_4)_2$ (D_{4h})	−1943.53893 (87.8) (1)	−1945.82982 (21.1) (1)	−1946.06978 (20.7) (1)	−1945.67337 (22.6) (1)	
$Ni(N_2)_4$ (T_d)	−1944.08104 (19.3) (0)	−1946.28446 (18.9) (0)	−1946.57301 (18.5) (0)	−1946.18202 (19.1) (0)	
$Ni(C_4H_4)_2$ (D_{4h})	−1815.49681 (88.3) (1)	−1817.67406 (81.2) (1)	−1817.88106 (80.5) (0)	−1817.54734 (83.7) (0)	−1817.92389 (80.7) (0)
$Ni(C_4H_4)_2$ (D_{4d})	−1815.49772 (88.1) (0)	−1817.67596 (81.4) (0)	−1817.88066 (80.3) (0)	−1817.54650 (83.6) (1)	−1817.92341 (80.6) (1)
$Ni(C_2O_2)_2$ (D_{2d})	−1958.69998 (18.7) (0)	−1961.07145 (17.8) (0)	−1961.33945 (17.0) (0)	−1960.97509 (18.8) (0)	
$Ni(CO)_4$ (T_d)	−1959.28060 (21.1) (0)	−1961.54774 (19.6) (0)	−1961.84005 (19.5) (0)	−1961.45982 (20.1) (0)	
TS1 (C_1)		−1945.76883 (19.3) (1)			
TS2 (C_2)		−1945.68993 (17.6) (1)			

[a] In the first parentheses. [b] In the second parentheses. [c] Only the eclipsed and staggered conformers of $Ni(C_4H_4)_2$ were calculated at the B3LYP/6-311+G(3df,3pd) level of theory.

TABLE 2: Relative Energy [kcal/mol] with ZPE Corrections Calculated at the MP2/6-31G*, B3LYP/6-31G*, B3LYP/6-311+G*, and BHLYP/6-311+G(3df,3pd) Levels of Theory

complexes	MP2/6-31G*	B3LYP/6-31G*	B3LYP/6-311+G*	BHLYP/6-311+G(3df,3pd)	complexes	MP2/6-31G*	B3LYP/6-31G*	B3LYP/6-311+G*	BHLYP/6-311+G(3df,3pd)
$Ni(N_4)_2$ (D_{4d})		0.0	0.0	0.0	$Ni(C_4H_4)_2$ (D_{4d})	−0.8	−1.0	0.1	0.4
$Ni(N_4)_2$ (D_{4h})		0.6	−0.002	−0.1	$Ni(C_2O_2)_2$ (D_{2d})	0.0	0.0	0.0	0.0
$Ni(N_2)_4$ (T_d)		−286.9	−318.0	−322.8	$Ni(CO)_4$ (T_d)	−361.0	−297.1	−311.6	−302.9
$Ni(C_4H_4)_2$ (D_{4h})	0.0	0.0	0.0	0.0					

TABLE 3: The Dissociation Energies [kcal/mol] of the Homolytic Bond Cleavage Calculated at the B3LYP/6-31G* Level of Theory

reactions	ΔH[a]	ΔH with ZPE[a]	exptl value
$Ni(N_4)_2$ (D_{4d}) → Ni + $2N_4$ (D_{2h})	145.9 (72.9)	142.4 (71.2)	
$Ni(C_4H_4)_2$ (D_{4d}) → Ni + $2C_4H_4$ (D_{2h})	167.7 (83.8)	163.1 (81.5)	
$Ni(C_2O_2)_2$ (D_{2d}) → Ni + $2C_2O_2$ (C_{2v})	87.7 (43.8)	84.9 (42.4)	
$Ni(N_2)_4$ (T_d) → Ni + $4N_2$	81.2 (20.3)	76.3 (19.1)	
$Ni(CO)_4$ (T_d) → Ni + 4CO	156.5 (39.1)	149.7 (37.4)	140,[b] 144[c]
$Ni(N_4)_2$ (D_{4d}) → Ni + $4N_2$	−202.6 (−50.6)	−209.9 (−52.5)	
$Ni(C_2O_2)_2$ (D_{2d}) → Ni + 4CO	−139.1 (−34.8)	−144.1 (−36.0)	
$Ni(C_4H_4)_2$ (D_{4d}) → Ni + $4C_2H_2$ ($D_{\infty h}$)	200.8 (50.2)	186.2 (46.6)	

[a] The average energies are listed in the parentheses. [b] Reference 40. [c] References 41 and 42.

atom and four C_2H_2 molecules is an endothermal reaction, which suggests that $Ni(C_4H_4)_2$ is not a high-energy species.

To understand the bonding between the metal and ligand in $Ni(N_4)_2$ (D_{4d}), as well as that in $Ni(C_4H_4)_2$ (D_{4h}) and $Ni(C_2O_2)_2$ (D_{2d}), qualitative frontier molecular orbital correlation diagrams calculated at the HF/STO-3G level of theory are shown in Figures 5−7, respectively. Our first expectation was that the bonding between the 2pπ orbitals of the ligand and the d orbitals of the metal would be the main bonding scheme for these three complexes. To further explore the orbital interactions between the ligand and metal, we analyzed the contribution of the orbitals of the ligand and atomic orbitals (AOs) of the Ni^{4+} to the frontier molecular orbitals (MOs) of these three complexes. For $Ni(N_4)_2$, 39% of the $4E_2$ MOs is from the $1E_2$ AOs (d_{xy} and $d_{x^2-y^2}$) of the Ni^{4+} and only 0.4% is from the virtual $4E_2$ orbitals of $2(N_4)^{2-}$ (besides, 54% is from the $3E_2$ orbitals of $2(N_4)^{2-}$ composed of 2s and 2p hybrid orbitals that are not depicted in Figure 5), which suggests that the metal → ligand E_2 back-donation will be very weak. This might result from the high energy of the virtual $4E_2$ orbitals of the ligand and the large positive charge of +4 of the metal. The $6E_1$ MOs of $Ni(N_4)_2$ consist mainly of the orbitals of the ligand, including 22% from the $4E_1$ and 68% from the $3E_1$ ($3E_1$ orbitals are formed from the 2s and 2p hybrid orbitals that are not depicted in Figure 5). The virtual $3E_1$ AOs (p_x and p_y) of the metal only account for 3% of the $6E_1$ MOs of $Ni(N_4)_2$, indicating that the ligand → metal E_1 donation will not be strong. This might be attributed to the fact that the virtual $3E_1$ AOs of the Ni^{4+} are not as important acceptors as the empty d orbitals. The $4E_3$ MOs of $Ni(N_4)_2$ consist mostly of the orbitals of the ligand, including 33% from the $4E_3$ and 48% from the $3E_3$ ($3E_3$ orbitals are formed from the 2s and 2p hybrid orbitals of $2(N_4)^{2-}$, which are not exhibited in Figure 5). The virtual $1E_3$ AOs (d_{xz} and d_{yz}) of the Ni^{4+} account for 14% of the $4E_3$ MOs of $Ni(N_4)_2$, suggesting that there exists strong ligand → metal π donation. This strong ligand → metal π donation contributes to stabilization of $Ni(N_4)_2$. For $Ni(C_4H_4)_2$, 73% of the $4E_g$ MOs is from the $4E_g$ orbitals of $2(C_4H_4)^{2-}$ and 20% is from the virtual $1E_g$ AOs (d_{xz} and d_{yz}) of the Ni^{4+}. And 45% of the $5E_u$ MOs is from the $4E_u$ orbitals of the $2(C_4H_4)^{2-}$, and 32% is from the virtual $3E_u$ AOs (p_x and p_y) of the Ni^{4+}. Obviously, there exist very strong ligand → metal π donations in $Ni(C_4H_4)$, which greatly contribute to stabilization of $Ni(C_4H_4)_2$. In addition, almost all of the $3B_{1g}$ MO of $Ni(C_4H_4)_2$ is from the $1B_{1g}$ AO

TABLE 4: Harmonic Vibrational Frequencies [cm^{-1}] and IR Intensities [km/mol] for $Ni(N_4)_2$ (D_{4d}), $Ni(C_4H_4)_2$ (D_{4d}), and $Ni(C_2O_2)_2$ (D_{2d}) at the B3LYP/6-31G* Level of Theory[a]

$Ni(N_4)_2$ (D_{4d})			$Ni(C_4H_4)_2$ (D_{4d})			$Ni(C_2O_2)_2$ (D_{2d})		
mode	freq	IR	mode	freq	IR	mode	freq	IR
B_1	51	0	B_1	64	0	B_1	92	0
E_1	169	2	E_1	146	4	E	113	2
A_1	383	0	A_1	373	0	E	257	0
E_3	429	0	E_3	435	0	A_1	289	0
E_1	473	9	E_1	436	30	E	365	0
B_2	619	38	B_2	568	8	B_2	452	1
E_2	653	0	E_2	633	0	A_1	520	0
E_1	951	2	E_3	685	0	B_2	567	1
E_2	951	0	E_1	732	0	A_2	568	0
E_3	960	0	E_2	790	0	B_1	652	0
E_2	1156	0	B_2	798	98	E	873	140
A_1	1195	0	A_1	801	0	E	940	152
B_2	1199	3	E_2	924	0	A_1	972	0
			E_3	955	0	B_2	985	0
			E_1	958	57	A_1	1109	0
			E_2	989	0	B_2	1119	13
			A_2	1186	0			
			B_1	1188	0			
			E_2	1204	0			
			B_2	1263	45			
			A_1	1267	0			
			E_1	1359	2			
			E_3	1367	0			
			E_2	3254	0			
			E_3	3272	0			
			E_1	3272	15			
			B_2	3289	0			
			A_1	3289	0			

[a] The intensities of degenerate modes have been doubled.

($d_{x^2-y^2}$) of the Ni^{4+}, which indicates that there may be no B_{1g} back-donation from the Ni^{4+} to ligand. For $Ni(C_2O_2)_2$, 33% and 44% of the 10E MOs are from the 8E (composed of p_z orbitals of the C atoms) and 7E (composed of p_z orbitals of the O atoms) orbitals of the $2(C_2O_2)^{2-}$, and 4% and 15% are from the 5E (p_x and p_y) and 4E (d_{xz} and d_{yz}) AOs of the Ni^{4+}, respectively. While 16% and 50% of the 9E MOs of $Ni(C_2O_2)_2$ are formed from the 8E and 7E orbitals of $2(C_2O_2)^{2-}$, 10% and 9% are from the 5E and 4E AOs of the Ni^{4+}, respectively. Clearly, there exist very strong ligand $\rightarrow$ metal π donations, which greatly contribute to stabilization of $Ni(C_2O_2)_2$. In addition, almost all of the $8B_2$ MO of $Ni(C_2O_2)_2$ is from $3B_2$ (d_{xy}) AO of the metal, suggesting that there may be no B_2 back-donation from the Ni^{4+} to ligand. In conclusion, the MO component analyses show that there are strong ligand $\rightarrow$ metal π donations in $Ni(N_4)_2$, as well as in $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$, which greatly contribute to their stabilizations.

To facilitate the identification of the three NiL_2 ($L = N_4^{2-}$, $C_4H_4^{2-}$, and $C_2O_2^{2-}$) complexes, harmonic vibrational frequencies and their associated IR intensities at the B3LYP/6-31G* level of theory are listed in Table 4.

4. Summary

In the present quantum chemical study, the geometries, energies, harmonic vibrational frequencies, and nature of bonding of three isoeletronic-liganded NiL_2 ($L = N_4^{2-}$, $C_4H_4^{2-}$, and $C_2O_2^{2-}$) sandwich complexes were investigated by using the MP2 and DFT methods. Harmonic vibrational frequency analyses show that these three complexes are all local minima on their PES. The stable structure for $Ni(N_4)_2$ is a staggered conformer. The dissociation barriers at the B3LYP/6-31G* level of theory indicate that $Ni(N_4)_2$ is kinetically stable enough to resist dissociation. The calculated reaction energies for the dissociation of $Ni(N_4)_2$, $Ni(C_4H_4)_2$, and $Ni(C_2O_2)_2$ into their respective stable products suggest that $Ni(N_4)_2$ and $Ni(C_2O_2)_2$ are high-energy species; however, $Ni(C_4H_4)_2$ is not. According to the qualitative frontier MO correlation diagrams and quantitative frontier MO component analyses, we may come to a conclusion that there exist strong ligand $\rightarrow$ metal π donations in $Ni(N_4)_2$, as well as in $Ni(C_4H_4)_2$ and $Ni(C_2O_2)_2$. These strong π donations greatly contribute to the stabilizations of the three complexes.

Supporting Information Available: Figure S-1 shows some molecular orbitals that correspond to the MO correlation diagram for $Ni(N_4)_2$ (D_{4d}). This material is available free of charge via the Internet at http://pubs.acs.org.

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