

## Scandium Cycloheptanitride, ScN<sub>7</sub>: A Predicted High-Energy Molecule Containing an [ $\eta^7$ -N<sub>7</sub>]<sup>3-</sup> Ligand

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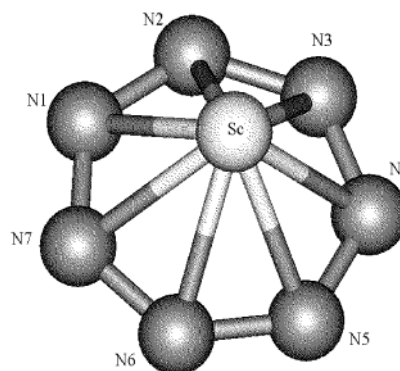
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Three all-nitrogen chemical species in bulk compounds are experimentally known from the three last centuries: N<sub>2</sub>, N<sub>3</sub><sup>-</sup>, and N<sub>5</sub><sup>+</sup>.<sup>2</sup> The last one was predicted in 1991.<sup>3</sup> Furthermore there is evidence for tetrahedral N<sub>4</sub> in matrixes.<sup>4</sup> Could further “nitrogens” exist? In recent years, the hypothetical existence of poly-nitrogen clusters has been the object of several theoretical investigations (refs 5–16 and references therein). Besides their theoretical interest, these structures have drawn attention because of their possible use as high energy-density materials (HEDM), that is, the large ratio between the energy released in a fragmentation reaction and the specific weight.

Pentazole derivatives N<sub>5</sub>-R have been synthesized<sup>17</sup> and theoretically studied.<sup>18</sup> No  $\eta^5$ -N<sub>5</sub><sup>-</sup> compounds, analogous to cyclopentadienes, cp = C<sub>5</sub>H<sub>5</sub>, are yet known. Corresponding  $\eta^5$ -E<sub>5</sub> compounds (E = P, As) have been prepared.<sup>19</sup> While these 6 $\pi$  systems have, around the symmetry axis, only occupied  $\sigma$  and  $\pi$  shells, the larger 10 $\pi$  systems also have an occupied  $\delta$  shell, capable of donation to the metal. Such N<sub>7</sub><sup>3-</sup> and N<sub>8</sub><sup>2-</sup> systems have not been discussed before. These three simultaneous interactions, in fact, were the idea behind the original synthesis of thorocene and uranocene, An(COT)<sub>2</sub>; An = Th, U; COT = C<sub>8</sub>H<sub>8</sub>.<sup>20</sup> The experimentally known<sup>21</sup> cycloheptatrienes, An(hp)<sub>2</sub>; hp =  $\eta^7$ -C<sub>7</sub>H<sub>7</sub>, have been theoretically studied by Li and Bursten.<sup>22</sup> We



**Figure 1.** The structure of the local minimum of ScN<sub>7</sub>.

**Table 1.** Bond Lengths (Å) and Angles (degrees) for LM

system	RSC-N	RN-N	∠NscN	∠NNN
LM C7v <sup>a</sup>	2.142	1.374	37.40	128.57
LM C7v <sup>b</sup>	2.144	1.371	37.28	128.57
LM C7v <sup>c</sup>	2.134	1.368	37.40	128.57
LM C7v <sup>d</sup>	2.163	1.399	35.64	128.57
TS C1 <sup>a</sup>	2.175 ScN1	1.273N1N2	33.42 N1ScN2	126.38 N1N2N3
	2.216 ScN2	1.297N2N3	34.35 N2ScN3	125.62 N2N3N4
	2.175 ScN3	1.537N3N4	43.16 N3ScN4	139.12 N3N4N5
	1.974 ScN4	1.533N4N5	41.60 N4ScN5	122.32 N4N5N6
	2.271 ScN5	1.280N5N6	32.75 N5ScN6	134.66 N5N6N7
	2.270 ScN6	1.271N6N7	32.90 N6ScN7	
	2.214 ScN7	2.103N7N1		

<sup>a</sup> B3LYP/6-31G\*. <sup>b</sup> B3LYP/6-31+G\*. <sup>c</sup> B3LYP/6-31G(3df,3pd). <sup>d</sup> MP2/631-G\*.

here report a theoretical search for optimum stability for MN<sub>n</sub> systems,  $n = 7, 8$ . The best results were found for Sc(III)( $\eta^7$ -N<sub>7</sub>). Some other M(III)( $\eta^7$ -N<sub>7</sub>) and further M(N<sub>n</sub>)<sub>x</sub> compounds are briefly discussed.

The calculations were carried out by using density functional theory (DFT) at the B3LYP<sup>23</sup> level of theory, and second-order perturbation theory (MP2), with a 6-31G\* split valence basis,<sup>24,25</sup> (specifically (22s,16p,4d,1f)/[5s,4p,2d,1f] for Sc and (10s,4p,1d)/[3s,2p,1d] for N). The Gaussian98 package was used. The B3LYP calculations were repeated with two larger basis sets, the 6-31+G\* split valence + polarization basis, namely (23s,18p,5d,1f)/[6s,6p,3d,1f] for Sc and (11s,5p,1d)/[4s,3p,1d] for N, and the 6-31G(3df,3pd) split valence + extended polarization basis, namely (22s,16p,4d,3f,1g)/[5s,4p,3d,3f,1g] for Sc and (10s,4p,3d,1f)/[3s2p3d1f] for N.

ScN<sub>7</sub> was found to have a local minimum (LM) with C<sub>7v</sub> symmetry (Figure 1) with all frequencies real at both the B3LYP and MP2 levels of theory. The calculation was run for ScN<sub>7</sub> as a singlet. The triplet was found to lie ca. 50 kcal/mol higher in energy than the singlet. The typical bond distances and angles of LM are reported in Table 1 and the harmonic frequencies with their intensities are reported in Table 2. The lowest frequency is 320 cm<sup>-1</sup> at B3LYP/6-31+G\* level and 322 cm<sup>-1</sup> at MP2/6-31G\* level. It is a degenerate e mode for the Sc–N deformation. The other three IR-active frequencies are predicted to occur around 454, 801, and 919 cm<sup>-1</sup>. ScN<sub>7</sub> formally corresponds to Sc(III) and cyclic N<sub>7</sub><sup>3-</sup>. According to a Mulliken population analysis, the charge is partitioned as +1.13 on scandium and –0.16 on each nitrogen atom. The analysis of the molecular orbitals shows

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**Table 2.** Harmonic Frequencies ( $\text{cm}^{-1}$ ) and Their Intensities ( $\text{km mol}^{-1}$ ) in Parenthesis for LM in the Last Column the  $^{14}\text{N}/^{15}\text{N}$  Ratio Is Reported

normal	a	b	c	d	$^{14}\text{N}/^{15}\text{N}$
$\nu_1(\text{e}) \alpha$	317.1(5)	320.2(7)	321.9(5)	314.2(7)	1.0191
$\nu_2(\text{e}) \beta$	366.4(0)	371.6(0)	345.4(0)	359.4(0)	1.0339
$\nu_3(\text{e}) \beta$	398.4(0)	408.5(0)	473.4(0)	394.7(0)	1.0350
$\nu_4(\text{a}) \gamma$	453.8(60)	454.1(61)	419.9(59)	448.8(59)	1.0118
$\nu_5(\text{e}) \beta$	490.0(0)	493.4(0)	500.4(0)	476.7(0)	1.0350
$\nu_6(\text{a}) \delta$	798.2(6)	800.7(6)	727.5(14)	774.8(7)	1.0334
$\nu_7(\text{e}) \epsilon$	914.1(41)	918.7(41)	838.6(34)	887.9(39)	1.0347
$\nu_8(\text{e}) \epsilon$	926.7(0)	931.5(0)	930.0(0)	900.0(0)	1.0350
$\nu_9(\text{e}) \epsilon$	938.9(0)	949.1(0)	996.8(0)	917.0(0)	1.0350
$\nu_{10}(\text{e}) \epsilon$	1116.4(0)	1121.6(0)	1131.5(0)	1084.3(0)	1.0344

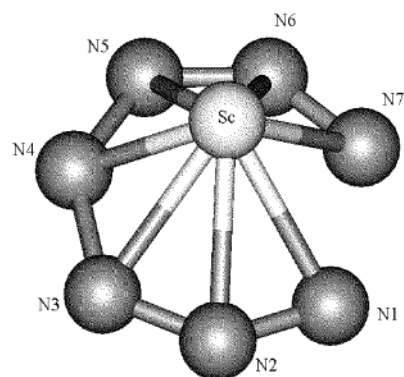
<sup>a</sup> B3LYP/6-31G\*. <sup>b</sup> B3LYP/6-31+G\*. <sup>c</sup> MP2/631-G\*. <sup>d</sup> Sc<sup>15</sup>N: B3LYP/6-31G\*  $\alpha$ :Sc–N deformation;  $\beta$ : ring out of plane bend;  $\gamma$ : Sc-ring stretch;  $\delta$ : ring in plane breath;  $\epsilon$ : ring in plane stretch.

that the bond is mainly formed by linear combinations of nitrogen p orbitals and scandium  $d\delta$  orbitals.

An experiment with laser-ablated Sc atoms and solid nitrogen<sup>26</sup> did produce ScN and other complexes but did not reveal any frequencies characteristic of ScN<sub>7</sub>. Peaks at 803–807 and 898  $\text{cm}^{-1}$  were assigned to (ScN)<sub>2</sub><sup>+</sup> and its N<sub>2</sub> complexes, and to N<sub>2</sub> complexes of ScN. Our two lowest frequencies are below the experimental range. The  $^{14}\text{N}/^{15}\text{N}$  ratios in Table 2 would also give a clear signature for ScN<sub>7</sub>. Especially the intensive  $\nu_4(\text{a})$  stretch has a ratio of 1.0118, only, compared with the experimental ratio of 1.0262 for ScN.

Various neutral N<sub>7</sub> isomers have been investigated at theoretical level<sup>14</sup> (and references there). A diazidamine-type N<sub>7</sub><sup>−</sup> was found to be a local minimum.<sup>6</sup> We found the naked cyclic N<sub>7</sub><sup>3−</sup> to be a local minimum ( $D_{7h}$  symmetry and  $R(\text{N}–\text{N}) = 1.373 \text{ \AA}$  at the B3LYP level) with all frequencies real at the B3LYP (lowest frequency is 324  $\text{cm}^{-1}$ ) and MP2 levels of theory, with the same AO basis as for ScN<sub>7</sub>.

The dissociation of ScN<sub>7</sub> was investigated at B3LYP/6-31G\* level of theory. A transition state (TS) (Figure 2) with one imaginary frequency was found lying ca. 20 kcal/mol above ScN<sub>7</sub>. This value already includes a zero point energy correction of ca. 2 kcal/mol. The typical bond distances and angles of TS are reported in Table 1. The TS leads to the formation of the ionic species ScN<sup>2+</sup> and two N<sub>3</sub><sup>−</sup> fragments. This is rather evident by looking at the structure of the TS and its imaginary frequency which corresponds to the breaking of the N3N4 and N4N5 bonds. The Mulliken analysis confirms the presence of two N<sub>3</sub> moieties, (N1N2N3) and (N5N6N7) which have a charge of ca. −0.40 each. (ScN4) has a charge of +0.80. However, in the vicinity of the TS, the ionic reaction path crosses a reaction path that leads to neutral products. We investigated two possible sets of neutral

**Figure 2.** The structure of the transition state of ScN<sub>7</sub>.

products, namely ScN + 3N<sub>2</sub> (reaction A), and Sc + [7/2] N<sub>2</sub> (reaction B). The dissociation products of reaction A were found to lie ca. 103 kcal/mol lower in energy than ScN<sub>7</sub>, while the dissociation products of reaction B lie ca. 125 kcal/mol lower in energy than ScN<sub>7</sub>. Per N<sub>2</sub> unit the latter corresponds to only 36 kcal/mol.

Our previous studies on nitrogen clusters<sup>16</sup> (and references therein) showed that in general the N<sub>n</sub> species ( $n = 6, 8, 10$ ) lie ca. 200 kcal/mol per N<sub>2</sub> unit above  $[n/2]$  N<sub>2</sub> molecules. The barrier to break one N–N bond is ca. 10–20 kcal/mol, as in the present work. However, the presence of the Sc metal seems to lead to much higher energetic stability with respect to the dissociation products.

We will extend the present study to other metal–polynitrogen compounds to investigate the stability with different metals and different polynitrogen clusters. Preliminary results at B3LYP level show that below scandium, YN<sub>7</sub> dissociates, while LaN<sub>7</sub> is stable with all frequencies real, and AcN<sub>7</sub> dissociates. We have also considered some “sandwich” complexes, such as U(N<sub>7</sub>)<sub>2</sub> which dissociates and Th(N<sub>8</sub>)<sub>2</sub> which is a stationary point but with four imaginary frequencies corresponding to the bending of the N<sub>8</sub> rings. Some cationic species have also been considered, among them ThN<sub>7</sub><sup>+</sup> and Sc(N<sub>5</sub>)<sub>2</sub><sup>2+</sup>, which are both stable minima.

Summarizing, our calculations suggest that the  $\eta^7$ -scandium cycloheptanitride, ScN<sub>7</sub>, should have a fair chance of existing. It would contain a new homonuclear polynitrogen ligand, bound to the metal by  $\sigma$ -,  $\pi$ -, and  $\delta$ -type interactions, corresponding to a five-fold metal–ring bond. The new IUPAC name of this predicted molecule is “scandium heptaazy-[07] cyclate”.

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**Supporting Information Available:** This material is available free of charge via the Internet at <http://pubs.acs.org>.

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