N_4 Ring as a Square Planar Ligand in Novel MN_4 Species

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Ab initio (MP2) and density functional theory (DFT) methods are used to examine a series of MN_4 compounds, where M is an alkaline-earth cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), and N_4^{2-} is a six-π-electron ring. All pyramidal structures except MgN_4 are the most energetically favored for all singlet MN_4 systems considered here. For MgN_4, the C_S structure with dicoordinated Mg out of the N_4 ring plane is the most stable of all. Among these systems, the pyramidal CaN_4, SrN_4, BaN_4 and the planar C_S structure containing dicoordinated Ba are stable as singlet molecules due to their significant isomerization or dissociation barriers (21.3−94.1 kcal/mol). Structural, natural bond orbital (NBO), and molecular orbital (MO) analyses indicate that the bonding in the BaN_4 system has a larger covalent character as compared with other MN_4 systems. In addition, substantial *d* character is found in the bonding of the MN_4 (M = Ca^{2+}, Sr^{2+}, Ba^{2+}) species.

Introduction

Metal nitrides have received increasing attention in recent years because of their fascinating structures and properties.[1] While traditionally, perhaps, the unique redox chemistry of the transition metals plays a dominant role in many branches of inorganic chemistry, it is also apparent in nitride chemistry.[2] Recently, the hypothetical existence of transition metal nitrides has been a focus of several theoretical studies.[3−6] Gagliardi and Pyykkö[3] have predicted the possible existence of the ScN_7 molecule, which contains a new structural unit, the $\eta^7{-}N_7^{3-}$ ten-π-electron ring, and has a relatively high energy barrier of decomposition of 20 kcal/mol. They have then predicted the possible existence of some sandwich compounds with the general formula N_5MN_7 (M = Ti, Zr, Hf, Th),[4] in which N_5-ThN_7 is the most stable of all and has a fair chance of existing. Lein et al.[5] predicted the ferrocene-like Fe $(\eta^5{-}N_5)_2$ to be a strongly bonded complex with D_{5d} symmetry. Straka[6] performed a theoretical study on the possibility of stabilizing the N_6 species as a planar hexagonal ring in M $(\eta_6{-}N_6)$ (M = Ti, Zr, Hf, Th) systems. However, the frequently neglected *s*-block-metal nitrides also have provoked some interesting and fundamental questions. Schleyer et al.[7] reported that the lithium salt, N_5Li, favors the planar C_{2v} structure containing dicoordinated lithium. Zhao et al.[8] performed a theoretical study of MN_5 (M = Li^+, Na^+, K^+, Rb^+) by using hybrid density functional methods. They pointed out that the planar complex containing dicoordinated M is the most energetically favored, but the pyramidal structures are less stable, and they rapidly rearrange to the most stable planar structures. Pentazole metal compounds, like NaN_5, KN_5, Mg $(N_5)_2$, and Ca $(N_5)_2$, have also been recently predicted by Burke et al.[9] Gregory[2] pointed out that the compounds formed from group 2 metals with nitrogen appear in many respects to become less ionic with atomic number. Gagliardi[10] gave a striking observation that a well-defined triple bond between the Ba 5d and N 2p orbitals exists in the CsNBa molecule. Gagliardi and Pyykkö[11] pointed out that the CsN_7Ba molecule (in which the $\eta^7{-}N_7^{3-}$ is a ten-π-electron ring) is stable and presents a barrier of 35 kcal/mol to dissociation toward CsNBa and three N_2 molecules. They also found substantial 5d character in the bonding of the CsN_7Ba species.

As Zandwijk et al. [12] reported, the perfect square planar N_4^{2-} dianion has six delocalized π-electrons, thus conforming to the $(4n + 2)$ rule for aromaticity. Therefore, analogous to the recently discussed aromatic nitrogen ring systems, N_5^-, N_6^{4-}, and N_7^{3-}, the N_4^{2-} planar ring might be stabilized as a π-system ligand by the metal−ligand interaction. Related works[6,12,13] on metal cation−N_4^{2-} compounds have been reported. Zandwijk et al.[12] pointed out that N_4^{2-} in the neutral Li_2N_4 remains planar. We have investigated recently some nitrogen-rich compounds such as M_2N_4 (M = Li^+, Na^+, K^+, Rb^+, Cs^+),[13] and our computational results show that the N_4^{2-} ring still exhibits characteristics of aromaticity in the M_2N_4 compounds. Furthermore, we found that the bipyramidal M_2N_4 structures are likely to be stable and to be observed experimentally due to their significant isomerization or dissociation barriers (39.2−48.6 kcal/mol). As part of a project to investigate new metal cation-N_4^{2-} compounds, the compounds with the general formula MN_4 (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) containing one N_4^{2-} six-π-electron ring are now considered. The nature of the M−N_4 bonding in these compounds is also explored.

Computational Methods

All calculations were performed using the *Gaussian 98* program package.[14] We initially optimized geometries and calculated the harmonic vibrational frequencies for MN_4 (M = Mg^{2+} and Ca^{2+}) at the B3LYP/6-311+G* level of theory, where B3LYP is the DFT method using Becke's three-parameter gradient-corrected functional[15] with the gradient-corrected correlation of Lee et al.[16], and 6-311+G* is the split-valence triple-ζ plus polarization basis set augmented with diffuse functions.[17] Then, the geometries were refined, and the vibrational frequencies were calculated at the level of the second-order Møller−Plesset perturbation theory (MP2)[18] with the 6-311+G* basis set. The SrN_4 and BaN_4 systems were

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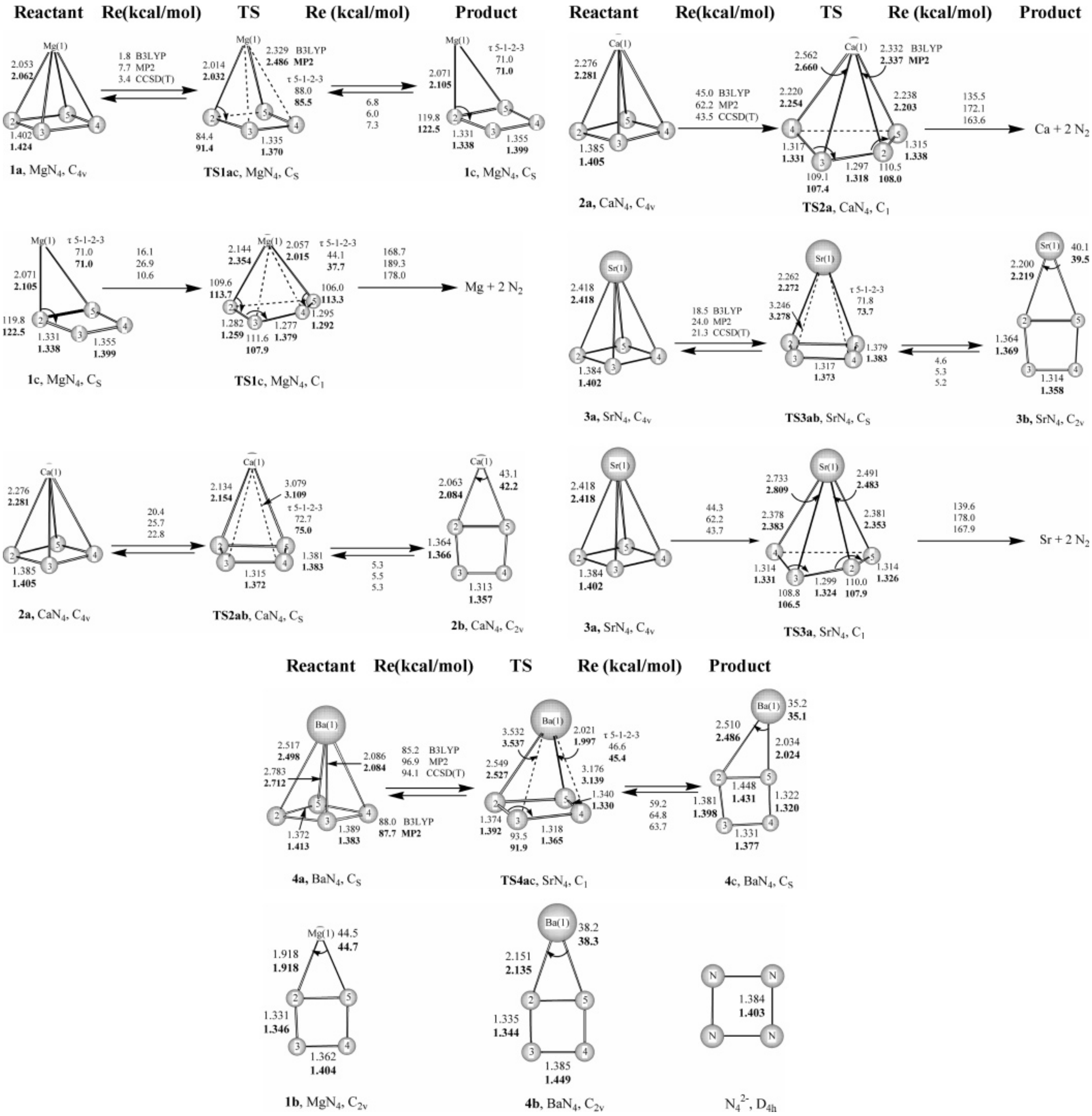

Figure 1. Optimized geometries for reactants, transition states, products, and relative energies (RE) of MN_4 systems and the optimized geometries of N_4^{2-}.

calculated at the B3LYP and MP2 levels of theory, where the 6-311+G* basis set was employed for nitrogen, and the energy-adjusted Stuttgart ECPs were used on the heavier atoms Sr ($Z = 38$) and Ba ($Z = 56$).[19,20] Stationary points were characterized as minima without any imaginary vibrational frequency and a transition state with only one imaginary vibrational frequency. For transition states, the minimum energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez−Schlegel second-order algorithm.[21,22] Final energies were refined at the CCSD (T)[23]/6-311+G*//MP2/6-311+G* + ZPE (MP2/6-311+G*) level of theory.

In addition to the structural and energetic investigations, the natural population and Wiberg bond indices (WBIs) analyses were also presented using the NBO procedure.[24,25]

Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, total energies in Hartrees, and relative and zero-point vibrational energies in kcal/mol.

Results and Discussion

The optimized structures for four MN_4 systems are illustrated in Figure 1. For comparison, the geometric structure of N_4^{2-} dianion[13] is also shown in Figure 1. The total energies, zero-point energies (ZPE), relative energies (with ZPE corrections), and number of imaginary frequencies are listed in Table 1.

Structures and Stabilities of the MN_4 Species. Geometric Structures and Energies of the MN_4 Species. We performed ab initio calculations on a wide variety of singlet structures and found that all pyramidal structures (**1a**−**4a**) (Figure 1) except

TABLE 1: Total Energies (E),[a] Zero-Point Energies (ZPE),[b] and Relative Energies (RE)[c] for MN_4 Species

	B3LYP/6-311+G*			MP2/6-311+G*			CCSD(T)/6-311+G*//MP2/6-311+G*	
species	E[a]	ZPE[b]	RE[c]	E[a]	ZPE[b]	RE[c]	E[a]	RE[c]
1a (C_{4v})	−418.96626	10.0 (0)	0.0	−417.98174	10.0 (0)	0.0	−418.00289	0.0
1b (C_{2v})	−418.95430	9.5 (1)	7.0	−417.95632	9.5 (1)	15.5	−417.98193	12.7
1c (C_S)	−418.97366	9.7 (0)	−4.9	−417.97809	9.4 (0)	1.7	−418.00812	−3.9
2a (C_{4v})	−896.55673	10.4 (0)	0.0	−895.37711	10.4 (0)	0.0	−895.41455	0.0
2b (C_{2v})	−896.53221	10.1 (0)	15.1	−895.34428	10.0 (0)	20.2	−895.38604	17.5
3a (C_{4v})[d]	−249.66734	10.2 (0)	0.0	−248.92932	10.1 (0)	0.0	−248.95369	0.0
3b (C_{2v})[d]	−249.64457	9.8 (0)	13.9	−248.89890	9.7 (0)	18.7	−248.92725	16.2
4a (C_S)[d]	−244.22100	11.4 (0)	0.0	−243.47044	11.5 (0)	0.0	−243.49951	0.0
4b (C_{2v})[d]	−244.11893	10.6 (1)	63.2	−243.35494	10.6 (1)	71.6	−243.38308	72.2
4c (C_S)[d]	−244.17989	11.6 (0)	26.0	−243.41934	11.6 (0)	32.2	−243.45126	30.4

[a] Total energies in Hartree. [b] Zero-point energies in kcal/mol. The integers in parentheses are number of imaginary frequencies (NIMAG). [c] The relative energies with ZPE corrections in kcal/mol. [d] The 6-311+G* basis set was used for the nitrogen atom and for M = Mg and Ca, and the energy-adjusted Stuttgart ECPs were used for M = Sr and Ba.

MgN_4 (**1a**) are the most energetically favored for all singlet MN_4 systems considered here. It should be noted that, different from the other C_{4v} pyramidal MN_4 (M = Mg^{2+}, Ca^{2+}, Sr^{2+}) structures, the structure of BaN_4 (**4a**) is a leaning pyramidal with C_S symmetry. The calculation for the C_{4v} pyramidal BaN_4 was also carried out, but we found that this structure is unstable as a local minimum with three imaginary frequencies at the B3LYP and MP2 levels of theory. Each MN_4 system was also located in one planar C_{2v} structure (**1b**−**4b**) containing one N_4^{2-} ring. As shown in Table 1, the pyramidal MN_4 (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) species (**1a**−**4a**) are all local minima on their potential energy surfaces (PES) at the B3LYP and MP2 levels of theory. Species **1b**−**4b** are the local minima for CaN_4 and SrN_4 systems at the two used levels of theory, but they are first-order saddle points for the MgN_4 and BaN_4 systems. As shown in Figure 1, besides the previously mentioned MN_4 structures, we have located a C_S structure with dicoordinated Mg out of the N_4 ring plane (**1c**) and a planar C_S structure containing dicoordinated Ba (**4c**) for MgN_4 and BaN_4 systems, respectively. They are all local minima at the B3LYP and MP2 levels of theory. As shown in Table 1, the planar C_{2v} structures containing dicoordinated Mg, Ca, Sr, and Ba are 12.7, 17.5, 16.2, and 72.2 kcal/mol higher in energy than their pyramidal structures at the CCSD(T) level of theory, respectively. The pyramidal MgN_4 (**1a**) was found to be 1.7 kcal/mol lower in energy than the MgN_4 (**1c**) at the MP2/6-311+G* level of theory, but it is 4.9 kcal/mol higher in energy at the B3LYP/6-311+G* level of theory. To further analyze their relative stabilities, we have refined their energies at the CCSD(T)/6-311+G*//MP2/6-311+G* + ZPE (MP2/6-311+G*) level of theory. As seen from Table 1, **1c** is indeed more stable than **1a**. The relative energy is 3.9 kcal/mol. Therefore, it is the isomer **1c** rather than the pyramidal structure that is the global minimum of the MgN_4 species considered here. The planar C_S BaN_4 (**4c**) is energetically higher than the pyramidal **4a** by 30.4 kcal/mol at the CCSD(T) level of theory.

A comparison of the relative stabilities of different geometrical MN_4 complexes and those of recently predicted M_2N_4[13] (M = Li^+, Na^+, K^+, Rb^+, Cs^+), MN_5[8,9] (M = Li^+, Na^+, K^+, Rb^+), and $M(N_5)_2$[9] (M = Mg^{2+}, Ca^{2+}) can be made. For the complexes of the N_4^{2-} ligand, energy analysis shows that most structures with metal cations over the ring are the global minima, whereas for the complexes of the N_5^- ligand, the structures containing dicoordinated metal are the most energetically favored. This trend may be attributed to the lone pair repulsion. As compared with cyclic N_5^-, the N_4^{2-} ring is smaller, and it has a larger lone pair repulsion. Thus, structures in which metal cations and the N_4^{2-} ligand are coplanar are not the most energetically favored.

TABLE 2: Enthalpies of Formations (kcal/mol) of the MN_4 Species at the B3LYP Level of Theory (Including ZPE Corrections)

species	$\Delta_f H$[a]
Mg + $2N_2$ → **1a** (C_{4v})	157.6 (78.8)
Mg + $2N_2$ → **1b** (C_{2v})	164.6 (82.3)
Mg + $2N_2$ → **1c** (C_S)	152.7 (76.3)
Ca + $2N_2$ → **2a** (C_{4v})	90.4 (45.2)
Ca + $2N_2$ → **2b**(C_{2v})	105.5 (52.8)
Sr + $2N_2$ → **3a** (C_{4v})	95.3 (47.6)
Sr + $2N_2$ → **3b** (C_{2v})	109.2 (54.6)
Ba + $2N_2$ → **4a** (C_S)	209.9 (104.9)
Ba + $2N_2$ → **4b** (C_{2v})	273.1 (136.6)
Ba + $2N_2$ → **4c** (C_S)	235.9 (117.9)

[a] The kcal/mol per N_2 unit is given in parentheses.

To understand the high-energy nature of the MN_4 species, we have calculated their enthalpies of formations at the B3LYP level of theory. The calculation results are listed in Table 2. The suggested ScN_7 lies approximately 36 kcal/mol per N_2 unit higher in energy above a Sc atom and $7/2N_2$.[3] The energy of N_5ThN_7 lies about 22 kcal/mol per N_2 unit higher than that of a Th atom and six N_2 molecules.[4] The calculated reaction energy for the decay of $Fe(N_5)_2$ into an Fe atom and five N_2 molecules is 45 kcal/mol per N_2 unit.[5] The predicted ThN_6 gives the energy of 24 kcal/mol per N_2 unit above the Th and $3N_2$.[6] As shown in Table 2, the MN_4 species lie about 45.2−136.6 kcal/mol per N_2 unit above the energy of the metal atom and two N_2 molecules, which are energetically substantially higher than the predicted ScN_7, N_5ThN_7, $Fe(N_5)_2$, and ThN_6 molecules. So if the MN_4 species could be prepared, they would be effective HEDMs.

As shown in Figure 1, for each set of the similar structural MN_4 species, along group 2, going from Mg to Sr, the heavier the M atom is, the longer the M−N distances are. But the Ba−N2 (N5) distances (2.135−2.151 Å) in BaN_4 (**4b**) are shorter than the corresponding Sr−N2 (N5) distances (2.219−2.200 Å) in SrN_4 (**3b**), despite the larger atomic radii of the heavier element, suggesting that the bonding in BaN_4 (**4b**) has a larger covalent character than that in SrN_4 (**3b**). The covalent radius for nitrogen is 0.7 Å,[26] and the corresponding values for Mg, Ca, Sr, and Ba are 1.36, 1.74, 1.92, 1.98 Å,[26] respectively. Obviously, except for the Ba−N5 bond in the pyramidal BaN_4 (**4a**) and the Mg−N2 (N5) bonds in MgN_4 (**1c**), all M−N bond distances are shorter than the sum of the covalent radii of the corresponding M atom and nitrogen atom at the B3LYP level of theory. Regarding the N−N bond distances in the MN_4 compounds, for the C_{4v} pyramidal structures, the N−N bond distances in the MgN_4, CaN_4, and SrN_4 systems are all either close to those in the bare N_4^{2-} ring or slightly longer (Figure

TABLE 3: Zero-Point Corrected B3LYP Energies (kcal/mol) for Hypothetical $MN_4 \rightarrow M^{2+} + N_4^{2-}$ Reactions

MgN_4			CaN_4		SrN_4		BaN_4		
1a	**1b**	**1c**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**4c**
591.0	584.0	596.0	544.0	528.9	511.2	497.3	356.7	293.4	330.7

1). For the C_S pyramidal BaN_4, the N−N distances in this structure are alternate and close to those in the N_4^{2-} dianion. For other nonpyramidal MN_4 structures, the presence of the metal cation on the side of the ring induces alternating N−N distances and thus less aromatic character. In addition, like the case of the isolated N_4^{2-} dianion, all N−N−N bond angles are about 90° in the N_4 rings of the MN_4 species. Mulliken charge analysis shows that all positive charges are located on the alkaline-earth metal atoms, and all negative charges are on the N_4 rings for all the MN_4 species. In terms of NBO analysis, for the pyramidal MN_4 species (**1a**−**4a**), the calculated NN WBIs range from 1.2 to 1.4, indicating delocalization. For the planar C_{2v} structures containing dicoordianted M (**1b**−**4b**), MgN_4 (**1c**), and BaN_4 (**4c**) (except for the bonds of N2−N5, whose WBIs are very close to that of the N−N single bond (1.0)), the calculated WBIs of the other NN bonds range from 1.2 to 1.5, which is between the standard values of a single bond (1.0) and a double bond (2.0). That all WBIs of the metal−nitrogen bonds range from 0.1 to 0.7 supports that all metal−ligand bonds are possibly partly ionic and partly covalent. On the other hand, among each set of the similar structural MN_4 species, the WBIs of Ba−N in the BaN_4 compounds are largest, again indicating that the bonding in the BaN_4 system has a larger covalent character as compared with other MN_4 systems, in agreement with the opinion of Gregory.[2]

Stabilities of the MN_4 Systems. To estimate the strength of the interactions between the alkaline-earth cations and the N_4^{2-} ligand, we performed the calculations on the binding energies of various MN_4 complexes. The zero-point corrected B3LYP energies for hypothetical $MN_4 \rightarrow M^{2+} + N_4^{2-}$ reactions are given in Table 3. All reactions are endothermic, indicating a substantial energy stabilization of the MN_4 species as compared to the bare N_4^{2-} dianion and the M^{2+} cations. Furthermore, the binding energy order is $MgN_4 > CaN_4 > SrN_4 > BaN_4$, suggesting that the more electropositive the alkaline-earth metal is, the less interaction with the ring would be. On the other hand, as compared with our previous data[13] for the complexes of N_4^{2-} with alkali metals Na, K, Rb, Cs, we found that the interaction between the metal cations and the N_4^{2-} ligand in the MN_4 ($M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$) complexes is stronger than that in the M_2N_4 ($M = Na^+, K^+, Rb^+, Cs^+$) complexes for the same row metals. This trend may be attributed to the electronegativity of metals. Group I metals are more electropositive than group II and can be expected to interact less with the ring.

We have investigated the isomerization and decomposition reactions for some MN_4 species using the B3LYP and MP2 methods. The optimized structures for reactants, transition states, and products are shown in Figure 1. The energy differences (with ZPE corrections) between reactants and transition states and transition states and products are inserted between their corresponding structures.

As shown in Figure 1, the isomerization of MgN_4 **1a** and **1c** is expected to occur easily through **TS1ac** (C_S) because the transition-state barrier from **1c** to **1a** is 7.3 kcal/mol, and from **1a** to **1c**, it is only 3.4 kcal/mol at the CCSD(T) level of theory. **TS1c** is a transition structure of the dissociation of MgN_4 (**1c**) with an imaginary frequency. The barrier for the decomposition reaction **1c** → **TS1c** → Mg + $2N_2$ is predicted to be 26.9 kcal/mol at the MP2 level. But, it is only 10.6 kcal/mol at the CCSD(T) level. Such low barriers imply that MgN_4 (**1c**) can easily dissociate into a magnesium atom and smaller nitrogen molecules through the located transition states. Possible isomerization reactions between CaN_4 **2a** and **2b** have been investigated. The two conformers interconvert through a transition structure **TS2ab** (C_S) (seen in Figure 1). Conformer **2a** converts to **2b** with a barrier of 22.8 kcal/mol, and conformer **2b** converts to **2a** with a barrier of 5.3 kcal/mol. Thus, species **2b** is not likely to be stable, and if it is formed in any process, it will rapidly rearrange to the most stable pyramidal **2a**. Similarly, the isomerizaion reaction path analysis indicates that the species SrN_4 (**3b**) is unstable, and it will transform into the pyramidal **3a**. Possible decomposition mechanisms were studied for pyramidal MN_4 ($M = Ca^{2+}$ and Sr^{2+}) molecules, in analogy with what was previously done for SrN_7,[3] by considering the opening of the nitrogen ring and locating the transition states (TS) (Figure 1). The TS for CaN_4 (**2a**) occurs when the N4−N5 bond opens to 2.247 (2.224) Å, and the TS for SrN_4 (**3a**) occurs when the N4−N5 bond opens to 2.232 (2.204) Å. IRC calculations performed at the B3LYP and MP2 levels directly lead to dissociation into Ca, Sr, and two N_2 molecules, respectively, from these two transition structures. The barriers for the two decomposition reactions **2a** → **TS2a** → Ca + $2N_2$ and **3a** → **TS3a** → Sr + $2N_2$ are predicted to be 43.5 and 43.7 kcal/mol at the CCSD(T) levels of theory, respectively, indicating highly stabilities.

Figure 1 also shows that **TS4ac** connects **4a** and **4c**. The isomerization barrier from **4a** to **4c** is 94.1 kcal/mol, and from **4c** to **4a**, it is 63.7 kcal/mol at the CCSD(T) level of theory. Such high barriers show that species **4a** and **4c** are highly stable toward isomerization.

The previous analysis indicates that the pyramidal CaN_4, SrN_4, BaN_4, and the planar C_S BaN_4 (**4c**) species are likely to be stable and to be observed experimentally.

Nature of the M−N_4 Bonding. In this section, we will explore the nature of the M−N_4 bonding by MO analysis. Natural population configurations show that all the MN_4 species except MgN_4 exhibit substantial M[$(n-1)d$] (n is the number of electron shell) populations, indicating the back donation from N_4^{2-} to M-$d(pi)$. Furthermore, the $(n-1)d$ character in the BaN_4 compounds is the largest one among the four MN_4 systems.

MO analysis on various MN_4 species has been performed. In the following, we will take the pyramidal MN_4 as an example and discuss in some detail the results of the MO analysis. Our main consideration was the bonding between the ring $2p\pi$ orbitals and the d orbitals of the metal. In an orbital picture of the pyramidal BaN_4, the combined σ, π, and δ bonding around the C_4 axis is observed. The Ba−N_4 bonds should not only be interpreted as ionic interactions; it is striking to see how Ba in its formal valence of +2 can interact so strongly with the N_4 ring, by forming σ, π, and δ bonds, similar to what is observed for CsN_7Ba.[11] The 5d orbitals of Ba take an active role in the formation of this multiple bond, intervening especially in the δ bond. The MOs of the pyramidal SrN_4 and CaN_4 look rather similar to those of BaN_4; however, the character of the δ MOs is small on the alkaline-earth metal (Sr or Ca) and rests mainly on the N_4 ring.

Conclusion

We investigated a series of compounds with general formula MN_4, where M is a group II cation, Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}.

Among all known MN_4 species, the pyramidal structures except MgN_4 are the most energetically favored for all singlet MN_4 systems considered here. For MgN_4, the C_S structure (**1c**) with the dicoordinated Mg out of the N_4 ring plane is the most stable of all. This study suggests that the pyramidal CaN_4, SrN_4, BaN_4, and the planar C_S BaN_4 (**4c**) species have the potential to be used as HEDMs because of their moderate dissociation or isomerization barriers (21.3−94.1 kcal/mol). Structural, NBO, and MO analyses indicate that the bonding in the BaN_4 system has a larger covalent character as compared with other MN_4 systems. The M−N_4 bonding in these compounds can be understood using simple molecular orbital pictures and noting that substantial d character is found in the bonding of the MN_4 (M = Ca^{2+}, Sr^{2+}, Ba^{2+}) species.

References and Notes

(1) DiSalvo, F. J. *Science* **1990**, *247*, 649.

(2) Gregory, D. H. *Cood. Chem. Rev.* **2001**, *215*, 301.

(3) Gagliardi, L.; Pyykkö, P. *J. Am. Chem. Soc.* **2001**, *123*, 9700.

(4) Gagliardi, L.; Pyykkö, P. *J. Phys. Chem. A* **2002**, *106*, 4690.

(5) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem.*−*Eur. J.* **2001**, *7*, 4155.

(6) Straka, M. *Chem. Phys. Lett.* **2002**, *358*, 531.

(7) Glukhovtsev, M. N.; Schleyer, P. v. R.; Maerker, C. *J. Phys. Chem.* **1993**, *97*, 8200.

(8) Zhao, J. F.; Li, N.; Li, Q. S. *Theor. Chem. Acc.* **2003**, *110*, 10.

(9) Burke, L. A.; Butler, R. N.; Stephens, J. C. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1679.

(10) Gagliardi, L. *J. Am. Chem. Soc.* **2002**, *124*, 8757.

(11) Gagliardi, L.; Pyykkö, P. *Theor. Chem. Acc.* **2003**, *110*, 205.

(12) Zandwijk, G. v.; Janssen, R. A. J.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4155.

(13) Li, Q. S.; Cheng, L. P. *J. Phys. Chem. A* **2003**, *107*, 2882.

(14) Frisch, M. J. et al. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(17) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(19) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(20) Fuentealba, P.; Preuss, H.; Stoll, H.; Szentpaly, L. v. *Chem. Phys. Lett.* **1982**, *89*, 418.

(21) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(22) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(23) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(24) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.* **1988**, *169*, 41.

(25) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(26) http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch7/size.html#cov.