Scandium Cycloheptanitride, ScN₇: A Predicted High-Energy Molecule Containing an [η⁷-N₇]³⁻ Ligand

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Three all-nitrogen chemical species in bulk compounds are experimentally known from the three last centuries: N₄, N₅−,¹ and N₇⁻.² The last one was predicted in 1991.³ Furthermore there is evidence for tetrahedral N₄ in matrices.⁴ Could further "nitrigen" 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 N₅−R have been synthesized¹⁷ and theoretically studied.¹⁸ No η⁷−N₇− compounds, analogous to cyclopentadienes, Cp = C₅H₅, are yet known. Corresponding η⁷−E₇− compounds (E = P, As) have been prepared.¹⁹ While these 6π systems have, around the symmetry axis, only occupied σ and π shells, the larger 10π systems also have an occupied δ shell, capable of donation to the metal. Such N₇− and N₅− 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)₂; An = Th,U; COT = C₅H₅.²⁰ The experimentally known¹¹ cycloheptatrienes, An(hp); hp = η⁷−C₅H₅, have been theoretically studied by Li and Bursten.²² We here report a theoretical search for optimum stability for MnN₇ systems, n = 7, 8. The best results were found for Sc(III)(η⁷−N₇−N₅). Some other M(III)(η⁷−N₇−) and further M(N₅−N₇−) compounds are briefly discussed.

The calculations were carried out by using density functional theory (DFT) at the B3LYP²³ level of theory, and second-order perturbation theory (MP2), with a 6-31G* split valence basis,²⁴ 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 6-31G* and MP2/6-31+G*.⁵

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

<table>
<thead>
<tr>
<th></th>
<th>RSC-N</th>
<th>RN-N</th>
<th>∠NScN</th>
<th>∠NNN</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM C7v^a</td>
<td>2.142</td>
<td>1.374</td>
<td>37.40</td>
<td>128.57</td>
</tr>
<tr>
<td>LM C7v^b</td>
<td>2.144</td>
<td>1.371</td>
<td>37.28</td>
<td>128.57</td>
</tr>
<tr>
<td>LM C7v^c</td>
<td>2.134</td>
<td>1.368</td>
<td>37.40</td>
<td>128.57</td>
</tr>
<tr>
<td>TS C1^a</td>
<td>2.163</td>
<td>1.399</td>
<td>35.64</td>
<td>128.57</td>
</tr>
</tbody>
</table>

^a B3LYP/6-31G*.  ^b B3LYP/6-31+G*.  ^c B3LYP/6-31G(3df,3pd).

The other three IR-active frequencies are predicted to occur around 454, 801, and 919 cm⁻¹. The calculated frequencies of ScN₇ are 2.175 ScN₁ 1.273N₁N₂ 33.42 N₁ScN₂ 126.38 N₁N₂N₃ 2.163 1.399 35.64 128.57.

The structure of the local minimum of ScN₇.

Figure 1. The structure of the local minimum of ScN₇.

The typical bond distances and angles of the triplet were found to lie ca. 50 kcal/mol higher in energy than the singlet. The lowest frequency is 320 cm⁻¹ at B3LYP/6-31+G* level and 322 cm⁻¹ 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⁻¹. ScN₇ formally corresponds to Sc(III)(η⁷−N₇) and cyclic N₇⁻. 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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³ Curtius, T. Ber. 1890, 23, 3023.
products, namely ScN + 3N₂ (reaction A), and Sc + [7/2] N₅ (reaction B). The dissociation products of reaction A were found to lie ca. 103 kcal/mol lower in energy than ScN₇, while the dissociation products of reaction B lie ca. 125 kcal/mol lower in energy than ScN₇. Per N₂ unit the latter corresponds to only 36 kcal/mol.

Our previous studies on nitrogen clusters²⁶ (and references therein) showed that in general the Nₙ species (n = 6, 8, 10) lie ca. 200 kcal/mol per N₂ unit above [n/2] N₅ 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, YN₇ dissociates, while LaN₇ is stable with all frequencies real, and ACN₇ dissociates. We have also considered some “sandwich” complexes, such as U(N₇)₂ which has the 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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**Table 2.** Harmonic Frequencies (cm⁻¹) and Their Intensities (km mol⁻¹) in Parenthesis for LM in the Last Column the ¹⁴N/¹⁵N Ratio Is Reported

<table>
<thead>
<tr>
<th>Normal</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>¹⁴N/¹⁵N</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁(e) α</td>
<td>317.1(5)</td>
<td>320.2(7)</td>
<td>321.9(5)</td>
<td>314.2(7)</td>
<td>1.0191</td>
</tr>
<tr>
<td>v₂(e) β</td>
<td>366.4(0)</td>
<td>371.6(0)</td>
<td>345.4(0)</td>
<td>359.4(0)</td>
<td>1.0339</td>
</tr>
<tr>
<td>v₃(e) β</td>
<td>398.4(0)</td>
<td>408.5(0)</td>
<td>473.4(0)</td>
<td>394.7(0)</td>
<td>1.0350</td>
</tr>
<tr>
<td>v₄(a) γ</td>
<td>453.8(60)</td>
<td>454.1(61)</td>
<td>419.9(59)</td>
<td>448.8(59)</td>
<td>1.0118</td>
</tr>
<tr>
<td>v₅(e) β</td>
<td>490.0(0)</td>
<td>493.4(0)</td>
<td>500.4(0)</td>
<td>476.7(0)</td>
<td>1.0350</td>
</tr>
<tr>
<td>v₆(a) δ</td>
<td>798.2(6)</td>
<td>800.7(6)</td>
<td>727.5(14)</td>
<td>774.8(7)</td>
<td>1.0334</td>
</tr>
<tr>
<td>v₇(e) β</td>
<td>914.1(41)</td>
<td>918.7(41)</td>
<td>838.6(34)</td>
<td>887.9(39)</td>
<td>1.0347</td>
</tr>
<tr>
<td>v₈(e) δ</td>
<td>926.7(0)</td>
<td>931.5(0)</td>
<td>930.0(0)</td>
<td>900.0(0)</td>
<td>1.0350</td>
</tr>
<tr>
<td>v₉(e) ε</td>
<td>938.9(0)</td>
<td>949.1(0)</td>
<td>996.8(0)</td>
<td>917.0(0)</td>
<td>1.0350</td>
</tr>
<tr>
<td>v₁₀(e) ε</td>
<td>1116.4(0)</td>
<td>1121.6(0)</td>
<td>1131.5(0)</td>
<td>1084.3(0)</td>
<td>1.0344</td>
</tr>
</tbody>
</table>