η^3-Sandwich-Like Complexes Based on the Smallest Polynitrogen Ring

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Over the past decades, polynitrogen chemistry has witnessed rapidly growing progress. Unfortunately and to our great surprise, η^3-assembled species based on the simplest polynitrogen ring (N_3) have never been reported. In this paper, we report the first successful assembly design of the long-escaped N_3-based compounds, that is, $[N_3NiN_3]^{2-}$, $[N_3M(CO)_2N_3]^q$ ((M,q), = (Fe,0) (Mn,−1)), $[N_3M(CO)_3]^q$ ((M,q) = (Co,0), (Fe,−1)), and $[N_3MCp]^q$ ((M,q) = (Ni, 0), (Co,−1)), at the density functional level. The conversion and dissociation of them need to overcome considerable barriers kinetically. To our surprise, the detailed structural, charge distribution, and orbital analyses consistently reveal a triplet polynitrogen unit, *cyclic*-$^3N_3^-$, rather than another simplest trinitrogen unit *cyclic*-$^1N_3^+$. The two unpaired spins within the naked *cyclic*-$^3N_3^-$ have effectively participated in the bonding interaction with the central transition-metal atoms (here, M is Ni, Fe, Co, and Mn). Moreover, the possible experimental routes of $N_3Co(CO)_3$ were proposed. The diradical-like polynitrogen ring, *cyclic*-$^3N_3^-$, would add to the polynitrogen family as a novel building block. The assembly-designed species await future experimental verification.

1. Introduction

In cluster science, "polynitrogen" compounds represent a unique and hotly pursued class, and are important in various fields including atmospheric chemistry,[1] inorganic chemistry,[2] and energetic materials.[3] Chemists have been striving to characterize and design diverse polynitrogen compounds.[4−17] Among, the conjugated polynitrogen rings have received considerable interest, due to their structural analogue to hydrocarbons. Up to now, various aromatic polynitrogen rings with average N−N bonds, that is, N_3^+,[5] N_4^{2-},[6] N_5^-,[7] N_6,[4−8] and N_7^{3-} [9] have been theoretically characterized as stable inorganic units. A breakthrough is the gas-phase mass spectrometric detection of the long-sought pentazole anion, *cyclic*-N_5^-,[2d] whose existence half-time has been evaluated to be as long as $t_{1/2}$ = 2.2 days in methanol solution at 0 °C.[2d] In addition, a neutral *cyclic*-N_3 radical with one N═N and two identical N−N bonds, though not aromatic, has recently been characterized in the gas phase via the velocity map imaging (VMI) and time-of-flight (TOF) spectra.[10]

The η^n-sandwich-like or half-sandwich-like complexes with four to seven-membered regular polynitrogen rings have been successfully assembly-designed. They include $[N_4MN_4]^q$ (M = Ti, V, Cr, Fe, Co, Ni),[11] MN_4 (M = Mg, Ca, Sr, Ba),[12] N_5FeN_5,[13] $[MN_5]^+$ (M = Be, Mg, Ca, Sr, Ba),[14] MN_6 (M = Ti, Zr, Hf, and Th),[8] ScN_7,[9] and N_5MN_7 (M = Ti, Zr, Hf, Th).[15] Understanding the structural and bonding properties of these polynitrogen-based complexes has greatly enriched our knowledge of the aromaticity in the inorganic realm. Unfortunately and to our great surprise, η^3-assembled species based on the simplest polynitrogen ring (N_3) have never been reported.[16] Searching for the N_3-based η^3-sandwich-like complexes would thus present a challenge for the polynitrogen chemistry. In this paper, we report the first successful calculation of the long-escaped N_3-based assembled compounds. The diradical-like polynitrogen ring *cyclic*-$^3N_3^-$ has only been considered by Bartlett[17] by calculating its structure and frequencies. Our results show that *cyclic*-$^3N_3^-$ could act as a new polynitrogen building unit in cluster assembly.

2. Theoretical Methods

A total of seven sandwich-like (**I-1** to **V-1**) and half-sandwich-like (**VI-1** to **VII-1**) N_3-based compounds, that is, (**I-1**) $N_3NiN_3^{2-}$ (D_{3d}), (**II-1**) $N_3Fe(CO)_2N_3$ (C_{2v}), (**III-1**) $N_3Mn(CO)_2N_3^-$ (C_{2v}), (**IV-1**) N_3NiCp (C_s), (**V-1**) N_3CoCp^- (C_s), (**VI-1**) $N_3Co(CO)_3$ (C_{3v}), and (**VII-1**) $N_3Fe(CO)_3^-$ (C_{3v}), were calculated at the B3LYP/6-311++G(d,p) level using the Gaussian 03 program package.[18] Note that (**II-1**) and (**III-1**) are carbonyl-assisted sandwich-like forms. They all correspond to the local minima with all real frequencies. Among each of the calculated complexes, the central transition-metal atom can be viewed as η^3- and η^5-coordinated to the N_3-ring and Cp-ring, respectively. Also, each CO group can be considered as a two-electron donator. Therefore, all of the assembly-designed complexes accord to the well-known 18-valence-electron rule.[19] The natural bond orbital analyses of **I-1**, **II-1**, **IV-1**, and **VI-1** are obtained at the B3LYP/6-311++G(d,p) level. The NICS(1) of these four structures, *cyclic*-N_3^+, and *cyclic*-$^3N_3^-$ were predicted with the same basis sets as those employed in geometry optimization.

3. Result and Discussion

3.1. Kinetic Stability. The bond lengths of η^3-N_3 units in **I-1**, **II-1**, **III-1**, **IV-1**, **V-1**, **VI-1**, and **VII-1** are shown in Figure 1. The schematic potential energy surfaces (PESs) of the seven systems have been described and are shown in Figure 2−8. For each system, the total energy of the sandwich-like isomer **1** is set at zero for reference. It is natural to take the evolution of one N_3-ring as the rate-controlling process. Three kinds of processes associated with the N_3-ring are identified, that is, (1) deck opening to isomer **2** followed by N_2-extrusion, (2) ring opening to isomer **3** followed by N_2-extrusion, and (3) direct N_2-extrusion. Therefore, overall, the lowest-energy N_2-exrusion

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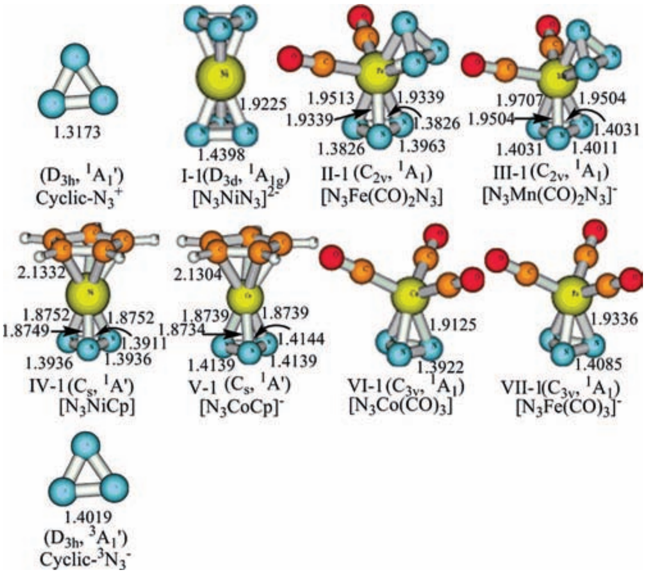


Figure 1. The geometries for *cyclic*-N_3^+, **I-1**, **II-1**, **III-1**, **IV-1**, **V-1**, **VI-1**, **VII-1**, and *cyclic*-$^3N_3^-$ units in this paper. Bond lengths are in angstroms.

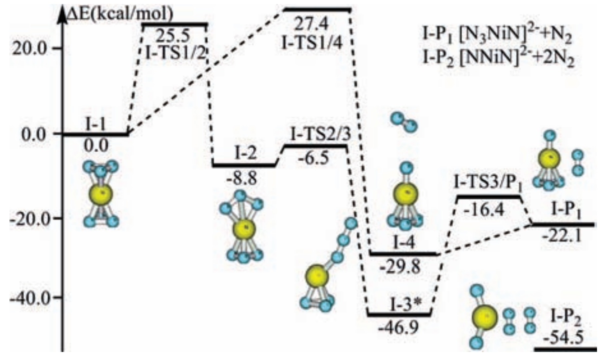


Figure 2. Schematic potential energy surface of the $[N_3NiN_3]^{2-}$ system at the B3LYP/6-311++G(d,p) level.

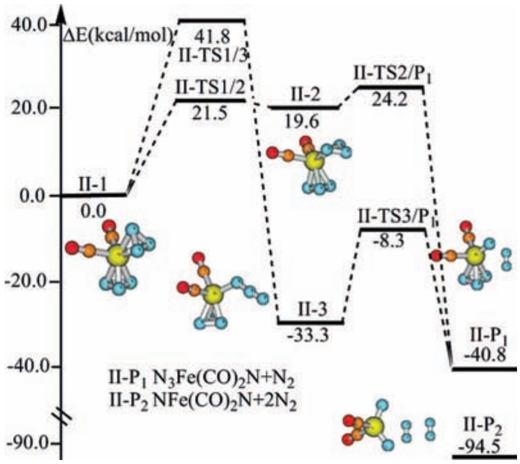


Figure 3. Schematic potential energy surface of the $[N_3Fe(CO)_2N_3]$ system at the B3LYP/6-311++G(d,p) level.

step should govern the lifetime of isomer **1**. The rate-determining barrier for each sandwich-like isomer is collected in Table 1. We can find that all of the assembly-designed sandwich-like forms have considerable barriers (24.2−38.7 kcal/mol) toward conversion or dissociation. Thus, the structures (**I-1**)−(**VII-1**) are all kinetically stable, which is very pleasing for their laboratory characterization. It is worthy of note that the complex **I-1** is a dianionic species, which might be subject to the electron autoionization as result of coulomb repulsion. The charge compensation is necessary in experiment. Yet, we believe that in addition to increasing the electronic stability, the counterions would not change the kinetic stability.

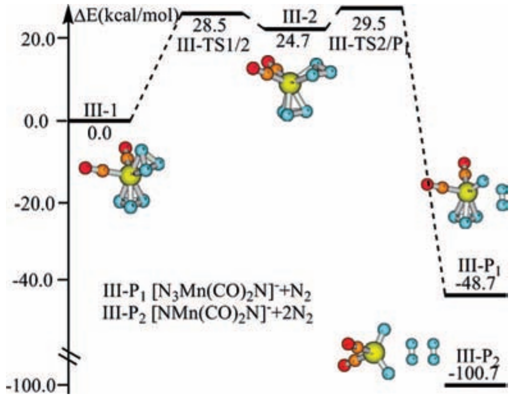


Figure 4. Schematic potential energy surface of the $[N_3Mn(CO)_2N_3]^-$ system at the B3LYP/6-311++G(d,p) level.

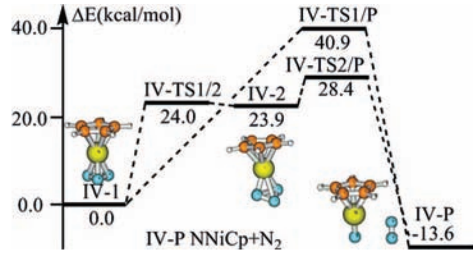


Figure 5. Schematic potential energy surface of the [N_3NiCp] system at the B3LYP/6-311++G(d,p) level.

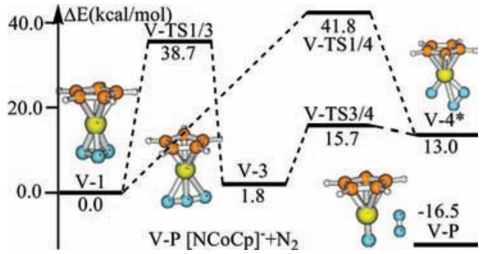


Figure 6. Schematic potential energy surface of the $[N_3CoCp]^-$ system at the B3LYP/6-311++G(d,p) level. **V-4** marked with "*" are calculated at the B3LYP/6-31G(d) level, and the single-point calculations are performed at the B3LYP/6-311++G(d,p) level.

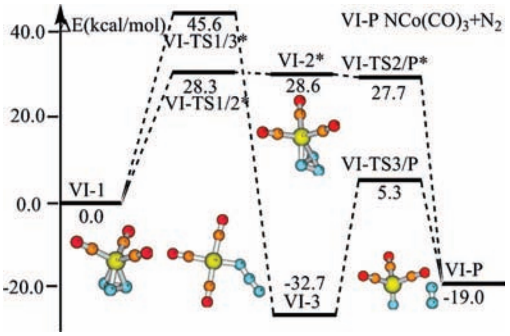


Figure 7. Schematic potential energy surface of the $[N_3Co(CO)_3]$ system at the B3LYP/6-311++G(d,p) level. The isomers and transition states marked with "*" are calculated at the B3LYP/6-31G(d) level, and the single-point calculations are performed at the B3LYP/6-311++G(d,p) level.

3.2. Nature of the Assembled N_3-Ring.

What is the nature of the assembled N_3-ring? The calculated nuclear-independent

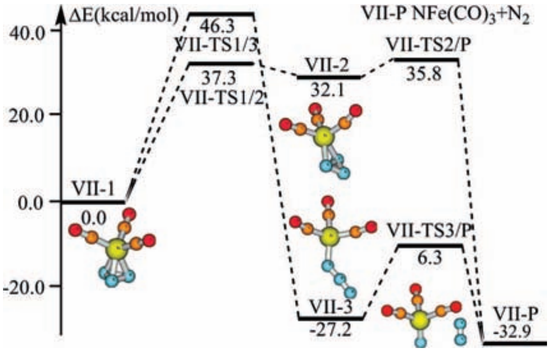


Figure 8. Schematic potential energy surface of the $[N_3Fe(CO)_3]^-$ system at the B3LYP/6-311++G(d,p) level.

chemical shielding values at 1.0 Å above the center of the N_3-ring, that is, NICS(1),[20] show that the η^3-assembled N_3-rings are all aromatic. Thus, we preliminarily consider it as the *cyclic*-$^1N_3^+$, which is the well-known (theoretically) and the simplest aromatic form of the polynitrogen family.[5,17] At the B3LYP/6-311++G(d,p) level, *cyclic*-$^1N_3^+$ has a D_{3h} structure with the N−N distance 1.3173 Å, and its NICS(1) value is −20.46. However, as shown in Figure 1, nearly all of the assembled N_3-rings have the N−N distances of around 1.40 Å (except $[N_3NiN_3]^{2-}$), significantly longer than that of *cyclic*-$^1N_3^+$ (1.3173 Å). Moreover, the natural charge distribution (see Table 1) shows that all of the assembled N_3-rings are negatively charged. Thus, it is inappropriate to view the assembled N_3-ring as being *cyclic*-$^1N_3^+$ with 2π electrons. This prompts us to study the *cyclic*-N_3^- unit with 4π electrons. Being antiaromatic, the D_{3h}-symmetrized singlet *cyclic*-N_3^- is not a minimum point and would lead to the ring opening due to the Jahn−Teller effect. At the B3LYP/6-311++G(d,p) level, the two identical short N−N bonds of *cyclic*-$^1N_3^-$ are 1.2895 Å, and the long N−N bond is 1.7409 Å. Clearly, the η^3-assembled N_3-ring does not correspond to the singlet *cyclic*-N_3^-, either. Therefore, we have to turn to the triplet *cyclic*-N_3^-, the electronic state of which is $3A_1'$. At the B3LYP/6-311++G(d,p) level, *cyclic*-$^3N_3^-$ is indeed an equilateral triangle with the N−N bond distance of 1.4019 Å, which is very close to those of the assembled N_3-rings. The calculated NICS(1) value of −11.46 is indicative of the aromaticity of *cyclic*-$^3N_3^-$, which results from a set of delocalized π orbitals, as depicted in Figure 9. The two unpaired electrons evenly spread over the whole N_3-ring, showing the diradical character.

All in all, on the basis of the structural, natural charge, and NICS(1) analyses, we can conclude that the N_3-ring within the seven η^3-assembled complexes is associated with a cyclic triplet polynitrogen unit, that is, *cyclic*-$^3N_3^-$. The exceptionality of (**I-1**) $[N_3NiN_3]^{2-}$ could be ascribed to the existence of two additional negative charges and the large electronegativity of nitrogen that attracts more charges to the N_3-ring. As a result, (**I-1**) $[N_3NiN_3]^{2-}$ has the relatively longer N−N bond (1.4404 Å), smaller NICS(1) value (−9.69), and more negatively charged N_3-ring (−1.427 e).

Of particular note, the seven η^3-sandwich-like complexes of N_3 have the singlet ground state. This indicates that the two unpaired spins within the naked *cyclic*-$^3N_3^-$ have effectively participated in the bonding interaction with the central transition-metal atoms (here, M is Ni, Fe, Co, and Mn). In order to describe the process of spin pairing, the absolute energy diagrams of $^1[N_3NiN_3]^{2-}$, $^3[N_3NiN_3]^{2-}$, $^5[N_3NiN_3]^{2-}$, and $^7[N_3NiN_3]^{2-}$ against the distance between the Ni-atom and the center of *cyclic*-N_3 plane have been calculated, as shown in Figure 10. We can see that when the two N_3^- units are far from the Ni-atom, the singlet state is significantly higher in energy than the high spin states. At roughly $r = 2.16$ Å, one comes to a cross point between the curve of $^1[N_3NiN_3]^{2-}$ and those of $^3[N_3NiN_3]^{2-}$, $^5[N_3NiN_3]^{2-}$, $^7[N_3NiN_3]^{2-}$. That is to say, when "r" is around 2.16 Å, the unpaired electrons of the *cyclic*-$^3N_3^-$ ligands interact with the Ni atom, and simultaneously, the spin is annihilated. As shown in Figure 9, in free *cyclic*-$^3N_3^-$, the HOMO and HOMO-1 orbitals are degenerate and associated with the π-bonding and π-antibonding orbitals between the two N-atoms, respectively. Both HOMO and HOMO-1 are occupied by an unpaired electron. HOMO-4 and HOMO-5 belong to the delocalized σ and π orbitals, respectively, and both contribute to the structural rigidity of the $^3N_3^-$. In the assembled complexes, HOMO and HOMO-1 of **I-1**, HOMO, HOMO-1, HOMO-2, and HOMO-3 of **II-1**, HOMO, HOMO-1, HOMO-5, and HOMO-6 of **IV-1**, and HOMO, HOMO-1, and HOMO-3 of **VI-1** represent the bonding orbitals between the N_3-moiety and the central transition-metal atom. The remaining orbitals are well-retained σ and π characteristic orbitals.

3.3. Experimental Viability. It would be a great and attractive challenge to detect our assembly-designed N_3-based complexes. We are aware that the previously theoretically assembly-designed complexes (e.g., $[N_4MN_4]^q$ (M = Ti, V, Cr, Fe, Co, Ni; $q = -2, -1, 0$),[11] N_5FeN_5,[13] and N_5MN_7 (M = Ti, Zr, Hf, Th)[15]) have not been experimentally available up to now. A clear reason for the absence of these species could be their rather high thermodynamic instability with respect to the dissociation of N_2, which makes it highly difficult to choose suitable synthetic techniques, although these species might be kinetically stable. By comparison, the present assembly-designed N_3-based complexes **I-1** $[N_3NiN_3]^{2-}$, **IV-1** $[N_3NiCp]$, **V-1** $[N_3CoCp]^-$, **VI-1** $[N_3Co(CO)_3]$, and **VII-1** $[N_3Fe(CO)_3]^-$ have the exothermic energies of −13.6 to −54.5 kcal/mol, much smaller than the previous all-nitrogen-based species (e.g., 202 kcal/mol for $N_4NiN_4 \rightarrow Ni + 4N_2$,[11b] 132 kcal/mol for $N_5ThN_7 \rightarrow Th + 6N_2$, and 177 kcal/mol for $N_5HfN_7 \rightarrow Hf + 6N_2$[15]). In particular, **IV-1** $[N_3NiCp]$ (−13.6 kcal/mol) and **V-1** $[N_3CoCp]^-$ (−16.5 kcal/mol) could become the first ones to be experimentally accessible that might not lead to explosion. Thus, the combined good kinetic stability and superior thermodynamic stability should render the assembly-designed N_3-based complexes experimentally tractable. The synthetic condition of **II-1** $[N_3Fe(CO)_2N_3]$ and **III-1** $[N_3Mn(CO)_2N_3]^-$ would be more rigorous because of their high exothermicities (−94.5 and −100.7 kcal/mol).

In order to provide more information for experimental detection, for **VI-1** $N_3Co(CO)_3$, we propose two possible routes, that is

$$\text{Route 1:}\quad cyclic\text{-}N_3\bullet + Co(CO)_4\bullet \rightarrow N_3Co(CO)_3(\textbf{VI-1}) + CO$$

$$\text{Route 2:}\quad cyclic\text{-}N_3\bullet + Co(CO)_3\bullet \rightarrow N_3Co(CO)_3(\textbf{VI-1})$$

The above three radicals, that is, *cyclic*-N_3•, $Co(CO)_4$•, and $Co(CO)_3$•, have been already detected.[21] As shown in Table 2, the exothermic energies are −20.9 and −44.4 kcal/mol, respectively. In view of the large lowest conversion barrier of **VI-1** (28.6 kcal/mol), both routes are possible to generate and stabilize the complex **VI-1**. Surely, we expect that route 1 is superior to route 2.

In fact, despite the significant difficulties, there has been accumulating evidence for the nitrogen-rich compounds either in the gas phase or in crystals, for example, N_5^+,[2a−c] N_5^-,[2d,7] *cyclic*-N_3 radical,[10] and the more complicated forms **1−6** as shown in Scheme 1.[22] These reports strongly provide hope for

TABLE 1: The B3LYP/6-311++G(d,p) Properties of the Sandwich-Like/Half-Sandwich-Like Complexes[a]

species	$Q_1(N_3)$	$Q_2(N_3)/Q_2(Cp)$	$Q(M)$	NICS(1)	E^{+2}	E_1	E_2
cyclic-N_3^+				−20.46			
cyclic-$^3N_3^-$				−11.46			
I-1 $[N_3NiN_3]^{2-}$	−1.427	−1.427	+0.856	−9.69	25.5	−22.1	−54.5
II-1 $[N_3Fe(CO)_2N_3]$	−0.266	−0.266	+0.532	−13.40	24.2	−40.8	−94.5
III-1 $[N_3Mn(CO)_2N_3]^-$					29.5	−48.7	−100.7
IV-1 $[N_3NiCp]$	−0.458	−0.424	+0.882	−15.53	28.4	−13.6	
V-1 $[N_3CoCp]^-$					38.7	−16.5	
VI-1 $[N_3Co(CO)_3]$	−0.433		+0.433	−12.24	28.6	−19.0	
VII-1 $[N_3Fe(CO)_3]^-$					37.3	−32.9	

[a] Q means the natural charge. E^{+2} means the lowest-energy barrier. E_1 and E_2 mean the released energy for one N_2-extrusion and two N_2-extrusion processes, respectively.

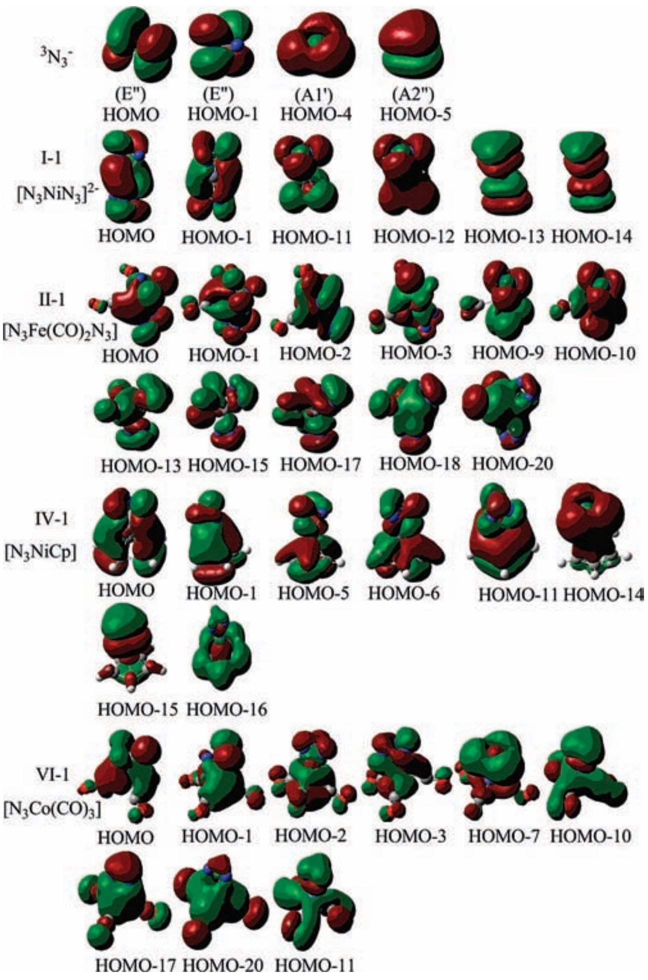


Figure 9. The pictures of characteristic orbitals of *cyclic*-$^3N_3^-$, **I-1**, **II-1**, **IV-1**, and **VI-1**.

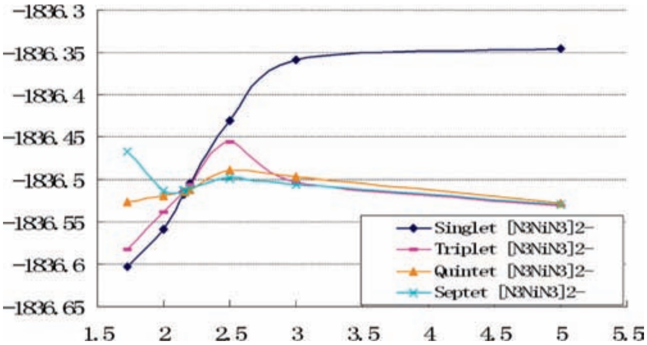
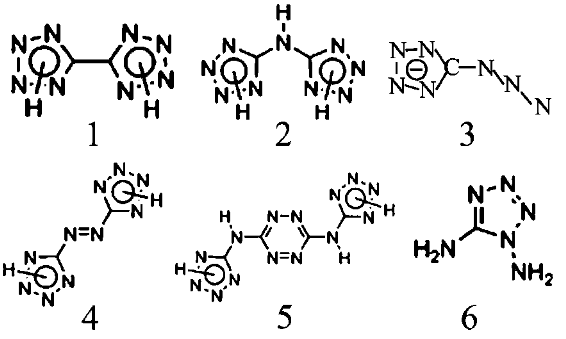


Figure 10. The absolute energy diagrams of $^1[N_3NiN_3]^{2-}$, $^3[N_3NiN_3]^{2-}$, $^5[N_3NiN_3]^{2-}$, and $^7[N_3NiN_3]^{2-}$ against the distance between the Ni-atom and the center of the *cyclic*-N_3 plane.

TABLE 2: The relative energies (kcal/mol) of route 1 and route 2

route	ΔE
route 1: *cyclic*-N_3• + $Co(CO)_4$• → $N_3Co(CO)_3$ + CO	−20.9
route 2: *cyclic*-N_3• + $Co(CO)_3$• → $N_3Co(CO)_3$	−44.4

SCHEME 1



the generation of our assembly-designed η^3-N_3-sandwich-like complexes, and we optimistically expect that our assembly designed species, especially **IV-1** $[N_3NiCp]$ and **V-1** $[N_3CoCp]^-$, could be synthesized in the future.

3.4. Implication. While there have been numerous studies on the η^n-sandwich-like complexes comprising a regular polynitrogen ring N_n^q ((n,q)=(4,−2), (5,−1), (6,−4), (7,−3)), η^3-sandwich-like complexes based on the simplest polynitrogen ring, i.e., N_3, still remain absent. The first successful calculation of the η^3-N_3-sandwich-like complexes, described in the present work, fills in the "blank" of the sandwich-like polynitrogen family. The diradical-like nature of the regular polynitrogen ring, $^3N_3^-$ (D_{3h}), is revealed by analyzing the structural, charge distribution and NICS(1) properties of the η^3-assembled N_3-complexes. Therefore, the *cyclic*-N_3 ligand is quite different from the known singlet ligands, such as N_4^{2-},[6] N_5^-,[7] N_6^{4-},[8] and N_7^{3-},[9] and no investigations based on diradical-like ligands have been reported, to our knowledge from a literature survey. Together with other polynitrogen rings, that is, N_4^{2-},[6] N_5^-,[7] N_6^{4-},[8] and N_7^{3-},[9] novel kinds of assembled compounds could be designed, for example, $N_3MN_5^q$ ((M,q) = (Fe,−2), (Co,−1), (Ni,0)). Moreover, with the embedded spins, *cyclic*-$^3N_3^-$ could be combined with main-group metals to form paramagnetic molecules since unlike transition metals, main-group metals will not quench the spins of *cyclic*-$^3N_3^-$. Finally, as to the simplest N_3-ring class, chemists now know the $^1N_3^+$ (D_{3h}) cation and the $^2N_3$• (C_{2v}) radical. Here, we have put forward the $^3N_3^-$ (D_{3h}) anion as a N_3-ring and have provided various kinetically stable sandwich-like examples for future synthesis.

4. Conclusion

In this paper, a series of η^3-sandwich-like complexes based on the N_3-based have been assembly designed.

The results are summarized as follows:

(1) Sandwich-like isomers **I-1**, **II-1**, **III-1**, **IV-1**, **V-1**, **VI-1**, and **VII-1** possess good kinetic stability against both isomerization and dissociation.

(2) The structural, natural charge, and NICS(1) analyses suggest that the N_3-ring within the seven η^3-assembled complexes is a cyclic triplet polynitrogen unit, that is, *cyclic*-${}^3N_3^-$.

Future laboratory investigations are expected.

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Supporting Information Available: Total, relative, absolute, and zero-point energies and coordinates of all isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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