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ARTICLES

$[N_3MN_5]^q$: A Type of Low-Lying Sandwich-like Isomer on $[N_8M]^q$ Hypersurface with (M, q) = (Ni, 0), (Co, −1), and (Fe, −2)

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Recently, design and assembly of small, high-energy-density, all-nitrogen units into more complex sandwich-like forms have received growing attention. In this paper, we report a type of heterodecked sandwich-like structures $[N_3MN_5]^q$ containing two odd-membered all-nitrogen rings (N_3 and N_5) on the hypersurface of $[N_8M]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2)]. At the B3LYP/6-311+G(d) level, the new isomers are energetically more stable than the previously reported homodecked sandwich-like isomers $[N_4MN_4]^q$ based on the even-membered all-nitrogen ring N_4^{2-}. In particular, the $\eta^3-\eta^2$ ($\eta^3-\eta^1$) isomers of $[N_3MN_5]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2)] possess considerable kinetic stability for laboratory characterization. The bond length and natural charge analysis of $[N_3MN_5]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2)] indicate that each complex possesses the smallest triplet all-nitrogen ring $^3N_3^-$. The unique stability of the presently designed heterodecked sandwich-like complexes await future laboratory investigations.

1. Introduction

Neutral and charged polynitrogen have received attention for more than 20 years,[1] due to their potential use as possible candidates for environment-friendly high-energy-density materials (HEDM).[1] Design and assembly of potential sandwich-like complexes starting from small and simple all-nitrogen units have continued to attract considerable attention.[2] The recent significant breakthrough that the all-nitrogen species N_5^-,[3] N_5^+,[1d,e] and N_3[4] can be experimentally isolated has raised much hope for HEDM chemistry. Besides the interest in potential energetic materials, the study of all-nitrogen unit-based compounds has fundamental importance. The penta-atomic N_5^- possesses a perfect polypentangle ring, and its electronic structure is quite similar to the isoelectronic and well-known cylcopentadieyl ($C_5H_5^-$) with 6π electrons. Thus, N_5^- is an energetic noncarbon aromatic unit.[5] Similarly, the tetra-atomic N_4^{2-} is isoelectronic to another 6π-aromatic hydrocarbon, $C_4H_4^{2-}$.[6] Understanding the structural, stability, and electronic properties of both the naked and assembled all-nitrogen compounds should help in rational designing of more complex energetic species.

Up to now, a number of studies have been reported on the design of sandwich-like and half-sandwich-like complexes comprising the N_4,[2] N_5,[7] N_6,[8] and N_7[9] cyclic units, among which only cyclic-N_5^- is experimentally known. Recently, we for the first time found that the η^3-N_3 ring can be effectively assembled into novel sandwich-like compounds $[N_3MN_3]^q$, $[N_3MCp]^q$, $[N_3M(CO)_2N_3]^q$, and $[N_3M(CO)_3]^q$ (M = Fe, Co, Ni).[10] The natural bond analysis indicate that the assembled η^3-N_3 ring can be viewed as a diradical-like D_{3h}-symmetrized anion ($^3N_3^-$), which was first calculated by Bartlett.[11] The $^3N_3^-$ ring should be promising as a building block for designing various complex HEDM species.

In this paper, we further our study on the η^3-assembled N_3-ring. In order to propose potential HEDM candidates, two theoretical groups[2] have studied the sandwich-like complexes $[N_4MN_4]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2)] in homodecked form containing the even-membered aromatic ring N_4^{2-}. Here, we show that on the hypersurface of $[N_8M]^q$, another kind of isomer, i.e., $[N_3MN_5]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2), which involve the same central metal atom as previous reports], which takes the heterodecked form with two odd-membered rings ($^3N_3^-$ and N_5^-), not only have good kinetic stability but also are energetically more stable than the corresponding homodecked form $[N_4MN_4]^q$, which was previously reported.[2]

2. Theoretical Methods

All the calculations are carried out using the Gaussian 98[12] and Gaussian 03[13] program packages. The initial structural search for isomers and transition states is performed at the B3LYP[14]/6-31G(d)[15] level. The final structures, energies, and frequencies of the local minima and transition states are calculated at the B3LYP/6-311+G(d)[14d,15b,16] level. Connections of the transition states between designated local minima are carefully confirmed by intrinsic reaction coordinate (IRC)[17] calculations at the B3LYP/6-31G(d) level. For some crucial structures, the single point energies are obtained at B3LYP/6-311+G(3df)[18]//B3LYP/6-311+G(d) level. Moreover, when computationally feasible, the CCSD(T)[19]/6-311+G(d) calculations are carried out with specific species using the B3LYP/6-311+G(d) structures. In order to characterize the bonding of some crucial isomers, the natural bond orbital (NBO) are calculated at the B3LYP/6-311+G(d) level.

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TABLE 1: Total Energies (atomic units), Relative Energies (in Parentheses, kcal/mol), and the $\|t_1\|$ Diagnostics for All Isomers and Transition States for $[N_3MN_5]^q$ (M, *q*) = (Ni, 0), (Co, −1), and (Fe, −2)

species	B3LYP/6-311+G(d)	B3LYP/6-311+G(3df)// B3LYP/6-311+G(d)	CCSD(T)/6-311+G(d)// B3LYP/6-311+G(d)	$\|t_1\|$
Ni-1	−1946.180 04 (0.0)	−1946.222 996 (0.0)	−1943.966 112 (0.0)	0.022
Ni-2	−1946.213 33 (−20.9)	−1946.251 734 (−18.0)	−1944.007 875 (−26.2)	0.075
Ni-3	−1946.272 029 (−57.7)	−1946.30726 (−52.9)	−1944.025 327 (−37.2)	0.054
Ni−P	−1946.285 12 (−65.9)	−1946.321 14 (−61.6)	−1944.054 219 (−55.3)	
Ni-TS1/2	−1946.178 36 (1.1)	−1946.220 316 (1.7)	−1943.962 431 (2.3)	0.022
Ni-TS1/P	−1946.155 36 (15.5)	−1946.195 511 (17.2)	−1943.952 222 (8.7)	0.074
Ni-TS2/P	−1946.185 63 (−3.5)	−1946.221 02 (1.2)	−1943.959 97 (3.9)	0.031
$[N_4NiN_4](D_{4d})$	−1946.070 104 (69.0)	−1946.115 05 (67.7)	−1943.850 57 (72.5)	0.027
Co-1	−1820.758 902 (0.0)	−1820.796 561 (0.0)	−1818.574 756 (0.0)	0.054
Co-2	−1820.788 843 (−18.8)	−1820.821 599 (−15.7)	−1818.597 419 (−14.2)	0.058
Co-4	−1820.834 723 (−47.6)	−1820.869 524 (−45.8)	−1818.644 225 (−43.6)	0.059
Co-5	−1820.839 386 (−50.5)	−1820.870 977 (−46.7)	−1818.667 678 (−58.3)	0.093
Co−P	−1820.835 096 (−47.8)	−1820.868 564 (−45.2)	−1818.638 163 (39.8)	
Co-TS1/2	−1820.757 795 (0.7)	−1820.795 392 (0.7)	−1818.570 779 (2.5)	0.053
Co-TS1/4	−1820.730 188 (18.0)	−1820.766 774 (18.7)	−1818.544 646 (18.9)	0.057
Co-TS2/5	−1820.750 237 (5.4)	−1820.782 64 (8.7)	−1818.555 992 (11.8)	0.071
Co-TS2/P	−1820.754 628 (2.7)	−1820.786 549 (6.3)	−1818.559 583 (9.5)	0.057
$[N_4CoN_4]^-(D_{4d})$	−1820.710 705 (30.2)	−1820.750 719 (28.8)	−1818.521 482 (33.4)	0.047
Fe-1	−1701.577 24 (0.0)	−1701.612 629 (0.0)		
Fe-2	−1701.586 678 (−5.9)	−1701.618 58 (−3.7)		
Fe-3	−1701.666 642 (−56.1)	−1701.697 605 (−53.3)		
Fe-4	−1701.663 263 (−54.0)	−1701.696 523 (−52.6)		
Fe-5	−1701.699 039 (−76.4)	−1701.729 989 (−73.6)		
Fe−P	−1701.624 766 (−29.8)	−1592.090 678 (−28.5)		
Fe-TS1/2	−1701.568 789 (5.3)	−1701.601 173 (7.2)		
Fe-TS1/4	−1701.550 22 (17.0)	−1701.583 916 (18.0)		
Fe-TS2/5	−1701.564 613 (7.9)	−1701.596 243 (10.3)		
Fe-TS2/P	−1701.555 765 (13.5)	−1701.586 356 (16.5)		
$[N_4FeN_4]^{2-}(D_{4d})$	−1701.573 337 (2.4)	−1701.610 511 (1.3)		

3. Results and Discussions

The total energies and the relative energies of $[N_3MN_5]^q$ and $[N_4MN_4]^q(D_{4d})$ complexes are listed in Table 1 [(M, *q*) = (Ni, 0) (Co, −1) (Fe, −2)]. The energies of **Ni-1** ($[N_3NiN_5]$), **Co-1** ($[N_3CoN_5]^-$), and **Fe-1** ($[N_3FeN_5]^{2-}$) are set to zero as reference, respectively. By means of the interrelation among the isomers and the corresponding relative energies, the schematic profiles of the potential energy surfaces (PESs), structures of isomer, and transition states are depicted as shown in Figure 1 for the $[N_3NiN_5]$ system, in Figure 2 for the $[N_3CoN_5]^-$ system, and in Figure 3 for the $[N_3FeN_5]^{2-}$ system, respectively. All the isomers are singlet state with closed shell except ^{3}**Co-2**.

3.1. $[N_3NiN_5]$ System. The **Ni-1** and **Ni-2** isomers can both be considered as the sandwich-like complexes of $[N_3NiN_5]$. The difference is that, in **Ni-1**, both the N_3 and N_5 units use their "face" to interact with the Ni atom, whereas in **Ni-2**, the face of N_3 and the side of N_5 interact with Ni. Thus, we call **Ni-1** the "$\eta^3-\eta^5$" form and **Ni-2** the "$\eta^3-\eta^2$ ($\eta^3-\eta^1$)" form. Compared with the homodecked $\eta^4-\eta^4$ isomer $[N_4NiN_4](D_{4d})$

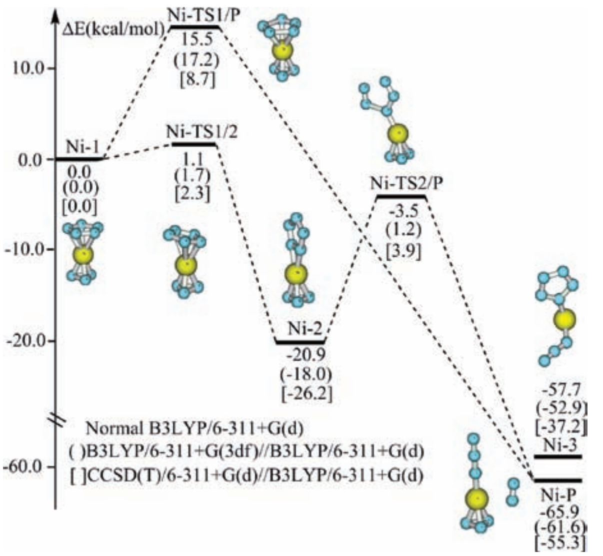

Figure 1. Schematic potential-energy surface of the $[N_3NiN_5]$ system.

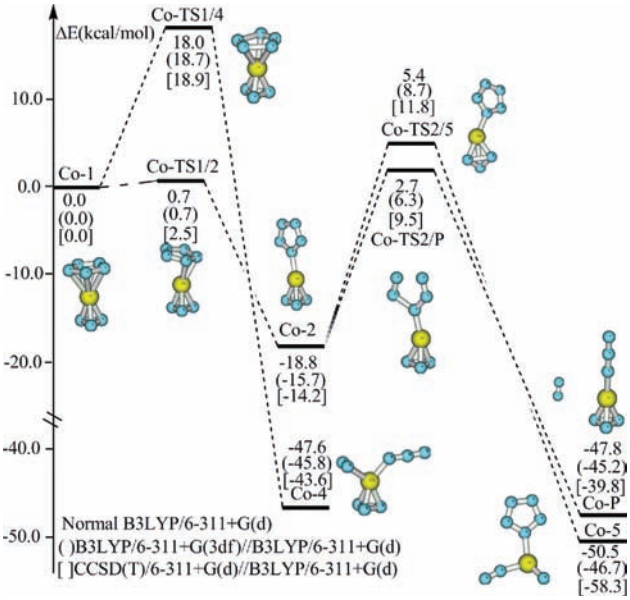

Figure 2. Schematic potential-energy surface of the $[N_3CoN_5]^-$ system.

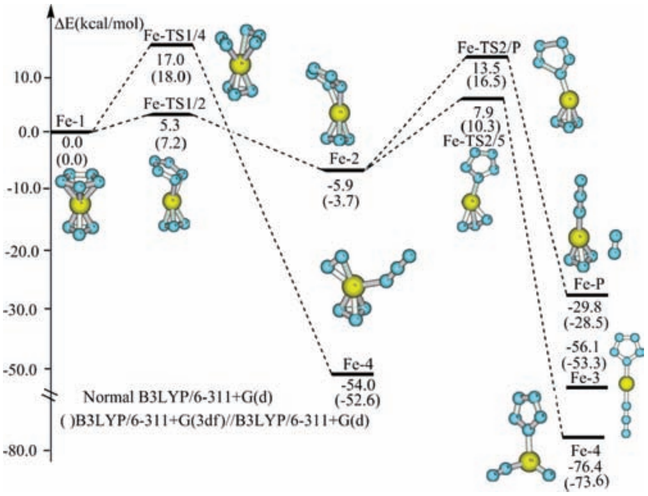

Figure 3. Schematic potential-energy surface of the $[N_3FeN_5]^{2-}$ system.

that was studied by Li et al.,[2a,b] our designed **Ni-1** and **Ni-2** are of the heterodecked sandwich type containing two odd-membered ring units (N_3 and N_5). Energetically, **Ni-1** is much less stable than **Ni-2** by 20.9 kcal/mol. Yet both forms are significantly lower in energy than $[N_4NiN_4](D_{4d})$ by 69.0 and 89.9 kcal/mol, respectively. Kinetically, **Ni-1** can very easily undergo a deck-opening process of N_5 to form **Ni-2** with a barrier of only 1.1 kcal/mol. Nevertheless, the fragmentation of **Ni-1** to **Ni−P** ($N_3NiN_3 + N_2$) (at −65.9 kcal/mol) is relatively difficult with a barrier of 15.5 kcal/mol. **Ni-2** has two evolution pathways, one is to isomerize back to the $\eta^3-\eta^5$ sandwich isomer **Ni-1** with the barrier 22.0 kcal/mol and the other is to fragmentize to **Ni−P** with the barrier 17.4 kcal/mol. The other low-lying isomer is **Ni-3**, which contains a η^1-N_5 ring and linear NNN, and no transition state between **Ni-2** and **Ni-3** has been found, in spite of numerous attempts. The optimization procedure suggests that the η^3-N_3 ring is kinetically very stable. Also, search of the M-insertion transition state to the N_5-ring always results in a N_2-extrusion process (i.e., **TS2/P**). According to our experience and previous reports, we expect that the complexes based on all-nitrogen ring, such as **Ni-2**, will not convert favorably to the complexes in which the metal atom is incorporated into the N_3 or N_5 rings.[2a,b,10,20]

The rate-determining process of **Ni-2** is the direct fragmentation rather than the N_5-closure. Therefore, the $\eta^3-\eta^2$ isomer **Ni-2** is more stable than **Ni-1** in both thermodynamics and kinetics. We note that the newly found isomer **Ni-2** in the heterodecked form $[N_3NiN_5]$ is thermodynamically much more stable than the previously reported homodecked isomer $[N_4NiN_4]$.[2]

3.2. $[N_3CoN_5]^-$ and $[N_3FeN_5]^{2-}$ Systems. The anionic $[N_3CoN_5]^-$ and $[N_3FeN_5]^{2-}$ systems are both isoelectronic to the neutral $[N_3NiN_5]$ system. The process of the N_5-opening followed by the N_2-extrusion is very similar to that of the Ni system. The former process is easy (the barrier is marginally zero as 0.7 kcal/mol for Co and 5.3 kcal/mol for Fe), while the latter is more difficult (the barrier is 21.5 kcal/mol for Co and 19.4 kcal/mol for Fe). The corresponding barriers for the back-rearrangement processes **Co-2**→**Co-1** and **Fe-2**→**Fe-1** are 19.5 and 11.2 kcal/mol. Yet, different features of PESs can also be found. In **Co-1** and **Fe-1**, the transition state for the breaking of the N_5-ring leads to an isomer with N_3 and N_2 moiety positioned on the M atom (Co, Fe), whereas for **Ni-1**, it leads to the direct extrusion of a N_2 molecule. Also, for both **Co-2** and **Fe-2**, we located a transition state that is associated with the breaking of the N_3-ring. Yet, this transition state cannot be located for **Ni-2**. Interestingly, breaking the N_3-ring is more competitive (by 2.7 kcal/mol) than breaking the N_5-ring for Co, yet the former process is less competitive (by 5.6 kcal/mol) than the latter for Fe. In all, the lowest barrier that determines the kinetic stability is now 19.5 kcal/mol for **Co-2** (via **Co-TS1/2**) and 11.2 kcal/mol for **Fe-2** (via **Fe-TS1/2**). The much lower kinetic stability of **Fe-2** may be associated with its structural feature, i.e., the planar N_5 bending with Fe atom, which differs from the upright in **Ni-2** and **Co-2**. We also should note that, in **Co-2**, the corner N atom of the N_5 unit interacts with the metal atom, whereas in **Ni-2** and **Fe-2**, the side N−N bond interacts with metal. **Co-3**, which is similar to **Ni-3**, is not a local minimum at B3LYP/6-311+G(d) level.

TABLE 2: Natural Populations of Atom Charge and HOMO−LUMO Gap of Ni-2 ($[N_3NiN_5]$), Co-2 ($[N_3CoN_5]^-$), and Fe-2 ($[N_3FeN_5]^{2-}$)

species	natural populations of atom charge (e)			HOMO−LUMO gap (eV)
	M atom	$^3N_3^-$ ring	N_5^- ring	
Ni-2 ($[N_3NiN_5]$)	0.9318	−0.2300	−0.7018	−4.4262
Co-2 ($[N_3CoN_5]^-$)	0.5510	−0.6780	−0.8730	−3.9772
Fe-2 ($N_3FeN_5]^{2-}$)	0.2608	−1.0724	−1.1884	−0.8237

3.3. Bonding Analysis. The structures and kinetic stability of **Ni-2**, **Co-2**, and **Fe-2** resemble each other. The N−N bond lengths of cyclic-N_3 are average in each isomer, i.e., 1.3570, 1.3568, and 1.4364 Å in **Ni-2** ($[N_3NiN_5]$); 1.4135, 1.3967, 1.4119 Å in **Co-2** ($[N_3CoN_5]^-$), and 1.4221, 1.4221, 1.4508 Å in **Fe-2** ($[N_3FeN_5]^{2-}$). $^3N_3^-$ has D_{3h} symmetry with the bond length 1.4018 Å and cyclic-$^1N_3^+$ has a D_{3h} structure with the N−N distance of 1.3173 Å at the B3LYP/6-311+G(d) level. Obviously, the bond lengths of N−N of cyclic-N_3 in **M-2** are much closer to that of the naked $^3N_3^-$. The natural charges are shown in Table 2, and they indicate that there is charge transfer from metal atom to all $^3N_3^-$ and N_5^- units. So we consider that the N_3 unit in **M-2** is cyclic-$^3N_3^-$.

All characteristic orbitals of $^3N_3^-$, N_5^-, and **Ni-2** and partial orbitals of **Co-2** and **Fe-2** (considering that the structure of **Ni-2**, **Co-2**, and **Fe-2** are analogous to each other) are shown in Figure 4. In $^3N_3^-$, the two single electrons of the out-of-plane 2p orbitals in N atoms form the delocalized π orbital (HOMO-5), and this causes the aromaticity of $^3N_3^-$. In $^3N_5^-$, the HOMO-2, HOMO-3, and HOMO-7 are delocalized π orbitals over the N_5-ring. Figure 4 shows that the MOs of $^3N_3^-$ and N_5^- can be easily recognized in all species, though some of the MOs rearranged. The **M-2** in this paper are all singlet isomers, indicating that the two unpaired spins within the naked cyclic-$^3N_3^-$ have effectively participated in the bonding interaction with the transition metal atoms (here M is Ni, Co, and Fe). Figure 5 shows a diagram of the absolute energies of singlet and triplet **Ni-2** against the distance between Ni atom and the center of the cyclic-N_3 plane. At roughly $r = 2.3$ Å, there is a cross point of singlet **Ni-2** and triplet **Ni-2**. That is to say, the spin is annihilated around 2.3 Å.

3.4. Test Calculations. The above discussions are based on the B3LYP/6-311+G(d) calculations. For better estimation of the stability of our designed heterodecked $[N_3MN_5]^q$ isomers **M-1** and **M-2**, we attempt to perform additional single-point calculations, i.e., B3LYP/6-311+G(3df) and CCSD(T)/6-311+G(d), at the relevant B3LYP/6-311+G(d) structures for M = Ni, Co, and Fe. Since we encounter iterative convergence difficulties (Link 913) in the CCSD(T) calculations for transition

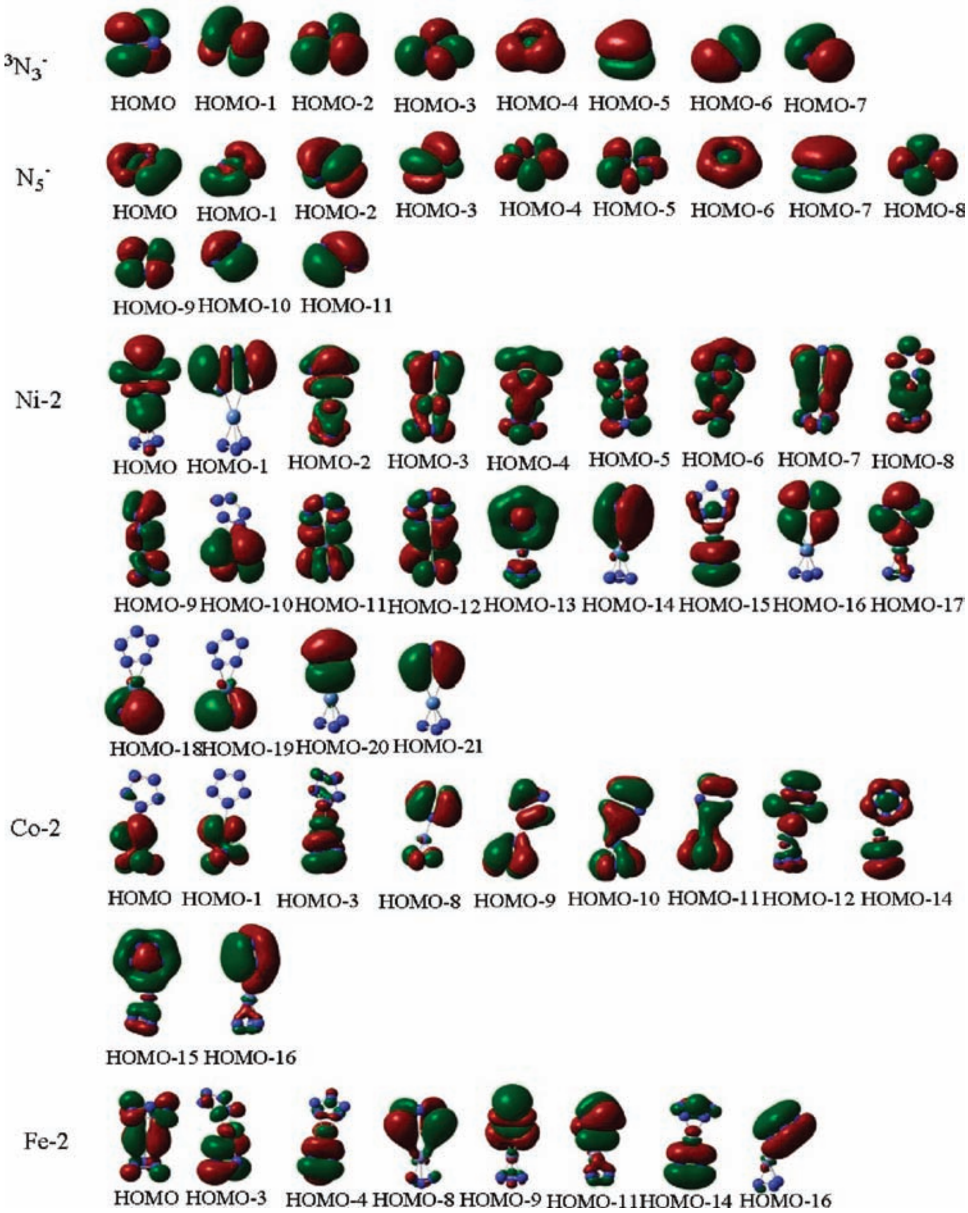

Figure 4. Molecular orbital figures of $^3N_3^-$, N_5^-, **Ni-2**, **Co-2**, and **Fe-2** obtained at the B3LYP/6-311+G(d) level.

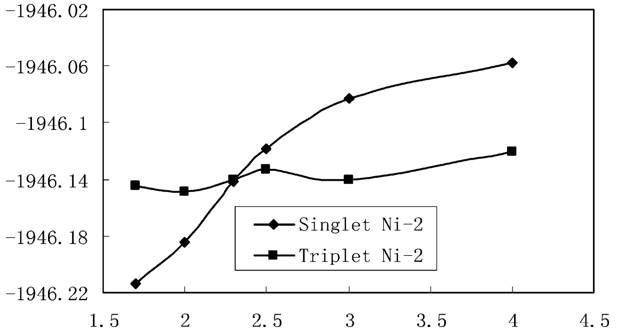

Figure 5. The absolute energies diagram of singlet **Ni-2** and triplet **Ni-2** against the distance between the Ni atom and the center of cyclic-N_3 plane.

states of $[N_3FeN_5]^{2-}$, we can only provide the B3LYP/6-311+G(3df) results for M = Fe. At the B3LYP/6-311+G(d), B3LYP/6-311+G(3df) and CCSD(T)/6-311+G(d) levels, the $\eta^3-\eta^5$ heterodecked sandwich-like isomer **M-1** has the respective **M-1**→**M-2** conversion barrier of 1.1, 1.7, and 2.3 kcal/mol for M = Ni and 0.7, 0.7, and 2.5 kcal/mol for M = Co. At the B3LYP/6-311+G(d) and B3LYP/6-311+G(3df) levels, **Fe-1** has the respective barrier of 5.3 and 7.2 kcal/mol for conversion to **Fe-2**. Clearly, all three levels predict **M-1** to be kinetically unstable toward arrangement to **M-2** for M = Ni, Co, Fe. For the lower-lying $\eta^3-\eta^2$ ($\eta^3-\eta^1$) sandwich-like form **Ni-2** and **Co-2**, B3LYP/6-311+G(d) and B3LYP/6-311+G(3df) predict close barrier height with respect to the N_2-extrusion process, i.e., 17.4 and 19.2 kcal/mol for M = Ni, 21.5 and 22.0 kcal/mol for M = Co, and 19.4 and 20.2 kcal/mol for M = Fe. At the CCSD(T)/6-311+G(d) level, **Co-2** has the N_2-extrusion barrier of 23.7 kcal/mol, also very close to both DFT results. Yet for **Ni-2**, CCSD(T)/6-311+G(d) gives a much higher barrier of 30.1 kcal/mol than DFT. This is because compared to B3LYP/6-311+G(d), the CCSD(T)/6-311+G(d) method lowers the relative energy of **Ni-2** by 5.3 kcal/mol, while increasing the relative energy of the N_2-exrusion transition state **Ni-TS2/P** by 7.4 kcal/mol. The dramatic energy change from DFT to CCSD(T) using the same basis set [i.e., 6-311+G(d)] may be ascribed to the structural difference between **Ni-2** and **Ni-TS2/P**. In isomer **Ni-2**, the central Ni atom is bonded to the N−N bond of N_5-ring; thus, the N−N π-bonding would preferably interact with Ni, which is usually influenced to a large extent by the electron correlative of B3LYP. Usually the DFT method considers much delocalization effect and results in the barrier being lower than the ones obtained at the CCSD level. Moreover, the deviation of the relative single point energies of **Ni-3** is up to 15.7, and it is also ascribed to the π-bonding of N═N═N. Yet in **Ni-TS2/P**, Ni atom is bonded to only one N atom of the N_5 ring. Luckily, such energetic influcence by the CCSD(T) method makes the **Ni-2** isomer kinetically more stable. Since the structural difference between **M-2** and **M-TS2/P** in M = Fe is similar to that in M = Ni, we expect that CCSD(T) would also predict a kinetically more stable **Fe-2** if the iterative convergence problem can be solved in other software packages. Moreover, CCSD(T) calculations at larger basis sets such as 6-311+G(3df) or aug-cc-pVTZ, which is presently unaccessible for such transition metal sandwich-like complexes due to our limited computational capacity, might introduce some quantitative changes. Yet we believe that they would not change the present conclusion, i.e., for M = Ni, Co, and Fe, the $\eta^3-\eta^2$ ($\eta^3-\eta^1$) sandwich-like form **M-2** is kinetically stable, whereas the $\eta^3-\eta^5$ sandwich form **M-1** is unstable against conversion to **M-2**. Note that both types of heterodecked sandwich-like isomers are energetically more stable than the previously reported homodecked sandwich-like isomer $N_4MN_4{}^q$.[2]

The multiconfigurational nature of $[N_3MN_5]^q$ (M, q = (Ni, 0), (Co, −1)) species have been calculated, as characterized by the T1 Diagnostics.[21] As shown in Table 1, the $||t_1||$; values in the CCSD(T) treatment with the 6-311+G(d) basis set distribute between 0.022 and 0.093. A value of $||t_1||$ higher than 0.02 indicates that the degree of multireference character is large enough to cast serious doubt on the reliability of single reference correlation treatments. Clearly, $[N_3MN_5]^q$ (M, q = (Ni, 0), (Co, −1)) have noticeable multireference effect. It is known that a reasonable multireference calculation requires inclusion of sufficient electrons of chemical interest. At present, we are not able to perform such study for the presently nitrogen-rich transition metal complexes containing many electron lone-pairs. Yet, in view of the considerable kinetic stability of **Ni-2** (17.4, 19.2, and 30.1) and **Co-2** (19.5, 16.4, and 16.7), we optimistically hope that future multiconfigurational calculations would not change the basic conclusions obtained by the present work. Note that the values in parentheses are the corresponding lowest conversion barriers at the B3LYP/6-311+G(d), B3LYP/6-311+G(3df), and CCSD(T)/6-311+G(d) levels.

Moreover, the triplet structures of **^{3}Ni-2**,**^{3}Co-2**, and **^{3}Fe-2** have been considered. They are not local minima except **^{3}Co-2**. The relative energy of **^{3}Co-2** is −16.5 kcal/mol at B3LYP/6-311+G(d) levels, which is somewhat higher than that of **^{1}Co-2** (−18.8).

The HOMO−LUMO gap can be viewed as an indicator of kinetic stability. A molecule with small HOMO−LUMO gap is chemically reactive,[22] so the HOMO−LUMO gap of **M-2** were calculated. As shown in Table 2, the gap of **Fe-2** (−0.8237) is much smaller than that of **Ni-2** (−4.4262) and **Co-2** (−3.9772), so **Fe-2** might be more active than **Ni-2** and **Co-2**. However, we note that the unusually small gaps should partly originate from the dianaions, which would lead to instability due to the Coulomb repulsion. In actual synthesis, the counterions should be incorporated to reduce such instability.

For a species generated experimentally, it is generally expected that the most detectable isomer should be the low-lying species, especially during the nucleation processes of clusters. However, though being thermodynamically less stable, if an isomer possesses good kinetic stability against both isomerization and fragmentation, they may still exist with carefully chosen synthetic precursors and under the suitably manipulated conditions (in particular the temperature should be low enough to suppress isomerization). In fact, a number of such kinds of isomers with less thermodynamic stability have been characterized in our laboratory. For relevance, we showed an example. Recently, the cyclic-pentanitrogen anion (N_5^-) has been successfully detected, though it lies 60 kJ/mol higher in energy than $N_3^- + N_2$.[3] The presently studied isomer $[N_5TMN_3]^q$ as well the previous $[N_4TMN_4]^q$ lie higher in energy than the N_2-extrusion products and thus belong to the so-called “high-energy and density materials (HEDM)”, for which the criteria “high-energy” yet “kinetically stable” should both be satisfied. The two points usually contradict each other. Consequently, detection of a HEDM molecule is challenging and has captured the attention of both experimental and theoretical chemists.

The complexes **M-2** in our paper are different from the classical sandwich complexes. They are highly energetic complexes with good kinetic stability. Worthy of note is that **M-2** possesses better thermodynamic stability than $[N_4MN_4]^q$. This point would be very attractive since, for synthesis, a favorable thermodynamic property is always appealing. Surely, we should admit that, being “energetic” molecules, **M-2** still lies higher in energy by the N_2-extrusion product. In fact, it has continued to be a great challenge to synthesize the high-energy-density materials, so we hope that the novel complexes reported in this paper will extend the idea of designing new high-energy-density materials. We optimistically hope that our designed **M-2** with good kinetic stability might be realized when suitable precursors can be found.

4. Conclusion

In summary, the present study described a type of heterodecked sandwich-like structures $[N_3MN_5]^q$ containing two all-nitrogen odd-membered rings N_3 and N_5, which are the isoelectronic isomers of $[N_4MN_4]^q$ [(M, q) = (Ni, 0), (Co, −1), (Fe, −2)]. The calculations show that the new isomers $[N_3MN_5]^q$ in heterodecked form are thermodynamically more stable than the previously reported homodecked sandwich-like isomers $[N_4MN_4]^q$ (D_{4d}) with even-membered ring $N_4{}^{2-}$ [(M, q) = (Ni,0), (Co, −1), (Fe, −2)]. The $\eta^3-\eta^2$ ($\eta^3-\eta^1$) isomers **Ni-2**, **Co-2**, and **Fe-2** possess considerable kinetic stability. Therefore, the sandwich-like complexes **Ni-2**, **Co-2**, and **Fe-2** might exist under low temperatures. The Natural Bond Orbital analysis shows that the N_3 unit in **Ni-2**, **Co-2**, and **Fe-2** are $^3N_3^-$, which is the smallest triplet all-nitrogen unit. We expect that $^3N_3^-$ should be a suitable building block in designing potential energetic materials. Future laboratory studies are desired.

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Supporting Information Available: The coordinates of all isomers shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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