η^5-N$_5$$^-$ −Metal−η^7-N$_7$$^{3-}$: A New Class of Compounds

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Ab initio calculations at the B3LYP and MP2 levels suggest that a series of compounds with the general formula N_5MN_7 (M = Ti, Zr, Hf, Th) are locally stable. These compounds are thermodynamically at least as stable as the recently suggested ScN_7 molecule. N_5ThN_7 seems the most stable of all. It lies 21.5 kcal/mol below a transition state, corresponding to the opening of one N−N bond in the N_7 ring, and only 132 kcal/mol above Th + 6 N_2, or 22 kcal/(mol N_2).

Introduction

The isolation of stable salts of the N_5^+ cation, the first new all-nitrogen species to be made in a century[1,2] has put the spotlight on the search for other stable polynitrogen species.

We have recently predicted the possible existence of the ScN_7 molecule,[3] which contains a new structural group, the η^7-N$_7$$^{3-}$ 10-π-electron ring, isoelectronic with the experimentally known η^7-(C$_7$H$_7$)$^{3-}$ ligand, and has a relatively low energy of formation of 36 kcal/mol per N_2 unit, above a Sc atom and N_2. The idea behind this study is that a 10π system like N_7^{3-} has occupied σ, π, and δ shells capable of donation to the M^{3+} metal. The interaction between the metal (M) and the poly-nitrogen cluster should thus stabilize the compound with respect to a N_n^q species.

In this study, we consider the further complexation of such a MN_7 moiety to a six-π-electron, η^5-N$_5$$^-$ pentazole ring. This gives rise to sandwich compounds with the general formula N_5MN_7 (Figure 1). We investigated the compounds containing a group 4 element, M = Ti, Zr, Hf, plus Th. Along row 4, the species containing Sc, Ti, and V, with a total charge of −1, 0, and +1, respectively, were also investigated.

It turns out that the energies of formation of this class of molecules are comparable with the previous ScN_7 case, even at the high N-to-M ratio of 12. Furthermore, the M atom in these new species is sterically shielded, whereas that of ScN_7 was open (unless the ScN_7 compound would crystallize as chains).

The transition-metal complexes of the η^5-N$_5$$^-$ ligand were briefly considered by us[3] and thoroughly studied by Lein et al.[4] in the case of the ferrocene analogue $Fe(N_5)_2$. Its energy of formation was, however, found to be somewhat higher, 40 kcal/mol per N_2 unit above the known Fe + 5N_2.

Computational Details

The calculations were carried out at the density functional theory (DFT) level, using the B3LYP exchange-correlation functional, with a 6-31G* basis set for the nitrogen atoms and metal atom, M = Sc, Ti, and V. When M belonged to the fifth,

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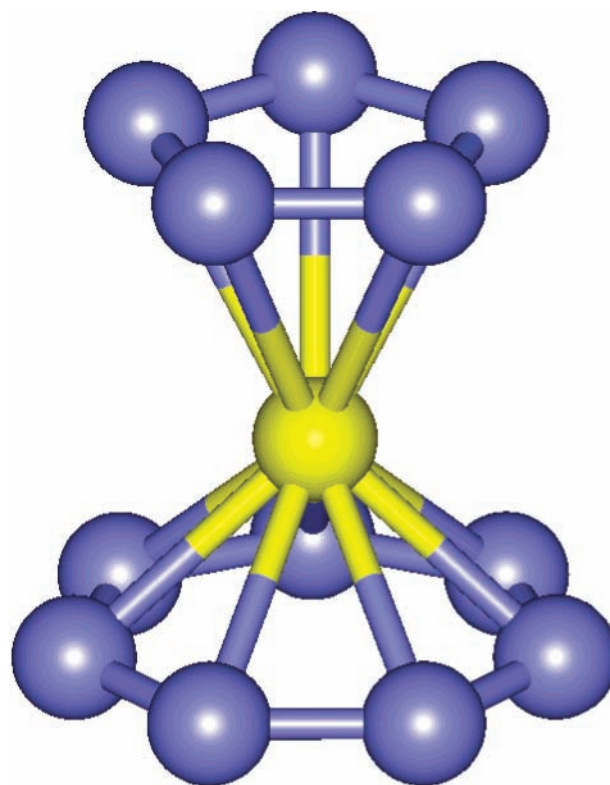* To whom correspondence should be addressed. E-mail: laura.g@ciam.unibo.it.
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Figure 1. Structure of the local minimum of N_5MN_7 (M = Ti, Zr, Hf, and Sc).

M = Zr, sixth, M = Hf, and seventh row, M = Th, effective core potentials (ECPs) were used on the metal atom. The energy-adjusted Stuttgart ECPs were used for this purpose.[5] The number of core electrons was 28 for Zr and 60 for Hf and Th. The accompanying basis set of the ECPs (8d,7p,6d,4f) was used to describe the valence electron density.[6] The program Gaussian 98 was employed.

Equilibrium geometries and harmonic frequencies were computed for all species. The calculations were performed using the ultrafine (99, 590) grid having 99 radial shells and 590 angular points per shell. At the same time, the weighting scheme of Becke has been used for numerical integration. The gradient

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TABLE 1: B3LYP Bond Lengths (Å) and Angles (degrees) for the N$_5$MN$_7$ Species, with M = Ti, Zr, Hf, and Sc[a]

system	N$_5$TiN$_7$	N$_5$ZrN$_7$	N$_5$HfN$_7$	N$_5$ThN$_7$	N$_5$ScN$_7^-$
R_{M-N7}	2.090 (2.109)	2.254	2.244 (2.228)	2.439	2.190
R_{M-N5}	2.342 (2.317)	2.540	2.520 (2.492)	2.823	2.573
R_{N7-N7}	1.370 (1.392)	1.375	1.378 (1.406)	1.367	1.370
R_{N5-N5}	1.344 (1.362)	1.342	1.342 (1.360)	1.336	1.337
$\angle$N7MN7	38.3 (38.5)	35.5	35.8 (36.8)	32.5	36.5
$\angle$N5MN5	33.4 (34.2)	30.6	30.9 (31.7)	27.4	30.1

[a] MP2 Values in Parenthesis for N$_5$TiN$_7$ and N$_5$HfN$_7$. N5 is a nitrogen atom lying on the N$_5$ ring, and N7 is a nitrogen atom lying on the N$_7$ ring.

tolerance was the default one in Gaussian which is set to be 10^{-6} on the largest component of the Cartesian gradient.

Comparative geometry optimizations and harmonic frequency calculations were performed using MP2 for some of the species.

Results

In Table 1, the typical bond distances and angles for the various molecules that were found to be stable are reported.

All of them have C_s symmetry (the symmetry plane of the molecules is a plane perpendicular to the N$_5$ and N$_7$ rings, containing the metal atom and one N atom on the N$_5$ and one on the N$_7$ ring). Along group 4, N$_5$TiN$_7$, N$_5$ZrN$_7$, and N$_5$HfN$_7$, together with N$_5$ThN$_7$, are local minima. Along row 4, N$_5$ScN$_7^-$ and N$_5$TiN$_7$ are local minima, whereas N$_5$VN$_7^+$ is not stable and dissociates into two N$_2$ groups, one N$_3$ moiety, one N$_5$ moiety, and a V atom. We checked the stability of the triplet for N$_5$TiN$_7$, and it was found to lie 15 kcal/mol higher in energy than the singlet. In all stable structures, the N$_7$ ring is closer to the M atom than the N$_5$ ring, with the typical M−N7 distance (N7 is a nitrogen atom lying on the N$_7$ ring) being ca. 0.3 Å shorter than the typical M−N5 distance (N5 is a nitrogen atom lying on the N$_5$ ring). In N$_5$TiN$_7$, these M−N distances are smaller than in any other system. Along group 4, going from Ti to Zr, the two M−N distances become ca. 0.2 Å longer, whereas they become 0.02 Å shorter in going from Zr to Hf. In N$_5$ThN$_7$, M−N7 is 0.2 Å longer and M−N5 is 0.3 Å longer, than in N$_5$HfN$_7$. Along row 4, in going from Sc to Ti, M−N7 becomes 0.1 Å longer and M−N5 becomes 0.2 Å longer. One

TABLE 2: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parenthesis for the N$_5$MN$_7$ Species (M = Ti and Zr), at the B3LYP and MP2 Levels of Theory[a]

normal mode	N$_5$TiN$_7$/B3LYP	N$_5$TiN$_7$/MP2	N$_5$ZrN$_7$/B3LYP
ν_1(a) N$_5$,N$_7$ rotation	i5.8 (0) (0)	i9.5 (0)	i8.7 (0)
ν_2(e) M−N$_5$,M−N$_7$ bend	78.3 (2) (2)	77.5 (2)	35.9 (5)
ν_3(e) M−N$_5$ bend	160.1 (0) (1)	194.5 (0)	130.3 (0)
ν_4(a) M−N$_5$, M−N$_7$ sym. stretch	236.3 (7) (2)	229.6 (2)	231.6 (15)
ν_5(e) N$_7$ out of plane breathing	297.3 (0) (3)	311.9 (0)	353.4 (0)
ν_6(e) M−N$_7$ stretch	312.6 (1) (1)	328.8 (1)	293.2 (0)
ν_7(e) N$_7$ out of plane bend	349.6 (0) (1)	443.3 (0)	382.6 (0)
ν_8(a) M−N$_5$, M−N$_7$ asym. stretch	473.5 (116) (17)	450.6 (99)	397.9 (104)
ν_9(e) N$_7$ out of plane bend	504.5 (0) (0)	509.2 (0)	521.8 (0)
ν_{10}(e) N$_5$ out of plane bend	746.3 (0) (0)	754.1 (0)	759.3 (0)
ν_{11}(a) N$_7$ in plane breathing	813.3 (13) (43)	737.0 (14)	792.6 (9)
ν_{12}(e) N$_7$ out of plane def	893.3 (0) (0)	915.3 (0)	923.0 (0)
ν_{13}(e) N$_5$, N$_7$ out of plane def	909.1 (0) (0)	926.9 (0)	930.7 (0)
ν_{14}(e) N$_7$ in plane breathing	926.7 (14) (2)	846.4 (8)	909.7 (21)
ν_{15}(e) N$_7$ in plane def	951.9 (0) (2)	908.4 (0)	939.0 (0)
ν_{16}(e) N$_7$ in plane asym def	1032.6 (0) (0)	1928.1 (0)	1069.3 (0)
ν_{17}(e) N$_5$ in plane asym stretch	1093.5 (0) (3)	1060.3 (0)	1092.4 (0)
ν_{18}(a) N$_5$ in plane breathing	1135.4 (0) (29)	1048.4 (0)	1141.7 (1)
ν_{19}(e) N$_5$ in plane breathing	1188.4 (3) (2)	1102.0 (2)	1199.3 (5)

[a] For N$_5$TiN$_7$/B3LYP, the Raman intensities are also reported as the second quantity in parentheses.

TABLE 3: Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parenthesis for the N$_5$MN$_7$ Species (M = Hf, Th, and Sc), at the B3LYP and MP2 Levels of Theory[a]

normal mode	N$_5$HfN$_7$/B3LYP	N$_5$HfN$_7$/MP2	N$_5$ThN$_7$/B3LYP	N$_5$ScN$_7^-$/B3LYP
ν_1(a)	3.4 (0) (0)	i9.7 (0)	i8.5 (0) (0)	i10.6 (0)
ν_2(e)	41.1 (4) (1)	37.1 (4)	35.7 (11) (0)	62.9 (5)
ν_3(e)	132.6 (0) (1)	161.8 (0)	108.3 (0) (2)	109.6 (0)
ν_4(a)	233.1 (17)(0)	238.9 (10)	217.7 (38)(0)	177.9 (8)
ν_5(e)	283.9 (0) (3)	302.3 (0)	236.1 (1) (3)	304.5 (3)
ν_6(e)	361.4 (0) (5)	334.6 (0)	401.9 (0) (3)	364.7 (0)
ν_7(e)	386.4 (0) (0)	507.1 (0)	399.5 (0) (2)	424.6 (0)
ν_8(a)	341.0 (66)(20)	334.3 (69)	348.7 (109) (13)	445.4 (134)
ν_9(e)	520.3 (0) (0)	513.4 (0)	502.3 (0) (0)	485.4 (0)
ν_{10}(e)	759.5 (0) (0)	762.1 (0)	766.5 (0) (0)	764.9 (0)
ν_{11}(a)	785.0 (6) (45)	705.3 (11)	786.5 (10) (37)	796.0 (14)
ν_{12}(e)	921.7 (0) (3)	910.1 (0)	960.2 (0) (3)	954.6 (0)
ν_{13}(e)	925.8 (0) (1)	931.4 (0)	944.7 (0) (0)	957.6 (0)
ν_{14}(e)	901.1 (24)(2)	812.4 (16)	922.6 (30) (1)	921.5 (43)
ν_{15}(e)	931.2 (0) (0)	960.8 (0)	964.6 (0) (2)	961.8 (0)
ν_{16}(e)	1078.1 (0) (0)	1072.7 (0)	1172.7 (0) (0)	1103.5 (0)
ν_{17}(e)	1091.1 (0) (3)	1060.8 (0)	1098.6 (0) (2)	1152.3 (0)
ν_{18}(a)	1137.8 (0) (34)	1052.4 (0)	1161.2 (1) (24)	1158.9 (0)
ν_{19}(e)	1195.3 (5) (1)	1111.6 (3)	1221.3 (4) (0)	1216.1 (9)

[a] For N$_5$HfN$_7$/B3LYP and N$_5$ThN$_7$/B3LYP the Raman intensities are also reported as the second quantity in parentheses. The assignment is the same as in Table 2.

TABLE 4: Partial Charges on N_5, M, and N_7 and Total Dipole Moment (Debye)

system/method	δ_{N_5}	δ_M	δ_{N_7}	dipole
N_5TiN_7/B3LYP	−0.40	+1.11	−0.71	0.44
N_5TiN_7/MP2	−0.50	+1.42	−0.92	0.71
N_5ZrN_7/B3LYP	−0.46	+1.49	−1.02	1.28
N_5HfN_7/B3LYP	−0.48	+1.60	−1.12	1.71
N_5HfN_7/MP2	−0.65	+2.20	−1.54	2.37
N_5ThN_7/B3LYP	−0.28	+0.90	−0.62	3.30
N_5ScN_7-/B3LYP[a]	−0.65	+1.01	−1.36	2.71
ScN_7/B3LYP[b]		+1.13	−1.13	7.62
ScN_7/MP2[b]		+1.39	−1.39	8.94

[a] The origin of the system is on the Sc atom. [b] Reference 3.

should bear in mind that the Sc compound has a total charge of (−1), whereas all other structures are neutral. The typical N−N distances in both the two rings are rather constant when varying the central metal. For the Ti and Hf compounds, the MP2 structures were also optimized. The MP2 bond distances are similar to the B3LYP values.

In Tables 2 and 3, the B3LYP harmonic frequencies of the molecules are reported, together with their IR intensities. All species except N_5HfN_7 have one very small imaginary frequency corresponding to the rotation of the two rings one with respect to the other. N_5HfN_7, on the other hand, has a small real frequency corresponding to this purely rotational mode. Local minima should show zero imaginary frequencies. However, in this case, the small imaginary frequency corresponds to a purely rotational mode. We followed this mode in N_5TiN_7 and ended up into a distorted structure which was less than 10 cm^{-1} lower in energy than the C_s one. We can thus safely say that the molecule might rotate, but statistically, it will assume most of the time the undistorted C_s conformation.

Most of the modes have zero IR intensities, except for a few modes: ν_2, corresponding to a M−N_7 and M−N_5 bending; ν_4 corresponding to a M−N_7 and M−N_5 symmetric stretching; ν_8 corresponding to a M−N_7 and M−N_5 antisymmetric stretching, which is the most intense mode in all molecules; ν_{11} corresponding to a N_7 in plane breathing; ν_{14} corresponding to a N_7 in plane breathing; and ν_{19} corresponding to a N_5 in plane breathing. For N_5TiN_7, N_5HfN_7, and N_5ThN_7, the B3LYP Raman intensities are also reported. Most of the modes have very little Raman intensity. The only modes having some Raman intensity are ν_8, ν_{11}, and ν_{18}.

The MP2 frequencies have also been calculated for N_5TiN_7 and N_5HfN_7, and they are similar to the B3LYP frequencies. In N_5HfN_7, ν_1 has an imaginary value of i9.7 cm^{-1}.

In Table 4, the partial charges on the N_5, M, and N_7 moieties, obtained by a Mulliken population analysis, are reported. Formally, they correspond to N_5^-, M^{4+} (except for Sc^{3+}), and N_7^{3-}. The real charge is however smaller than the formal charge. The total dipole moments are also reported. For the charged species $N_5ScN_7^-$, the origin of the system was placed on the Sc atom. At the B3LYP level, the ionicity increases in going from Ti to Zr to Hf, together with the total dipole moment. N_5ThN_7 has the largest dipole moment of all, but the partial charges on the moieties are lower than in all other systems. MP2 gives larger ionicity and dipole moment than B3LYP.

A possible dissociation mechanism was investigated for N_5TiN_7, in analogy with what was previously done for ScN_7.[3] We considered the opening of the N_7 ring and found a transition state (TS; Figure 2), with one imaginary frequency, which lies 9 kcal/mol higher in energy than the local minimum (LM) N_5TiN_7. This energy barrier of 9 kcal/mol already includes a zero-point energy correction of 1 kcal/mol. For ScN_7, the
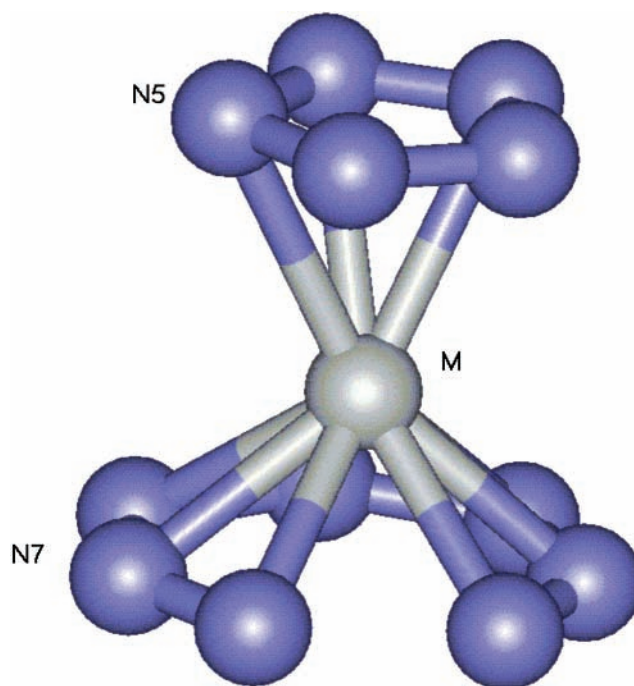

Figure 2. Structure of the transition state of N_5MN_7 (M = Ti and Hf).

analogous energy barrier was of 20 kcal/mol. Moreover, the TS for ScN_7 occurs when the N−N bond opens to 2.10 Å, whereas in the N_5TiN_7 TS, the N−N bond is only 1.86 Å. This indicates that presumably the opening process is easier to start in N_5TiN_7 than in ScN_7. As possible dissociation products of N_5TiN_7, we considered six N_2 molecules and a Ti atom. These lie 210 kcal/mol lower in energy than N_5TiN_7. Per N_2 unit, the latter corresponds to 35 kcal/mol. An analogous energy balance for ScN_7 gave 36 kcal/mol per N_2 unit.

The analysis of the structure and frequencies of N_5ZrN_7 did not suggest that the Zr compound could be more stable than the Ti compound. N_5HfN_7, on the other hand, has all real frequencies at the B3LYP level of theory. Compared to N_5ZrN_7, the two typical M−N bond distances are slightly shorter. The close chemical similarity between Zr and Hf can be attributed to a cancellation by shell-structure effects by relativistic effects.[7,8] We are not aware of any studies on the role of relativistic effects on the bonding of group 4 metals to 6π or 10π aromatic rings.

The usual opening of the N_7 ring presents a TS (Figure 2), with one imaginary frequency, which lies 15 kcal/mol higher in energy than the N_5HfN_7 local minimum, including a zero point energy correction of 1 kcal/mol. In the TS the N7−N7 bond is 2.03 Å. With respect to 6 N_2 molecules and Hf atom in its triplet ground state, N_5HfN_7 lies 180 kcal/mol higher in energy, which corresponds to only 30 kcal/mol per N_2 unit.

In N_5ThN_7 the ring opening presents a TS with one imaginary frequency which lies 21.5 kcal/mol higher in energy than the corresponding local minimum, already including a zero point energy correction of 2 kcal/mol. The N7−N7 bond is 2.06 Å in the TS. With respect to 6 N_2 molecules and Th atom in its triplet ground state, N_5ThN_7 lies 132 kcal/mol higher in energy, which corresponds to only 22 kcal/mol per N_2 unit. N_5ThN_7 is thus the most stable of all these N_5MN_7 molecules. It also seems that the dissociation process is more difficult to start in N_5ThN_7 in ScN_7, with its energy barrier of 20 kcal/mol.

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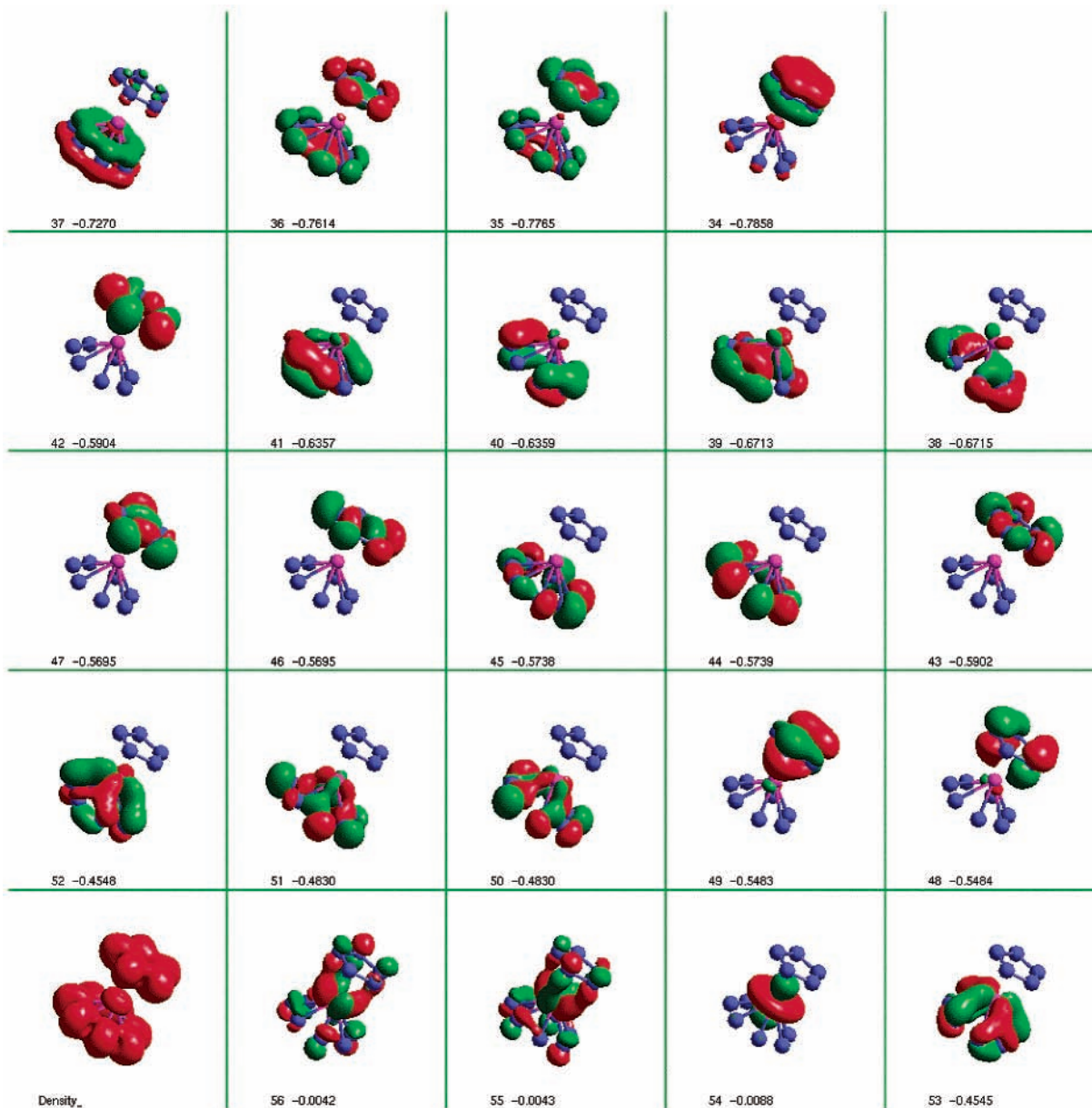*J. Phys. Chem. A, Vol. 106, No. 18, 2002* **4693**

Figure 3. Some Hartree−Fock molecular orbitals (MO) of N$_5$TiN$_7$: from MO 37 to MO 56. The orbital energy (a.u.) is also reported. MO 53 is the HOMO, and 54 is the LUMO. The total electron density in the bottom left-hand corner.

We performed an orbital analysis on the various species. As an example, we consider in detail the bonding of N$_5$TiN$_7$ using the Hartree−Fock orbitals. Including all of the 2s and 2p electrons of the rings and the four electrons of the metal, there are in all 64 electrons, or 32 doubly occupied MOs to analyze. These range from the HOMO, orbital 53, down to MO 21. The shapes of MOs from 53 to 34 are shown in Figure 3, together with three virtual orbitals, the LUMO, orbital 54, and MOs 55 and 56. A schematic qualitative energy-level diagram is reported in Figure 4. Our first expectation was that the bonding would mainly be between the ring 2pπ orbitals and the metal d orbitals. Around the molecular symmetry axis there would be σ and π orbitals binding to both the N$_5$ ring and the N$_7$ ring and, in addition a δ combination, binding to the N$_7$ ring. Such orbitals can indeed be identified. The two σ MOs are 34 and 37, respectively. The π bond to N$_5$ is formed by MOs 48−49. What complicates the situation is that the seven-ring N (2s+2p)σ orbitals also hybridize with the metal. From the N$_7$ ring, this yields the four axially π MOs, 38−41, and the four axially δ MOs, 50−53, all hybridized with the metal dδ. In addition, we

have MOs describing other intraring σ orbitals in this part of the eigenvalue spectrum. MO 54 is the metal d$_0$ LUMO that would receive an electron in an anion radical. The total electron density is shown in the lower left-hand corner of Figure 3.

Given the increasing of stability in going from lighter to heavier metals (form Ti to Th), we investigated the possibility that also the compound containing uranium (IV) could exist, but this turned out to be unstable.

We also studied the N$_5$ScN$_7^-$ anion. This system lies 69 kcal/mol lower in energy than ScN$_7$ and N$_5^-$. In Figure 5, the total energy of N$_5$ScN$_7^-$ as a function of the distance between ScN$_7$ and N$_5^-$ is reported. At each value of the distance between ScN$_7$ and N$_5^-$, the two moieties were reoptimized. The energy of the system increases with the distance up to 10 Å and then reaches the asymptotic value. It thus seems there is no barrier to the formation of the supersystem from the two fragments.

Conclusions

We presented the results of a study on some complexes with general formula N$_5$MN$_7$, where M is a group 4 atom, Ti, Zr,
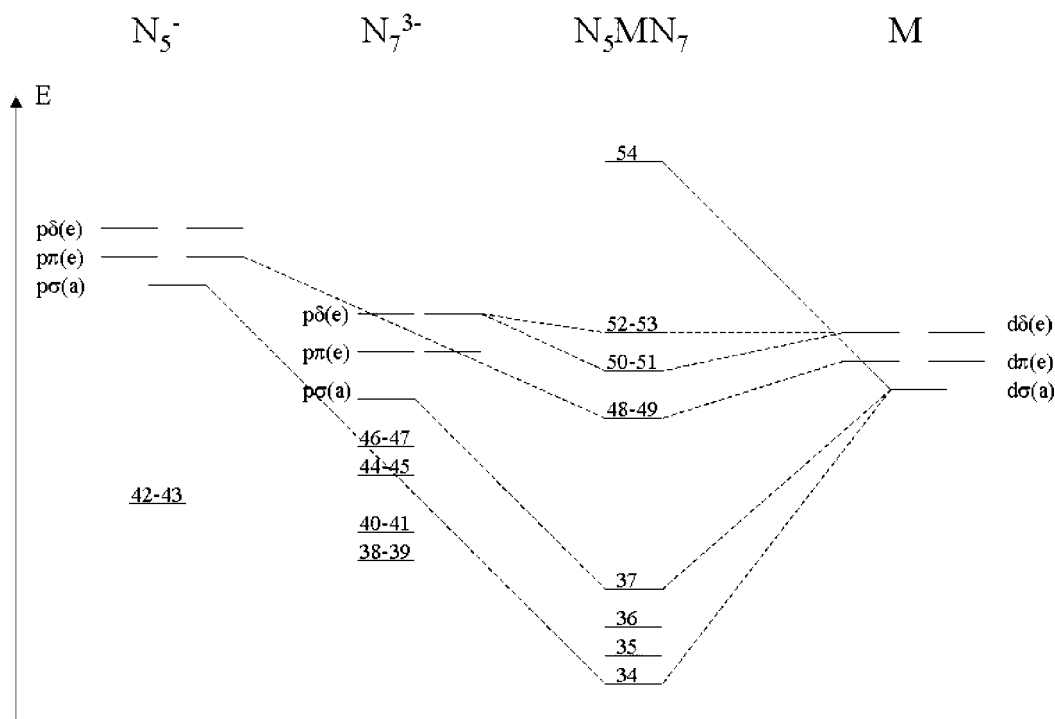
Figure 4. Qualitative energy-level diagram of N_5TiN_7 molecular orbitals.
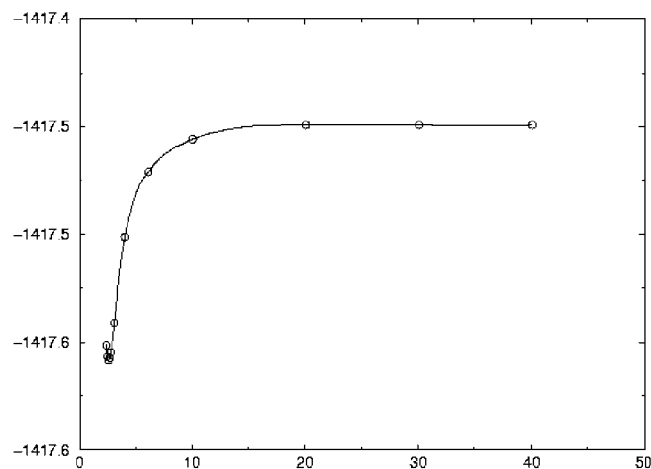

Figure 5. Total energy (a.u.) of $N_5ScN_7^-$ as a function of the distance (Å) between ScN_7 and N_5^-.

Hf, and also Th. These compounds are local minima. The system containing Th is the most stable of all. It presents a barrier to dissociation of 21.5 kcal/mol, corresponding to the breaking of a N–N bond on the N_7 ring, and it lies only 132 kcal/mol above Th + 6 N_2, or 22 kcal/(mol N_2). N_5HfN_7 has a barrier of 15 kcal/mol and lies 177 kcal/mol above Hf + 6 N_2, or 29.5 kcal/(mol N_2). The previously predicted ScN_7 molecule has a barrier to dissociation of 20 kcal/mol and lies 36 kcal/(mol N_2) above Sc and 7/2 N_2. The opening process presumably starts easier in ScN_7 than in the Th sandwich compound. Moreover, considering the lower energy of N_5ThN_7 with respect to the dissociation products compared to ScN_7, we suggest that N_5ThN_7 should have a chance of existing. The bonding in these N_5MN_7 species can be understood using simple molecular orbital concepts and noting that in the N_7 ring, a strong hybridization occurs between the ring σ and π systems.

The isoelectronic ionic species $N_5ScN_7^-$ turned also out to be interesting, because it can be formed via a barrierless reaction from N_5^- and ScN_7.

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