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

GAGLIARDI, Laura, PYYKKÖ, Pekka


DOI : 10.1021/ja016298q
Scandium Cycloheptanitride, ScN₇: A Predicted High-Energy Molecule Containing an [η⁷-N₇]³⁻ Ligand

Laura Gagliardi* and Pekka Pyynkö

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

Received May 29, 2001

Three all-nitrogen chemical species in bulk compounds are experimentally known from the three last centuries: N₂, N₄⁺,¹ and N₈². The last one was predicted in 1991.² Furthermore there is evidence for tetrahedral N₄ in matrices.³ 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 N₅-R have been synthesized¹⁷ and theoretically studied.¹⁸ No η⁷-N₇⁻ compounds, analogous to cyclopentadienides, cp = C₅H₅, are yet known. Corresponding η⁷-E₃ compounds (E = P, As) have been prepared.¹⁹ While these 6σ 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 N₉⁻ systems have not been discussed before. These three simultaneous investigations (refs 5–16 and references therein). Besides 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 cyclopentadienides, cp = C₅H₅, are yet known. Corresponding η⁷-E₃ compounds (E = P, As) have been prepared.¹⁹ While these 6σ 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 N₉⁻ systems have not been discussed before. These three simultaneous investigations (refs 5–16 and references therein). Besides 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.

The calculated parameters 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,3d,1f] for Sc and (10s,6p,3d,1f)/[6s,3p,1d] for N, and 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)/[3s,2p,3d,1f] for N.

Sc₇N₇ was found to have a local minimum (LM) with C₃ᵥ symmetry (Figure 1) with all frequencies real at both the B3LYP and MP2 levels of theory. The calculation was run for Sc₇N₇ 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 the triplet were found to lie ca. 50 kcal/mol higher in energy than the singlet. The typical bond distances and angles of the triplet were found to lie ca. 50 kcal/mol higher in energy than the singlet. The typical bond distances and angles of the triplet were found to lie ca. 50 kcal/mol higher in energy than the singlet.
Table 2. Harmonic Frequencies (cm⁻¹) and Their Intensities (km mol⁻¹) in Parentheses 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>ν1(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>ν2(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>ν3(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>ν4(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>ν5(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>ν6(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>ν7(e) ε</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>ν8(e) ε</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>ν9(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>ν10(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>

* B3LYP/6-31G*; † B3LYP/6-31+G*; ‡ MP2/631-G*; § Sc2N: B3LYP/6-31G*; ‡‡ Sc–N deformation; β: ring out of plane bend; γ: Sc–ring stretch; δ: ring in plane bend; ε: ring in plane stretch.

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

An experiment with laser-ablated Sc atoms and solid nitrogen did produce ScN and solid nitrogen did produce ScN and other complexes but did not reveal any frequencies characteristic of ScN₇. Peaks at 803–807 and 898 cm⁻¹ were assigned to (ScN)₂⁺ and its N₂ complexes, and to N₂ complexes of ScN. Our two lowest frequencies are below the experimental range. The ¹⁴N/¹⁵N ratios in Table 2 would also give a clear signature for ScN₇. Especially the intensive ν(a) stretch has a ratio of 1.0118, only, compared with the experimental ratio of 1.0262 for ScN.

Various neutral N₇ isomers have been investigated at theoretical level (and references therein). A diazidamine-type N₇⁻ was found to be a local minimum. We found the naked cyclic N₇⁻ to be a local minimum (D₉h symmetry and R(N–N) = 1.373 Å at the B3LYP level) with all frequencies real at the B3LYP (lowest frequency is 324 cm⁻¹) and MP2 levels of theory, with the same AO basis as for ScN₇.

The dissociation of ScN₇ 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 ScN₇. 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 ScN₇⁺ and two N₇⁻ 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 N₇⁻ 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 products, namely ScN + 3N₂ (reaction A), and Sc + [7/2] N₂ (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 clusters (and references therein) showed that in general the N₇ species (n = 6, 8, 10) lie ca. 200 kcal/mol per N₂ unit above [n/2] N₂ 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 dissociates and Th(N₈)₂ which is a stationary point but with four imaginary frequencies corresponding to the bending of the N₈ rings. Some cationic species have also been considered, among them ThN₇²⁺ and Sc(CN)₅, which are both stable minima.

Summarizing, our calculations suggest that the η⁷-scandium cycloheptanitride, ScN₇, should have a fair chance of existing. It would contain a new homonuclear polynitrogen ligand, bound to the metal by σ-, π-, and Δ-type interactions, corresponding to a five-fold metal–ring bond. The new IUPAC name of this predicted molecule is “scandium heptaazay-[07] cyclate”.

Acknowledgment. This work was partially supported by Ministero dell’Università e della Ricerca Scientifica, and the Academy of Finland.

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

JA016298Q