Predicted Group 4 Tetra-azides $M(N_3)_4$ ($M = \text{Ti, Hf, Th}$): The First Examples of Linear $M$–$NNN$ Coordination

Laura Gagliardi* and Pekka Pyykko†

Dipartimento di Chimica Fisica ‘F. Accascina’, Università di Palermo, Viale delle Scienze, I-90131 Palermo, Italy, and Department of Chemistry, University of Helsinki, P. O. B. 55 (A. I. Virtasen aukio 1), FIN-00014 Helsinki, Finland

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Quantum chemical calculations suggest that group 4 tetra-azides $M(N_3)_4$, where $M = \text{Ti, Zr, Hf, Th}$, are stable species. They present a unique structural feature; namely, the $M$–$N$–$N$–$N$ fragments are linear. These species are energetically more stable than the corresponding isomers with general formula $\eta^3$-$N_2$–$M$–$\eta^2$-$N_3$, and the Th species, $\text{Th}(N_3)_4$, is the most stable of all. Possible mixed nitride azides $\text{NNN}_4$ were also investigated.

1. Introduction

We have recently predicted the possible existence of novel nitrogen-containing molecules with general formula $\text{N}_n\text{M}_n\text{N}_n$, with $M = \text{Ti, Zr, Hf, Th}$. It is obvious that the same stoichiometry leads to a tetra-azide structure, $M(N_3)_4$, still binding 12 nitrogen atoms to a single metal atom. Although azides are known for most groups of the periodic table, the group 4 ones seem to be unknown so far. Therefore, their heats of formation and properties would be potentially interesting. A further possibility are the mixed nitride azides. For $\text{Mo}$, for instance, $\text{N}=\text{Mo}(N_3)_3$ is known in the bulk. For the group 4 metals, $\text{N}=\text{M}–\text{N}_3$ is a logical possibility. If such molecules could be made and could turn out to have suitable stabilities and volatilities, they might be interesting precursor molecules in material science, in view of the need to deposit either the metal $M$ or its nitrides $\text{MN}$ and $\text{M}_2\text{N}_4$, when making electronic circuits.

It should be noted that these $\text{MN}_n$ compounds could in principle disintegrate to deposit the desired $M$, $\text{MN}$, or $\text{M}_2\text{N}_4$, plus gaseous $\text{N}_2$. The metal nitrides $\text{TiN}$, $\text{ZrN}$, and $\text{HfN}$ are also used as thin layers on high-speed cutting tools, and the proposed compounds might be a useful way of depositing the layer. Further applications for metal azides are also known.

In this paper, we report the results of a theoretical study of the metal tetra-azides $M(N_3)_4$, where $M = \text{Ti, Zr, Hf, Th}$. These molecules turned out to be stable with all frequencies real, and they present a unique feature, namely the $M$–$N$–$N$–$N$ structure is linear, giving the tetra-azides a tetrahedral shape (see Figure 1). All the azide species, characterized previously, have bent $M$–$N$–$N$–$N$ angles. Recently, the hexa-azidosilicate(IV) ion has been synthesized and characterized. The analogous hexa-azidostannate(IV) was made much earlier. Diazides of certain group 4 metals are known. The crystal structure of bis($\eta^2$-cyclopentadienyl)titanium diazide has been determined. The $M$–$N$ distance is 2.03(1) Å, and the $M$–$NNN$ angle is bent. No earlier information of any kind was found on the present tetra-azides.

As a possible mixed nitride azide, we studied the species $\text{NUN}_3$, which also turned out to be stable.

2. Computational Details

The calculations were carried out at the density functional theory (DFT) level, using the B3LYP exchange-correlation functional, with various basis sets. A first set of calculations was performed with a smaller basis, BS1, consisting of a basis set of 6-31g* type for both the nitrogen (3s2p1d) and titanium (5s4p2d1f) atoms. For $M = \text{Zr, Hf, Th}$, the energy-adjusted Stuttgart ECPs were used.

* Corresponding author. E-mail: laurag@ciam.unibo.it.
† Università di Palermo.
‡ University of Helsinki.
(2) Godab, A. M.; Köhler, H.; Skopenko, V. V. Chemistry of Pseudo halides; Elsevier: Amsterdam, 1986.
Figure 1. Calculated structure of the local minimum of Ti(N\textsubscript{3}A\textsubscript{4}). The other M(N\textsubscript{3}A\textsubscript{4}) (M = Zr, Hf, Th) systems have similar structures.

Figure 2. Calculated structure of the local minimum of Zn(N\textsubscript{3}A\textsubscript{2})\textsuperscript{2-}.

Table 1. Bond Lengths (Å) for the M(N\textsubscript{3}A\textsubscript{4}) Species, with M = Ti, Zr, Hf, Th, with the Small, BS1, and Large, BS2, Basis (in Parentheses\textsuperscript{a,b}).

<table>
<thead>
<tr>
<th>M(N\textsubscript{3}A\textsubscript{4})</th>
<th>Ti(N\textsubscript{3}A\textsubscript{4})</th>
<th>Zr(N\textsubscript{3}A\textsubscript{4})</th>
<th>Hf(N\textsubscript{3}A\textsubscript{4})</th>
<th>Th(N\textsubscript{3}A\textsubscript{4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>R\textsubscript{N1-N2}</td>
<td>1.869 (1.879)</td>
<td>2.036 (2.030)</td>
<td>2.030 (2.023)</td>
<td>2.259</td>
</tr>
<tr>
<td>R\textsubscript{N2-N3}</td>
<td>1.210 (1.203)</td>
<td>1.213 (1.204)</td>
<td>1.212 (1.204)</td>
<td>1.219</td>
</tr>
<tr>
<td>R\textsubscript{N1-N3}</td>
<td>1.144 (1.135)</td>
<td>1.143 (1.131)</td>
<td>1.142 (1.131)</td>
<td>1.143</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In free N\textsubscript{3}A\textsuperscript{2-}; N–N = 1.18 Å. All structures are tetrahedral with the N1MN1 angle of 109.5° and the MN1N2 and N1N2N3 angles of 180°.

Three Results

In Table 1, the structures of the M(N\textsubscript{3}A\textsubscript{4}) species obtained with the two different basis sets are reported. All molecules were found to be local minima in \textit{T}d symmetry, with a linear M–N–N–N–N structure, in their singlet ground state. (From now on, we will refer to a tetrahedral–linear structure, meaning that the MNN and NNN angles are both 180° and the NNM angles are 109.5°). The calculations were also repeated with lowered \textit{D}_{4h} symmetry, and the molecules maintained the tetrahedral–linear structure. To our knowledge, linear polyazides have never been detected before. Some anionic tetra-azides are well-known, such as Zn(N\textsubscript{3}A\textsubscript{2})\textsuperscript{2-}. This system does not have a linear Zn–NNN coordination (see Figure 2), as confirmed by our calculations.

We checked the stability of the triplet for Ti(N\textsubscript{3}A\textsubscript{4}), and it was found to lie 60 kcal/mol above the singlet. Moreover, the optimized structure for the triplet is not perfectly tetrahedral–linear (MNN = 171.7°, NNN = 180°, and NNM = 108° or 110°).

As seen from Table 1, the larger BS2 basis set gives slightly different results compared to the smaller BS1 basis set. In Ti(N\textsubscript{3}A\textsubscript{4}), the Ti–N bond distance becomes 0.01 Å longer, while the N1–N2 and N2–N3 bond distances become ca. 0.01 Å shorter. In Zr(N\textsubscript{3}A\textsubscript{4}) and Hf(N\textsubscript{3}A\textsubscript{4}), all bond distances become slightly shorter with the larger basis set. For Th(N\textsubscript{3}A\textsubscript{4}), we performed only one set of calculations. In free N\textsubscript{3}A\textsuperscript{2-}, the N–N bond distance is calculated to be 1.18 Å.

References

(10) ECPs and corresponding valence basis sets; Institut für Theoretische Chemie, Universität Stuttgart: Stuttgart; http://www.theochem.uni-stuttgart.de/.
with BS2. Along the Ti–Th series, the M–N bond distances increase from Ti to Zr and from Zr to Th, while in the Zr and Hf case the M–N bond distance is very similar. The calculated Ti–N distance for the present titanium tetra-azide is 0.16 Å shorter than that measured for solid (C₅H₅)₂Ti-(N₃)₂, suggesting a very different bonding in the two compounds.

The linear MNNN bond is a unique feature, and it seems worth investigating. We performed RASSCF calculations in order to understand the molecular orbitals involved in the bonding. In Figure 3, the active MOs are reported.

In order to discuss the bonding of the azides to the metal, we first note that in each N₃ group the three 2pₓ orbitals lead to three molecular orbitals, MOs, denoted ψ₁–₃, having 0, 1, and 2 nodal surfaces perpendicular to the NNN axis, respectively. Among the eight occupied MOs, there are two of such ψ₁ combinations (49 and 50) and six ψ₂ combinations (47, 48, 44, 45, 46, 51). Among the eight external orbitals, there are some ψ₂ combinations (43, 39, 41, 36) along all the NNN bonds, and some mixed combinations, namely of ψ₁ type along certain NNN axes and of ψ₂ type along others (40, 42, 37, 38). The eight occupied orbitals are essentially azide orbitals, and the eight external orbitals are essentially azide orbitals with some Ti contribution. They give evidence for a M–N–N–N conjugation, which might explain the linear structure.

In Table 2, the D₂d harmonic frequencies of the M(N₃)₄ species, obtained with the largest basis sets of each series, are reported, together with their IR intensities. All frequencies are real. The same holds also when smaller basis sets are used. The lowest eight motions occur at ca. 20–30 cm⁻¹, and they correspond to wagging vibrations of the azides. Such low frequencies imply that at ambient temperature many of these modes will be thermally excited. The analogous modes in Zn(N₃)₂– vibrate at frequencies varying between 20 and 100 cm⁻¹. Thus, the wagging vibrations of this known system are comparable with the predicted ones, and the latter are not in this sense unusually “floppy”. The first mode with sizable IR intensity corresponds to MN₁ stretching and occurs at ca. 300–500 cm⁻¹. The most intense modes correspond to azide stretching modes. The azide bending occurs at 580–600 cm⁻¹, while in a free azide it occurs at 614 cm⁻¹. The symmetric azide stretching occurs at 1400–1500 cm⁻¹, while in a free azide it occurs at 1354 cm⁻¹. The asymmetric azide stretching occurs at 2200–2300 cm⁻¹, while in a free azide it occurs at 2100 cm⁻¹.

In Table 3, the partial charges on M, N₁, N₂, and N₃, obtained by a natural orbital (NO) population analysis, using the largest basis set, are reported. Formally, the systems correspond to M⁴⁺, and N₃⁻. The NO charge on the M center is, on the other hand, 1.37, 1.95, 2.08, and 2.04 for Ti, Zr, Hf, and Th, respectively.
previously investigated isomers with general formula $\text{N}_5\text{M}(\text{N}_3)_4$ summarized in Figure 4. With the inclusion of the zero point energy (ZPE) correction, the formation of $\text{M}(\text{N}_3)_4$ is endothermic for all species, with the exception of $\text{M} = \text{Th}$, and it requires ca. 50, 20, and 3 kcal/mol for $\text{M} = \text{Ti}$, $\text{Zr}$, $\text{Hf}$, respectively, and produces ca. 20 kcal/mol for $\text{M} = \text{Th}$. The non-ZPE corrected curve lies parallel to the ZPE corrected curve, ca. 10 kcal/mol below. It should, nevertheless, be noted that all the formation energies in Figure 4 could easily be reached by the kinetic energies of the laser-depleted $\text{M}$ atoms. (A strong laser can, in fact, create atoms with a few electronvolts of kinetic energy, and they still have this energy, when hitting the object molecules on the surface of the probe being condensed, before they thermalize. This is the way in which, for example, the $\text{NUN}$ molecule was created, by shooting an $\text{U}$ atom uphill to an $\text{N}_2$ molecule.)

A search for transition states was made for $\text{Ti}(\text{N}_3)_4$. The following reaction paths were studied at the unrestricted B3LYP level: (a) the dissociation of one $\text{N}_3^-$ group; (b) the dissociation of one $\text{N}_2$ group; (c) the concerted dissociation of one $\text{N}_2$ molecule and two $\text{N}_3^-$ groups. None of these yielded any transition states below 50 kcal/mol. This suggests that the dissociation of $\text{Ti}(\text{N}_3)_4$ might occur with a concerted mechanism, and unlike in the $\text{N}_2\text{TiN}_3$ case, it is not enough to elongate one bond to start a dissociation process. Therefore, we conclude that the present tetra-azides are not only thermodynamically but kinetically surprisingly stable.

The $\text{M}(\text{N}_3)_4$ systems are much more stable than the previously investigated isomers with general formula $\text{N}_5\text{M}\text{N}_3\text{N}_3\text{N}_3$, $\text{Th}(\text{N}_3)_4$, for example, is 150 kcal/mol lower in energy than $\text{N}_7\text{ThN}_7$. The dissociation/formation of the $\text{M}(\text{N}_3)_4$ systems to/from $\text{M} + 6\text{N}_2$ was investigated. The energy difference between $\text{M} + 6\text{N}_2$ and $\text{M}(\text{N}_3)_4$ varies according to the different nature of $\text{M}$. The energetics of the reactions are summarized in Figure 4. With the inclusion of the zero point energy (ZPE) correction, the formation of $\text{M}(\text{N}_3)_4$ is endothermic for all species, with the exception of $\text{M} = \text{Th}$, and it requires ca. 50, 20, and 3 kcal/mol for $\text{M} = \text{Ti}$, $\text{Zr}$, $\text{Hf}$, respectively, and produces ca. 20 kcal/mol for $\text{M} = \text{Th}$. The non-ZPE corrected curve lies parallel to the ZPE corrected curve, ca. 10 kcal/mol below. It should, nevertheless, be noted that all the formation energies in Figure 4 could easily be reached by the kinetic energies of the laser-depleted $\text{M}$ atoms. (A strong laser can, in fact, create atoms with a few electronvolts of kinetic energy, and they still have this energy, when hitting the object molecules on the surface of the probe being condensed, before they thermalize. This is the way in which, for example, the $\text{NUN}$ molecule was created, by shooting an $\text{U}$ atom uphill to an $\text{N}_2$ molecule.)

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The analogous $\text{U}$ compound, $\text{U}(\text{N}_3)_4$, was also investigated in several spin multiplicities. The system turned out to be bent, and it was not possible to converge the optimization procedure. Calculations were performed also on mixed nitride azides, $\text{N}_5\text{M}_3$, with $\text{M} = \text{Ti}$ and $\text{U}$. Both species were found to be stable in their singlet and triplet ground states, respectively. However, while $\text{NTiN}_3$ has a bent structure with a $\text{NTiN}_3$ angle of 119°, $\text{NUN}_3$ is linear. Typical bond distances are $\text{N(nitride)} - \text{M} = 1.66$ and 1.73 Å, $\text{M} - \text{N1}$-

### Table 2.

<table>
<thead>
<tr>
<th>Mode n</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\delta$(ZPE)</th>
<th>$\delta$(BS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(N$_3$)$_4$</td>
<td>31.12 (0)</td>
<td>31.72 (0)</td>
<td>27.81 (1)</td>
</tr>
<tr>
<td>Zr(N$_3$)$_4$</td>
<td>32.70 (0)</td>
<td>31.88 (0)</td>
<td>28.84 (0)</td>
</tr>
<tr>
<td>Hf(N$_3$)$_4$</td>
<td>32.74 (0)</td>
<td>31.91 (0)</td>
<td>28.98 (0)</td>
</tr>
<tr>
<td>Th(N$_3$)$_4$</td>
<td>32.7 (0)</td>
<td>31.99 (0)</td>
<td>32.62 (0)</td>
</tr>
</tbody>
</table>

* Harmonic frequencies and IR intensities for $\text{N}_3^-$: 667 (14) bend, 1354 (0) s stretch, 2100 (964) a stretch. s = symmetric stretch; a = antisymmetric stretch; op = out of plane.

### Table 3.

| M+6N$_2$ $\rightarrow$ M(N$_3$)$_4$ |
|-----------------|-----------------|--------------|--------------|
| $\delta$ M      | $\delta$ N$_1$  | $\delta$ N$_2$ | $\delta$ N$_3$ |
| Ti(N$_3$)$_4$   | 1.37            | 0.51          | 0.23         | -0.06        |
| Zr(N$_3$)$_4$   | 1.95            | 0.66          | 0.24         | -0.06        |
| Hf(N$_3$)$_4$   | 2.08            | 0.70          | 0.24         | -0.07        |
| Th(N$_3$)$_4$   | 2.04            | -0.54         | 0.29         | -0.26        |

Figure 4. Energy difference between $\text{M} + 6\text{N}_2$ and $\text{M}(\text{N}_3)_4$ as a function of the atomic number.
(azide) = 1.91 and 2.19 Å, N1–N2 = 1.21 and 1.22 Å, N2–N3 = 1.15 and 1.14 Å for M = Ti and U, respectively. The formation energy of NMN$_3$ from M + 2N$_2$, including ZPE correction, is +8.7 and +0.2 kcal/mol for M = Ti, U, respectively. This suggests that both these nitride azides are also experimentally feasible synthetic objects.

4. Conclusions

The existence of new group 4 tetra-azides, M(N$_3$)$_4$, with M = Ti, Zr, Hf, and Th, has been predicted. These species are quite stable, and far more stable that the recently proposed, novel N$_5$M$_7$ species. Furthermore, they present the unique feature of having linear M–NNN bonds. The present M(N$_3$)$_4$ molecules may be interesting spectroscopic objects in that their zero-temperature structure is predicted to be $T_d$, but at room-temperature, several rotational and high-amplitude vibrational states will be occupied and can lower the effective symmetry. The mixed nitride azides, NMN$_3$, with M = Ti and U were also investigated, and both species were found to be stable. In materials science, these predicted species could be useful reagents for depositing metal nitrides, or the metal itself. Finally, note that, compared to lead, titanium is nontoxic and hence not an environmental burden.

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Gagliardi and Pyykkö

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