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

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Quantum chemical calculations suggest that group 4 tetra-azides $M(N_3)_4$, where M = Ti, Zr, Hf, and 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 η^5-N_5 –M–η^7-N_7, and the Th species, $Th(N_3)_4$, is the most stable of all. Possible mixed nitride azides NMN_3 were also investigated.

1. Introduction

We have recently predicted the possible existence of novel nitrogen-containing molecules with general formula N_5MN_7, with M = Ti, Zr, Hf, Th.[1] 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,[2-4] 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 Mo, for instance, $N{\equiv}Mo(N_3)_3$ is known in the bulk.[3] For the group 4 metals, $N{\equiv}M{-}N_3$ 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 MN and M_3N_4, when making electronic circuits.

It should be noted that these MN_n compounds could in principle disintegrate to deposit the desired M, MN, or M_3N_4, plus gaseous N_2. The metal nitrides TiN, ZrN, and HfN are also used as thin layers on high-speed cutting tools,[5] 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 = 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−NN angles. Recently, the hexa-azidosilicate(IV) ion has been synthesized and characterized.[6] The analogous hexa-azidostannate(IV) was made much earlier.[7] Diazides of certain group 4 metals are known. The crystal structure of bis(η^5-cyclopentadienyl)titanium diazide has been determined.[8] 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 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 = Zr, Hf, and Th, the energy-adjusted Stuttgart ECPs were used

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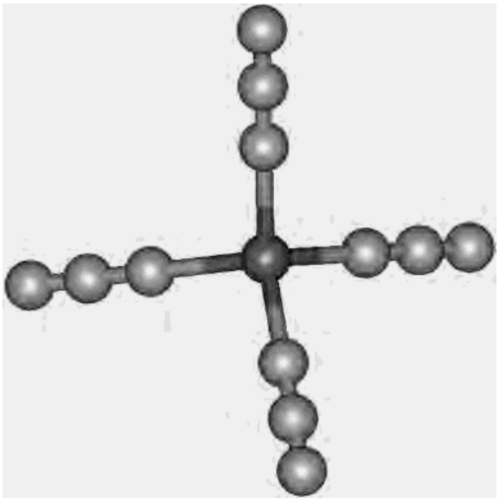

Figure 1. Calculated structure of the local minimum of Ti(N$_3$)$_4$. The other M(N$_3$)$_4$ (M = Zr, Hf, Th) systems have similar structures.

for this.[9] The number of valence electrons is 12 for Zr and Hf, and 30 for Th. The basis sets accompanying the ECPs, 6s5p3d for Zr and Hf, and 8s7p6d4f for Th, were used to describe them.[10]

A second set of calculations were performed using a larger basis, BS2, on Ti(N$_3$)$_4$, Zr(N$_3$)$_4$, and Hf(N$_3$)$_4$. This consists of an extended 6-31g* basis on N (6s3p2d) and Ti (8s5p4d1f), and a 6s5p5d3f basis set accompanying the ECPs for Zr and Hf.

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 integrations. The program Gaussian98[11] was employed.

Comparative calculations were performed at the multiconfigurational SCF level, of the restricted active space (RAS) SCF type,[12] for Ti(N$_3$)$_4$ using ANO type basis sets[13] on N (3s2p1d), and Ti atoms (5s4p3d1f). The active space used in the calculation is formed by the eight highest doubly occupied orbitals and the eight lowest external orbitals; single, double, and triple excitations were allowed from the occupied to the external orbitals. The program MOLCAS-5.2[14] was employed.

3. Results

In Table 1, the structures of the M(N$_3$)$_4$ species obtained with the two different basis sets are reported. All molecules

Table 1. Bond Lengths (Å) for the M(N$_3$)$_4$ Species, with M = Ti, Zr, Hf, Th, with the Small, BS1, and Large, BS2, Basis (in Parentheses)[a,b]

	Ti(N$_3$)$_4$	Zr(N$_3$)$_4$	Hf(N$_3$)$_4$	Th(N$_3$)$_4$
$R_{\mathrm{M-N1}}$	1.869 (1.879)	2.036 (2.030)	2.030 (2.023)	2.259
$R_{\mathrm{N1-N2}}$	1.210 (1.203)	1.213 (1.204)	1.212 (1.204)	1.219
$R_{\mathrm{N2-N3}}$	1.144 (1.135)	1.143 (1.131)	1.142 (1.131)	1.143

[a] In free N$_3^-$: N−N = 1.18 Å. [b] All structures are tetrahedral with the N1MN1 angle of 109.5° and the MN1N2 and N1N2N3 angles of 180°.

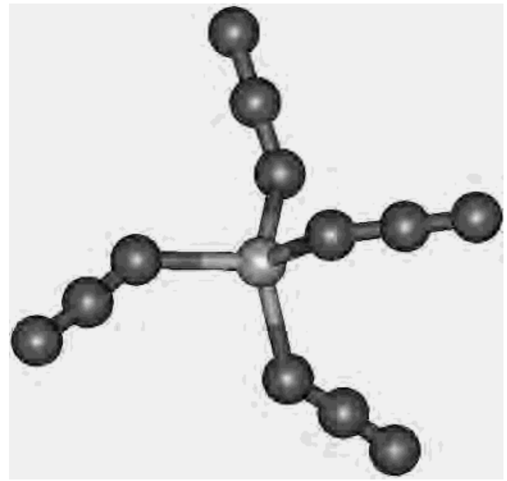

Figure 2. Calculated structure of the local minimum of Zn(N$_3$)$_4^{2-}$.

were found to be local minima in T_d symmetry, with a linear M−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 NMN angles are 109.5°). The calculations were also repeated with lowered D_{2d} 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$_3$)$_4^{2-}$. 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$_3$)$_4$, 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 NMN = 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$_3$)$_4$, 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$_3$)$_4$ and Hf(N$_3$)$_4$, all bond distances become slightly shorter with the larger basis set. For Th(N$_3$)$_4$, we performed only one set of calculations. In free N$_3^-$, the N−N bond distance is calculated to be 1.18 Å

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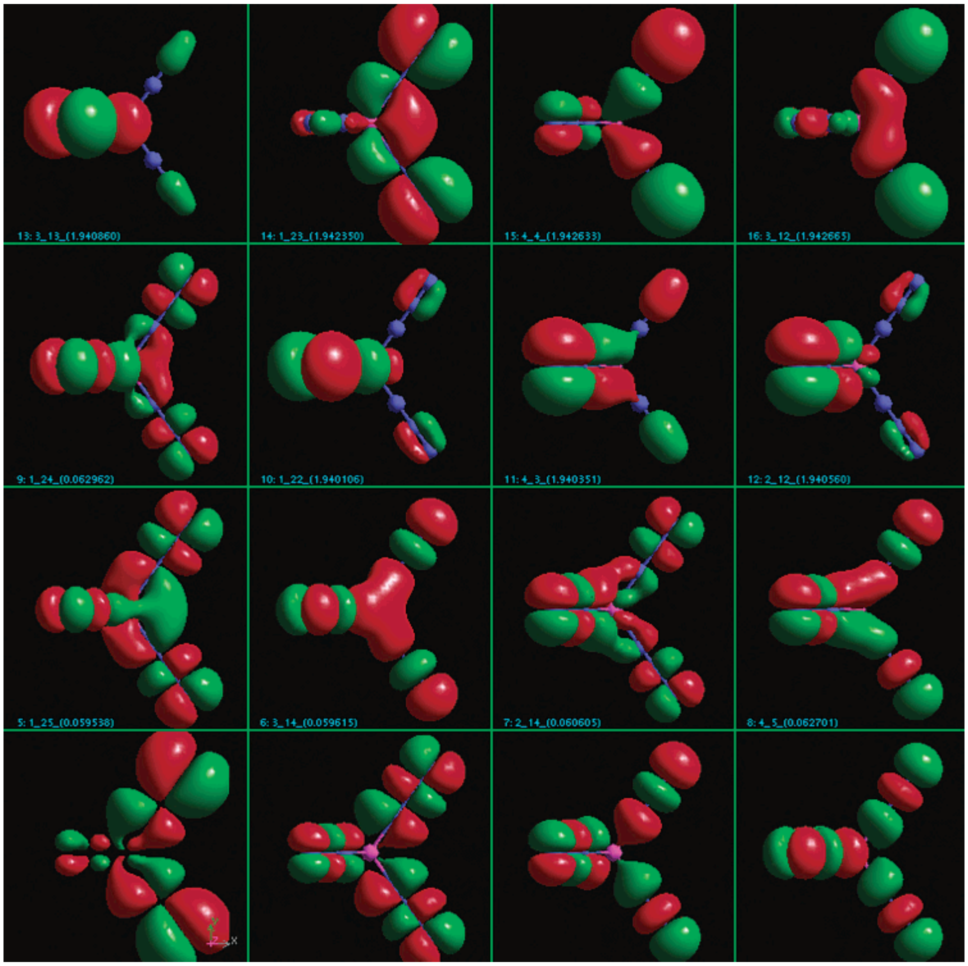

Figure 3. The 16 active orbitals of $Ti(N_3)_4$ and their occupation number in the RASSCF calculation.

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 $(C_5H_5)_2Ti(N_3)_2$,[8] 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 N_3 group the three $2p\pi_x$ orbitals lead to three molecular orbitals, MOs, denoted ψ_{1-3}, having 0, 1, and 2 nodal surfaces perpendicular to the NNN axis, respectively. Among the eight occupied MOs, there are two of such ψ_1 combinations (49 and 50) and six ψ_2 combinations (47, 48, 44, 45, 46, 51). Among the eight external orbitals, there are some ψ_3 combinations (43, 39, 41, 36) along all the NNN bonds, and some mixed combinations, namely of ψ_3 type along certain NNN axes and of ψ_2 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 D_{2d} harmonic frequencies of the $M(N_3)_4$ 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 $Zn(N_3)_4^{2-}$ 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 M^{4+}, and N_3^-. 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.

Table 2. D_{2d} Harmonic Frequencies (cm^{-1}) and Their IR Intensities (km mol^{-1}) in Parentheses for $Ti(N_3)_4$, $Zr(N_3)_4$, $Hf(N_3)_4$, and $Th(N_3)_4$, with the Larger Basis Set (BS2 for $Ti(N_3)_4$, $Zr(N_3)_4$, $Hf(N_3)_4$, and BS1 for $Th(N_3)_4$)[a]

mode n	description	$Ti(N_3)_4$	$Zr(N_3)_4$	$Hf(N_3)_4$	$Th(N_3)_4$
ν_1(e)	MN1N2N3 wag	20.21 (0)	31.12 (0)	31.72 (0)	27.81 (1)
ν_3(b_1)	MN1N2N3 wag	20.25 (0)	32.70 (0)	31.72 (0)	27.99 (1)
ν_4(b_2)	MN1N2N3 wag	20.59 (0)	32.72 (0)	31.88 (0)	28.84 (0)
ν_5(a_1)	MN1N2N3 wag	20.61 (0)	32.74 (0)	31.91 (0)	28.98 (0)
ν_6(e)	MN1N2N3 wag	34.00 (0)	75.15 (0)	75.99 (0)	83.12 (0)
ν_8(a_2)	MN1N2N3 wag	34.46 (0)	75.27 (0)	76.05 (0)	84.36 (0)
ν_9(b_1)	MN1N2 op bend	180.49 (0)	159.73 (0)	160.57 (0)	133.87 (0)
ν_{10}(a_1)	MN1N2 op bend	180.76 (0)	159.85 (0)	160.66 (0)	134.43 (0)
ν_{11}(e)	MN1N2 op bend	200.17 (3)	174.21 (8)	172.95 (12)	139.37 (13)
ν_{13}(b_2)	MN1N2 op bend	201.08 (3)	174.35 (8)	173.40 (12)	140.05 (13)
ν_{14}(a_1)	MN1 s stretch	375.12 (0)	365.41 (0)	372.75 (0)	333.94 (0)
ν_{15}(b_2)	MN1 a stretch	520.13 (293)	428.11 (214)	388.05 (152)	326.29 (192)
ν_{16}(e)	MN1 a stretch	520.16 (291)	428.32 (214)	388.14 (152)	326.29 (192)
ν_{18}(e)	N1N2N3 bend	582.18 (0)	604.44 (0)	604.60 (0)	600.17 (0)
ν_{20}(a_2)	N1N2N3 bend	582.23 (0)	604.51 (0)	604.64 (0)	600.21 (0)
ν_{21}(b_1)	N1N2N3 bend	584.36 (0)	606.99 (0)	607.19 (0)	604.81 (0)
ν_{22}(a_1)	N1N2N3 bend	584.76 (0)	607.05 (0)	607.36 (0)	604.92 (0)
ν_{23}(e)	N1N2N3 bend	586.61 (45)	608.78 (42)	608.79 (40)	605.27 (53)
ν_{25}(b_2)	N1N2N3 bend	587.01 (43)	608.83 (42)	608.99 (39)	605.46 (52)
ν_{26}(b_2)	N1N2N3 s stretch	1466.71(696)	1453.15 (649)	1462.21 (619)	1416.53 (611)
ν_{27}(e)	N1N2N3 s stretch	1466.78(685)	1453.25 (650)	1462.24 (610)	1416.53 (611)
ν_{29}(a_1)	N1N2N3 s stretch	1490.30(0)	1478.97 (0)	1488.69 (0)	1440.01 (0)
ν_{30}(b_2)	N1N2N3 a stretch	2239.95(1829)	2255.85 (1799)	2267.38(1825)	2267.82 (1516)
ν_{31}(e)	N1N2N3 a stretch	2239.95(1829)	2256.05 (1790)	2267.38(1793)	2267.87 (1497)
ν_{33}(a_1)	N1N2N3 a stretch	2280.61(0)	2291.79 (0)	2304.67 (0)	2293.66 (0)

[a] Harmonic frequencies and IR intensities for 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. Natural Orbital Population Analysis Partial Charges

	δ_M	δ_{N1}	δ_{N2}	δ_{N3}
$Ti(N_3)_4$	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

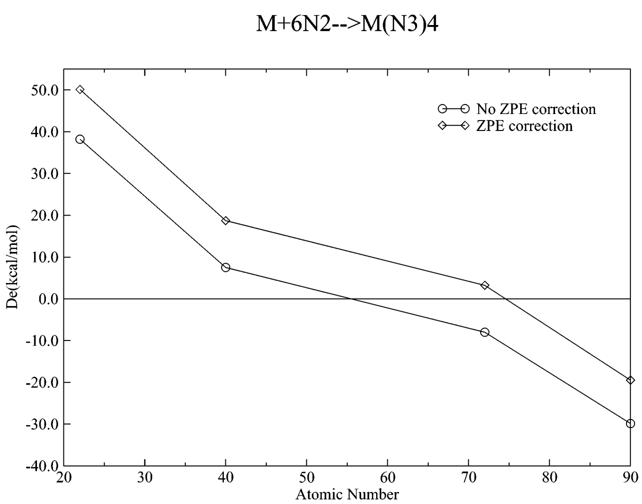

Figure 4. Energy difference between M + $6N_2$ and $M(N_3)_4$ as a function of the atomic number.

The $M(N_3)_4$ systems are much more stable than the previously investigated isomers with general formula N_5MN_7. $Th(N_3)_4$, for example, is 150 kcal/mol lower in energy than N_5ThN_7. The dissociation/formation of the $M(N_3)_4$ systems to/from M + $6N_2$ was investigated. The energy difference between M + $6N_2$ and $M(N_3)_4$ varies according to the different nature of M. The energetics of the reactions are summarized in Figure 4. With the inclusion of the zero point energy (ZPE) correction, the formation of $M(N_3)_4$ is endothermic for all species, with the exception of M = Th, and it requires ca. 50, 20, and 3 kcal/mol for M = Ti, Zr, Hf, respectively, and produces ca. 20 kcal/mol for M = 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 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 NUN molecule was created, by shooting an U atom uphill to an N_2 molecule.)

A search for transition states was made for $Ti(N_3)_4$. The following reaction paths were studied at the unrestricted B3LYP level: (a) the dissociation of one N_3^- group; (b) the dissociation of one N_2 group; (c) the concerted dissociation of one N_2 molecule and two N_3^- groups. None of these yielded any transition states below 50 kcal/mol. This suggests that the dissociation of $Ti(N_3)_4$ might occur with a concerted mechanism, and unlike in the N_7TiN_5 case,[1] 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 analogous U compound, $U(N_3)_4$, 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, NMN_3, with M = Ti and U. Both species were found to be stable in their singlet and triplet ground states, respectively. However, while $NTiN_3$ has a bent structure with a NTiN angle of 119°, NUN_3 is linear. Typical bond distances are N(nitride)−M = 1.66 and 1.73 Å, M−N1-

(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_5MN_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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