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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2002

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# $\eta^5\text{-N}_5^-$ –Metal– $\eta^7\text{-N}_7^{3-}$ : A New Class of Compounds

Laura Gagliardi<sup>\*,†</sup> and Pekka Pyykkö<sup>‡</sup>

Dipartimento di Chimica G. Ciamician, Università di Bologna, Viale F. Selmi 2, I-40126 Bologna, Italy, and  
Department of Chemistry, University of Helsinki, P.O.B. 55 (A. I. Virtasen aukio 1),  
FIN-00014 Helsinki, Finland

Received: November 12, 2001; In Final Form: February 20, 2002

Ab initio calculations at the B3LYP and MP2 levels suggest that a series of compounds with the general formula  $\text{N}_5\text{MN}_7$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Th}$ ) are locally stable. These compounds are thermodynamically at least as stable as the recently suggested  $\text{ScN}_7$  molecule.  $\text{N}_5\text{ThN}_7$  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  $\text{N}_7$  ring, and only 132 kcal/mol above  $\text{Th} + 6 \text{N}_2$ , or 22 kcal/(mol  $\text{N}_2$ ).

## Introduction

The isolation of stable salts of the  $\text{N}_5^+$  cation, the first new all-nitrogen species to be made in a century<sup>1,2</sup> has put the spotlight on the search for other stable polynitrogen species.

We have recently predicted the possible existence of the  $\text{ScN}_7$  molecule,<sup>3</sup> which contains a new structural group, the  $\eta^7\text{-N}_7^{3-}$  10- $\pi$ -electron ring, isoelectronic with the experimentally known  $\eta^7\text{-(C}_7\text{H}_7\text{)}^{3-}$  ligand, and has a relatively low energy of formation of 36 kcal/mol per  $\text{N}_2$  unit, above a Sc atom and  $\text{N}_2$ . The idea behind this study is that a 10 $\pi$  system like  $\text{N}_7^{3-}$  has occupied  $\sigma$ ,  $\pi$ , and  $\delta$  shells capable of donation to the  $\text{M}^{3+}$  metal. The interaction between the metal (M) and the poly-nitrogen cluster should thus stabilize the compound with respect to a  $\text{N}_n^q$  species.

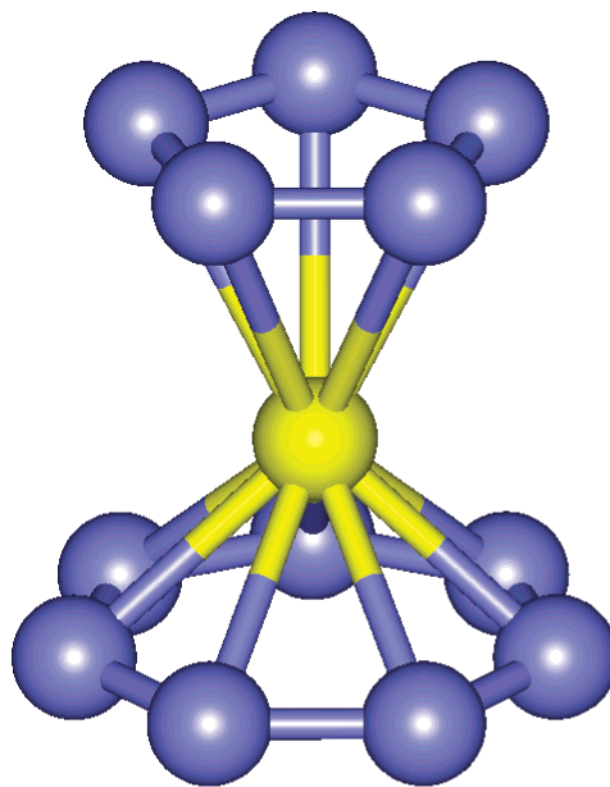
In this study, we consider the further complexation of such a  $\text{MN}_7$  moiety to a six- $\pi$ -electron,  $\eta^5\text{-N}_5^-$  pentazole ring. This gives rise to sandwich compounds with the general formula  $\text{N}_5\text{MN}_7$  (Figure 1). We investigated the compounds containing a group 4 element,  $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ , 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  $\text{ScN}_7$  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  $\text{ScN}_7$  was open (unless the  $\text{ScN}_7$  compound would crystallize as chains).

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

## 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,  $\text{M} = \text{Sc}, \text{Ti}$ , and V. When M belonged to the fifth,



**Figure 1.** Structure of the local minimum of  $\text{N}_5\text{MN}_7$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ , and Sc).

$\text{M} = \text{Zr}$ , sixth,  $\text{M} = \text{Hf}$ , and seventh row,  $\text{M} = \text{Th}$ , effective core potentials (ECPs) were used on the metal atom. The energy-adjusted Stuttgart ECPs were used for this purpose.<sup>5</sup> 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.<sup>6</sup> 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

\* To whom correspondence should be addressed. E-mail: laura.g@ciam.unibo.it.

<sup>†</sup> Università di Bologna.

<sup>‡</sup> University of Helsinki.

**TABLE 1: B3LYP Bond Lengths (Å) and Angles (degrees) for the  $\text{N}_5\text{MN}_7$  Species, with M = Ti, Zr, Hf, and Sc<sup>a</sup>**

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

<sup>a</sup> MP2 Values in Parenthesis for  $\text{N}_5\text{TiN}_7$  and  $\text{N}_5\text{HfN}_7$ . N5 is a nitrogen atom lying on the  $\text{N}_5$  ring, and N7 is a nitrogen atom lying on the  $\text{N}_7$  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  $\text{N}_5$  and  $\text{N}_7$  rings, containing the metal atom and one N atom on the  $\text{N}_5$  and one on the  $\text{N}_7$  ring). Along group 4,  $\text{N}_5\text{TiN}_7$ ,  $\text{N}_5\text{ZrN}_7$ , and  $\text{N}_5\text{HfN}_7$ , together with  $\text{N}_5\text{ThN}_7$ , are local minima. Along row 4,  $\text{N}_5\text{ScN}_7^-$  and  $\text{N}_5\text{TiN}_7$  are local minima, whereas  $\text{N}_5\text{VN}_7^+$  is not stable and dissociates into two  $\text{N}_2$  groups, one  $\text{N}_3$  moiety, one  $\text{N}_5$  moiety, and a V atom. We checked the stability of the triplet for  $\text{N}_5\text{TiN}_7$ , and it was found to lie 15 kcal/mol higher in energy than the singlet. In all stable structures, the  $\text{N}_7$  ring is closer to the M atom than the  $\text{N}_5$  ring, with the typical M–N7 distance ( $\text{N}_7$  is a nitrogen atom lying on the  $\text{N}_7$  ring) being ca. 0.3 Å shorter than the typical M–N5 distance ( $\text{N}_5$  is a nitrogen atom lying on the  $\text{N}_5$  ring). In  $\text{N}_5\text{TiN}_7$ , 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  $\text{N}_5\text{ThN}_7$ , M–N7 is 0.2 Å longer and M–N5 is 0.3 Å longer, than in  $\text{N}_5\text{HfN}_7$ . 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 ( $\text{cm}^{-1}$ ) and Their IR Intensities ( $\text{km mol}^{-1}$ ) in Parenthesis for the  $\text{N}_5\text{MN}_7$  Species (M = Ti and Zr), at the B3LYP and MP2 Levels of Theory<sup>a</sup>**

normal mode	$\text{N}_5\text{TiN}_7/\text{B3LYP}$	$\text{N}_5\text{TiN}_7/\text{MP2}$	$\text{N}_5\text{ZrN}_7/\text{B3LYP}$
$\nu_1(\text{a})$ $\text{N}_5, \text{N}_7$ rotation	i5.8 (0) (0)	i9.5 (0)	i8.7 (0)
$\nu_2(\text{e})$ M– $\text{N}_5$ , M– $\text{N}_7$ bend	78.3 (2) (2)	77.5 (2)	35.9 (5)
$\nu_3(\text{e})$ M– $\text{N}_5$ bend	160.1 (0) (1)	194.5 (0)	130.3 (0)
$\nu_4(\text{a})$ M– $\text{N}_5$ , M– $\text{N}_7$ sym. stretch	236.3 (7) (2)	229.6 (2)	231.6 (15)
$\nu_5(\text{e})$ $\text{N}_7$ out of plane breathing	297.3 (0) (3)	311.9 (0)	353.4 (0)
$\nu_6(\text{e})$ M– $\text{N}_7$ stretch	312.6 (1) (1)	328.8 (1)	293.2 (0)
$\nu_7(\text{e})$ $\text{N}_7$ out of plane bend	349.6 (0) (1)	443.3 (0)	382.6 (0)
$\nu_8(\text{a})$ M– $\text{N}_5$ , M– $\text{N}_7$ asym. stretch	473.5 (116) (17)	450.6 (99)	397.9 (104)
$\nu_9(\text{e})$ $\text{N}_7$ out of plane bend	504.5 (0) (0)	509.2 (0)	521.8 (0)
$\nu_{10}(\text{e})$ $\text{N}_5$ out of plane bend	746.3 (0) (0)	754.1 (0)	759.3 (0)
$\nu_{11}(\text{a})$ $\text{N}_7$ in plane breathing	813.3 (13) (43)	737.0 (14)	792.6 (9)
$\nu_{12}(\text{e})$ $\text{N}_7$ out of plane def	893.3 (0) (0)	915.3 (0)	923.0 (0)
$\nu_{13}(\text{e})$ $\text{N}_5$ , $\text{N}_7$ out of plane def	909.1 (0) (0)	926.9 (0)	930.7 (0)
$\nu_{14}(\text{e})$ $\text{N}_7$ in plane breathing	926.7 (14) (2)	846.4 (8)	909.7 (21)
$\nu_{15}(\text{e})$ $\text{N}_7$ in plane def	951.9 (0) (2)	908.4 (0)	939.0 (0)
$\nu_{16}(\text{e})$ $\text{N}_7$ in plane asym def	1032.6 (0) (0)	1928.1 (0)	1069.3 (0)
$\nu_{17}(\text{e})$ $\text{N}_5$ in plane asym stretch	1093.5 (0) (3)	1060.3 (0)	1092.4 (0)
$\nu_{18}(\text{a})$ $\text{N}_5$ in plane breathing	1135.4 (0) (29)	1048.4 (0)	1141.7 (1)
$\nu_{19}(\text{e})$ $\text{N}_5$ in plane breathing	1188.4 (3) (2)	1102.0 (2)	1199.3 (5)

<sup>a</sup> For  $\text{N}_5\text{TiN}_7/\text{B3LYP}$ , the Raman intensities are also reported as the second quantity in parentheses.

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

normal mode	$\text{N}_5\text{HfN}_7/\text{B3LYP}$	$\text{N}_5\text{HfN}_7/\text{MP2}$	$\text{N}_5\text{ThN}_7/\text{B3LYP}$	$\text{N}_5\text{ScN}_7^-/\text{B3LYP}$
$\nu_1(\text{a})$	3.4 (0) (0)	i9.7 (0)	i8.5 (0) (0)	i10.6 (0)
$\nu_2(\text{e})$	41.1 (4) (1)	37.1 (4)	35.7 (11) (0)	62.9 (5)
$\nu_3(\text{e})$	132.6 (0) (1)	161.8 (0)	108.3 (0) (2)	109.6 (0)
$\nu_4(\text{a})$	233.1 (17) (0)	238.9 (10)	217.7 (38) (0)	177.9 (8)
$\nu_5(\text{e})$	283.9 (0) (3)	302.3 (0)	236.1 (1) (3)	304.5 (3)
$\nu_6(\text{e})$	361.4 (0) (5)	334.6 (0)	401.9 (0) (3)	364.7 (0)
$\nu_7(\text{e})$	386.4 (0) (0)	507.1 (0)	399.5 (0) (2)	424.6 (0)
$\nu_8(\text{a})$	341.0 (66) (20)	334.3 (69)	348.7 (109) (13)	445.4 (134)
$\nu_9(\text{e})$	520.3 (0) (0)	513.4 (0)	502.3 (0) (0)	485.4 (0)
$\nu_{10}(\text{e})$	759.5 (0) (0)	762.1 (0)	766.5 (0) (0)	764.9 (0)
$\nu_{11}(\text{a})$	785.0 (6) (45)	705.3 (11)	786.5 (10) (37)	796.0 (14)
$\nu_{12}(\text{e})$	921.7 (0) (3)	910.1 (0)	960.2 (0) (3)	954.6 (0)
$\nu_{13}(\text{e})$	925.8 (0) (1)	931.4 (0)	944.7 (0) (0)	957.6 (0)
$\nu_{14}(\text{e})$	901.1 (24) (2)	812.4 (16)	922.6 (30) (1)	921.5 (43)
$\nu_{15}(\text{e})$	931.2 (0) (0)	960.8 (0)	964.6 (0) (2)	961.8 (0)
$\nu_{16}(\text{e})$	1078.1 (0) (0)	1072.7 (0)	1172.7 (0) (0)	1103.5 (0)
$\nu_{17}(\text{e})$	1091.1 (0) (3)	1060.8 (0)	1098.6 (0) (2)	1152.3 (0)
$\nu_{18}(\text{a})$	1137.8 (0) (34)	1052.4 (0)	1161.2 (1) (24)	1158.9 (0)
$\nu_{19}(\text{e})$	1195.3 (5) (1)	1111.6 (3)	1221.3 (4) (0)	1216.1 (9)

<sup>a</sup> For  $\text{N}_5\text{HfN}_7/\text{B3LYP}$  and  $\text{N}_5\text{ThN}_7/\text{B3LYP}$  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<sub>5</sub>, M, and N<sub>7</sub> and Total Dipole Moment (Debye)**

system/method	$\delta_{N_5}$	$\delta_M$	$\delta_{N_7}$	dipole
N <sub>5</sub> TiN <sub>7</sub> /B3LYP	-0.40	+1.11	-0.71	0.44
N <sub>5</sub> TiN <sub>7</sub> /MP2	-0.50	+1.42	-0.92	0.71
N <sub>5</sub> ZrN <sub>7</sub> /B3LYP	-0.46	+1.49	-1.02	1.28
N <sub>5</sub> HfN <sub>7</sub> /B3LYP	-0.48	+1.60	-1.12	1.71
N <sub>5</sub> HfN <sub>7</sub> /MP2	-0.65	+2.20	-1.54	2.37
N <sub>5</sub> ThN <sub>7</sub> /B3LYP	-0.28	+0.90	-0.62	3.30
N <sub>5</sub> ScN <sub>7</sub> <sup>a</sup> /B3LYP <sup>a</sup>	-0.65	+1.01	-1.36	2.71
ScN <sub>7</sub> /B3LYP <sup>b</sup>		+1.13	-1.13	7.62
ScN <sub>7</sub> /MP2 <sup>b</sup>		+1.39	-1.39	8.94

<sup>a</sup> The origin of the system is on the Sc atom. <sup>b</sup> 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.

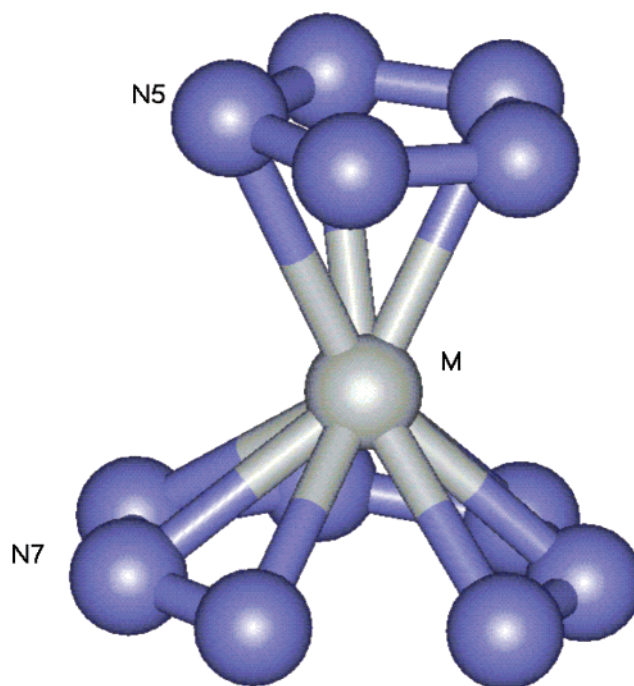
In Tables 2 and 3, the B3LYP harmonic frequencies of the molecules are reported, together with their IR intensities. All species except N<sub>5</sub>HfN<sub>7</sub> have one very small imaginary frequency corresponding to the rotation of the two rings one with respect to the other. N<sub>5</sub>HfN<sub>7</sub>, 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<sub>5</sub>TiN<sub>7</sub> and ended up into a distorted structure which was less than 10 cm<sup>-1</sup> lower in energy than the C<sub>s</sub> one. We can thus safely say that the molecule might rotate, but statistically, it will assume most of the time the undistorted C<sub>s</sub> conformation.

Most of the modes have zero IR intensities, except for a few modes:  $\nu_2$ , corresponding to a M–N<sub>7</sub> and M–N<sub>5</sub> bending;  $\nu_4$  corresponding to a M–N<sub>7</sub> and M–N<sub>5</sub> symmetric stretching;  $\nu_8$  corresponding to a M–N<sub>7</sub> and M–N<sub>5</sub> antisymmetric stretching, which is the most intense mode in all molecules;  $\nu_{11}$  corresponding to a N<sub>7</sub> in plane breathing;  $\nu_{14}$  corresponding to a N<sub>7</sub> in plane breathing; and  $\nu_{19}$  corresponding to a N<sub>5</sub> in plane breathing. For N<sub>5</sub>TiN<sub>7</sub>, N<sub>5</sub>HfN<sub>7</sub>, and N<sub>5</sub>ThN<sub>7</sub>, the B3LYP Raman intensities are also reported. Most of the modes have very little Raman intensity. The only modes having some Raman intensity are  $\nu_8$ ,  $\nu_{11}$ , and  $\nu_{18}$ .

The MP2 frequencies have also been calculated for N<sub>5</sub>TiN<sub>7</sub> and N<sub>5</sub>HfN<sub>7</sub>, and they are similar to the B3LYP frequencies. In N<sub>5</sub>HfN<sub>7</sub>,  $\nu_1$  has an imaginary value of i9.7 cm<sup>-1</sup>.

In Table 4, the partial charges on the N<sub>5</sub>, M, and N<sub>7</sub> moieties, obtained by a Mulliken population analysis, are reported. Formally, they correspond to N<sub>5</sub><sup>-</sup>, M<sup>4+</sup> (except for Sc<sup>3+</sup>), and N<sub>7</sub><sup>3-</sup>. The real charge is however smaller than the formal charge. The total dipole moments are also reported. For the charged species N<sub>5</sub>ScN<sub>7</sub><sup>-</sup>, 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<sub>5</sub>ThN<sub>7</sub> 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<sub>5</sub>TiN<sub>7</sub>, in analogy with what was previously done for ScN<sub>7</sub>.<sup>3</sup> We considered the opening of the N<sub>7</sub> 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<sub>5</sub>TiN<sub>7</sub>. This energy barrier of 9 kcal/mol already includes a zero-point energy correction of 1 kcal/mol. For ScN<sub>7</sub>, the

**Figure 2.** Structure of the transition state of N<sub>5</sub>MN<sub>7</sub> (M = Ti and Hf).

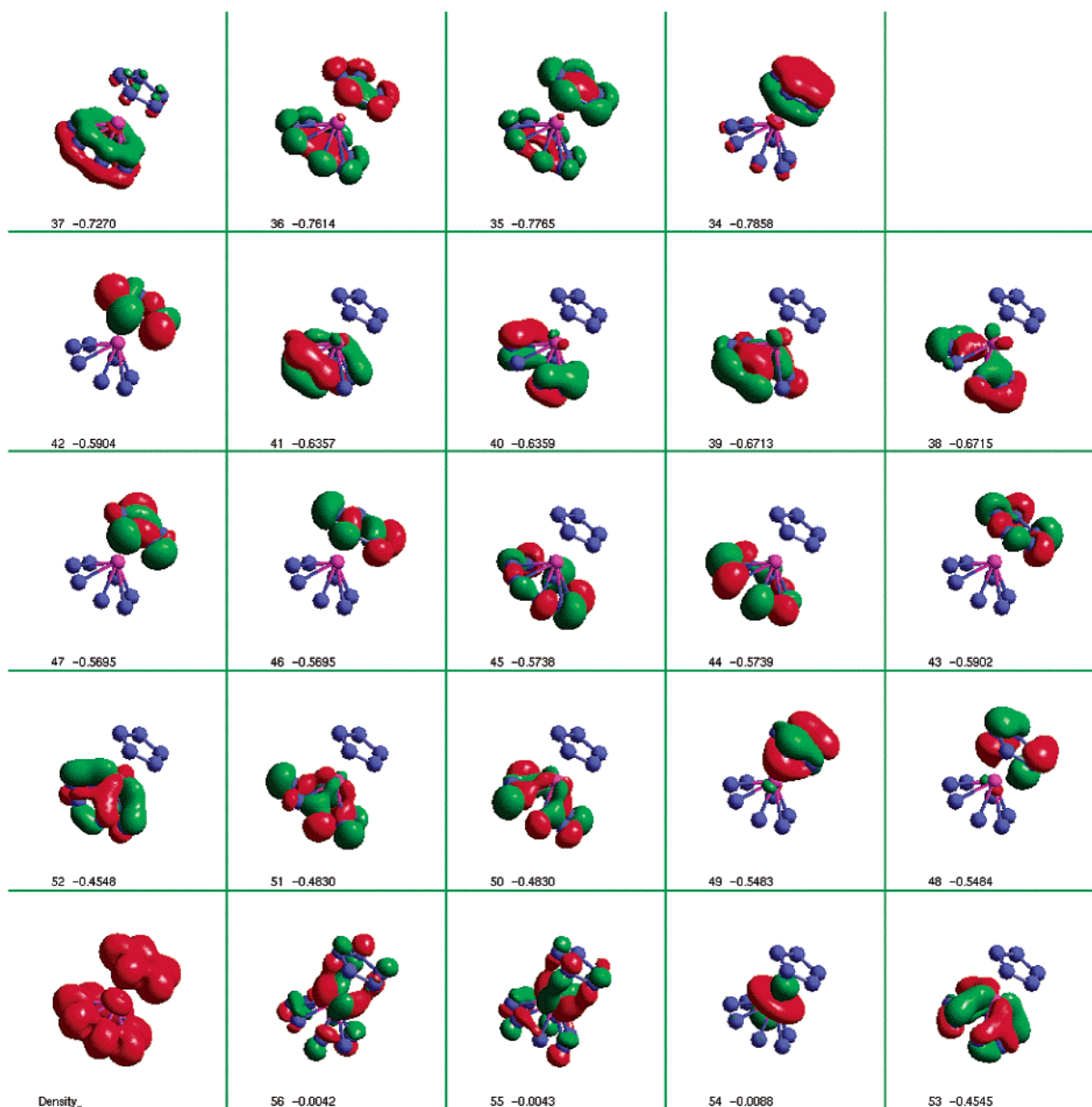
analogous energy barrier was of 20 kcal/mol. Moreover, the TS for ScN<sub>7</sub> occurs when the N–N bond opens to 2.10 Å, whereas in the N<sub>5</sub>TiN<sub>7</sub> TS, the N–N bond is only 1.86 Å. This indicates that presumably the opening process is easier to start in N<sub>5</sub>TiN<sub>7</sub> than in ScN<sub>7</sub>. As possible dissociation products of N<sub>5</sub>TiN<sub>7</sub>, we considered six N<sub>2</sub> molecules and a Ti atom. These lie 210 kcal/mol lower in energy than N<sub>5</sub>TiN<sub>7</sub>. Per N<sub>2</sub> unit, the latter corresponds to 35 kcal/mol. An analogous energy balance for ScN<sub>7</sub> gave 36 kcal/mol per N<sub>2</sub> unit.

The analysis of the structure and frequencies of N<sub>5</sub>ZrN<sub>7</sub> did not suggest that the Zr compound could be more stable than the Ti compound. N<sub>5</sub>HfN<sub>7</sub>, on the other hand, has all real frequencies at the B3LYP level of theory. Compared to N<sub>5</sub>ZrN<sub>7</sub>, 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.<sup>7,8</sup> We are not aware of any studies on the role of relativistic effects on the bonding of group 4 metals to 6 $\pi$  or 10 $\pi$  aromatic rings.

The usual opening of the N<sub>7</sub> ring presents a TS (Figure 2), with one imaginary frequency, which lies 15 kcal/mol higher in energy than the N<sub>5</sub>HfN<sub>7</sub> 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<sub>2</sub> molecules and Hf atom in its triplet ground state, N<sub>5</sub>HfN<sub>7</sub> lies 180 kcal/mol higher in energy, which corresponds to only 30 kcal/mol per N<sub>2</sub> unit.

In N<sub>5</sub>ThN<sub>7</sub> 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<sub>2</sub> molecules and Th atom in its triplet ground state, N<sub>5</sub>ThN<sub>7</sub> lies 132 kcal/mol higher in energy, which corresponds to only 22 kcal/mol per N<sub>2</sub> unit. N<sub>5</sub>ThN<sub>7</sub> is thus the most stable of all these N<sub>5</sub>MN<sub>7</sub> molecules. It also seems that the dissociation process is more difficult to start in N<sub>5</sub>ThN<sub>7</sub> in ScN<sub>7</sub>, with its energy barrier of 20 kcal/mol.





**Figure 3.** Some Hartree–Fock molecular orbitals (MO) of  $\text{N}_5\text{TiN}_7$ : 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  $\text{N}_5\text{TiN}_7$  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 2p $\pi$  orbitals and the metal d orbitals. Around the molecular symmetry axis there would be  $\sigma$  and  $\pi$  orbitals binding to both the  $\text{N}_5$  ring and the  $\text{N}_7$  ring and, in addition a  $\delta$  combination, binding to the  $\text{N}_7$  ring. Such orbitals can indeed be identified. The two  $\sigma$  MOs are 34 and 37, respectively. The  $\pi$  bond to  $\text{N}_5$  is formed by MOs 48–49. What complicates the situation is that the seven-ring N (2s+2p) $\sigma$  orbitals also hybridize with the metal. From the  $\text{N}_7$  ring, this yields the four axially  $\pi$  MOs, 38–41, and the four axially  $\delta$  MOs, 50–53, all hybridized with the metal d $\delta$ . In addition, we

have MOs describing other intraring  $\sigma$  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 (from 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  $\text{N}_5\text{ScN}_7^-$  anion. This system lies 69 kcal/mol lower in energy than  $\text{ScN}_7$  and  $\text{N}_5^-$ . In Figure 5, the total energy of  $\text{N}_5\text{ScN}_7^-$  as a function of the distance between  $\text{ScN}_7$  and  $\text{N}_5^-$  is reported. At each value of the distance between  $\text{ScN}_7$  and  $\text{N}_5^-$ , 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  $\text{N}_5\text{MN}_7$ , where M is a group 4 atom, Ti, Zr,

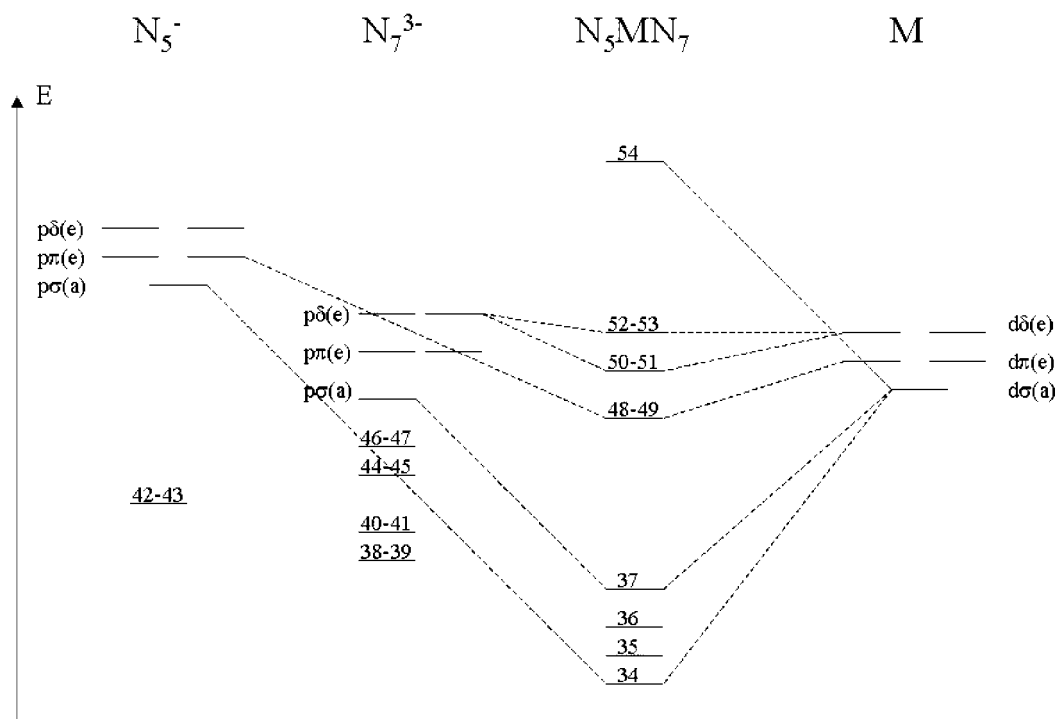


Figure 4. Qualitative energy-level diagram of  $N_5TiN_7$  molecular orbitals.

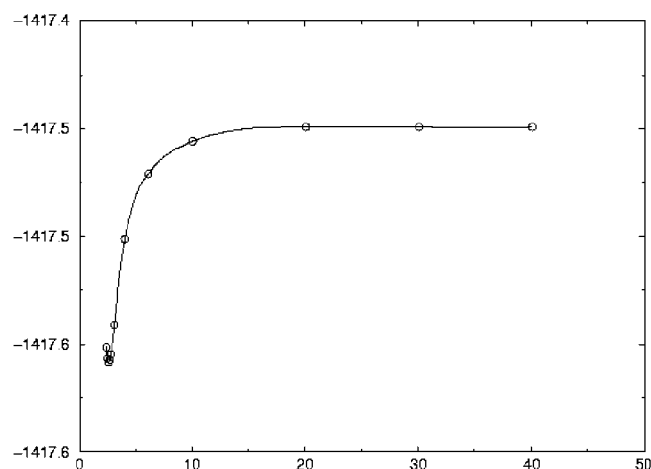


Figure 5. Total energy (a.u.) of  $N_5ScN_7^-$  as a function of the distance (Å) between  $ScN_7$  and  $N_5^-$ .

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  $\sigma$  and  $\pi$  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  $ScN_7$ .

**Acknowledgment.** This work was partially supported by Ministero dell'Università e della Ricerca Scientifica and The Academy of Finland. We thank Dr. Valera Veryazov, Lund University, for writing the interface to Cerius2 that was used to generate the picture of the molecular orbitals.

## References and Notes

- (1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2004.
- (2) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.
- (3) Gagliardi, L.; Pyykkö, P. *J. Am. Chem. Soc.* **2001**, *123*, 9700.
- (4) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem. Eur. J.* **2001**, *7*, 4155.
- (5) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
- (6) Institut für Theoretische Chemie, Universität Stuttgart. *ECPs and corresponding valence basis sets*. <http://www.theochem.uni-stuttgart.de/>.
- (7) Pyykkö, P.; Desclaux, J. P. *Chem. Phys. Lett.* **1977**, *50*, 503.
- (8) Pyykkö, P.; Snijders, J. G.; Baerends, E. J. *Chem. Phys. Lett.* **1981**, *83*, 432.