Azide Complexes

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The Binary Group 4 Azides $[PPh_4]_2[Zr(N_3)_6]$ and $[PPh_4]_2[Hf(N_3)_6]$

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Dedicated to Professor George A. Olah on the occasion of his 90th birthday

Abstract: *The binary zirconium and hafnium polyazides $[PPh_4]_2[M(N_3)_6]$ (M = Zr, Hf) were obtained in near quantitative yields from the corresponding metal fluorides MF_4 by fluoride–azide exchange reactions with Me_3SiN_3 in the presence of two equivalents of $[PPh_4][N_3]$. The novel polyazido compounds were characterized by their vibrational spectra and their X-ray crystal structures. Both anion structures provide experimental evidence for near-linear M-N-N coordination of metal azides. The species $[M(N_3)_4]$, $[M(N_3)_5]^-$ and $[M(N_3)_6]^{2-}$ (M = Ti, Zr, Hf) were studied by quantum chemical calculations at the electronic structure density functional theory and MP2 levels.*

Polyazides, due to their positive heats of formation and high energy content, are viable candidates for high-energy-density materials (HEDM).[1] The often highly sensitive and explosive nature of neutral binary polyazides can be greatly reduced by anion formation with ionic azides such as $[PPh_4][N_3]$ which strengthens the weak N_α–N_β bond and raises the activation energy barrier towards fatal N_2 elimination by increasing the ionic character of the azido ligands.[2] Partially azido-substituted titanium and zirconium compounds have been previously reported[3] and the first binary titanium polyazides were prepared in 2004.[4] In a theoretical study, the metal tetraazides $[M(N_3)_4]$ (M = Ti, Zr, Hf, Th) were predicted to be vibrationally stable,[5] exhibiting tetrahedral structures with unique linear M-N-N coordination of the metal. Linear M-N-N coordination had previously been predicted also for $[Nb(N_3)_5]$ and $[Ta(N_3)_5]$.[6] The first experimental evidence for a near-linear M-N-N coordination was provided by the structural characterization of the acetonitrile adduct $[Nb(N_3)_5{\cdot}CH_3CN]$.[6] Herein we report the synthesis of the first binary zirconium and hafnium polyazides, $[M(N_3)_6]^{2-}$ (M = Zr, Hf), which were isolated and characterized as their tetraphenylphosphonium salts, and comment on the observed and predicted M-N-N bond angles in the anions.

By analogy with our synthesis of other binary metal azides,[7] $[MF_4]$ was reacted at ambient temperature with an excess of Me_3SiN_3 and two equivalents of $[PPh_4][N_3]$ in acetonitrile solution. This resulted in rapid and quantitative fluoride–azide exchange and the formation of light yellow solutions of hexaazido-zirconate and -hafnate $[M(N_3)_6]^{2-}$ (M = Zr, Hf) anions, respectively [Eq. (1)].

$$[MF_4] + 4\,Me_3SiN_3 + 2\,[PPh_4][N_3] \xrightarrow[-\,4\,Me_3SiF]{CH_3CN} [PPh_4][M(N_3)_6] \quad (1)$$

M = Zr, Hf

Attempted reactions of the metal fluorides with an excess of Me_3SiN_3 in acetonitrile solution without the addition of $[PPh_4][N_3]$ yielded only the starting materials. This might be attributed to the low solubility of the metal fluorides in acetonitrile. Attempts to synthesize $[M(N_3)_5]^-$ (M = Zr, Hf) by reacting $[MF_4]$ with an excess of Me_3SiN_3 and only one equivalent of $[PPh_4][N_3]$ in acetonitrile at room temperature yielded a mixture of $[PPh_4]_2[M(N_3)_6]$ and $[MF_4]$ starting materials. The corresponding tetraphenylphosphonium salts were isolated from the reaction mixtures in quantitative yields after removal of all volatile compounds (Me_3SiF, CH_3CN and excess Me_3SiN_3) in vacuo. Both $[PPh_4]_2[M(N_3)_6]$ salts are room temperature stable, pale orange solids that are not friction or impact sensitive (FS > 360 N; IS > 100 J) and decompose exothermic but smooth with onset temperatures of 204 °C (M = Zr) and 280 °C (M = Hf) as determined by DTA (5 °C min^{-1} heating rate). These relatively high decomposition onset temperatures and the insensitivity to friction and impact can be attributed to the increased ionic character of the azido groups due to anion formation as well as the presence of two large organic counter-ions per anion.[8] The hexaazidometallate salts were identified and characterized by their crystal structures, vibrational and ^{14}N NMR spectra as well as the observed material balances. The experimental and calculated vibrational frequencies and intensities are given in the Supplementary Information.

The X-ray crystal structure of $[PPh_4]_2[Zr(N_3)_6]$ reveals the presence of isolated and well-separated $[PPh_4]^+$ and $[Zr(N_3)_6]^{2-}$ ions. The closest Zr···N contacts between neighboring anions are 7.242(1) Å and the closest cation–anion distance is 3.156(1) Å. The $[Zr(N_3)_6]^{2-}$ anion has a pseudo-octahedral coordination environment around the central zirconium atom (Figure 1) with ligand arrangement different than in the related anion $[Ti(N_3)_6]^{2-}$.[4] Out of the four equatorial azido groups of the $[Zr(N_3)_6]^{2-}$ anion, two opposing groups are pointing at an angle of about 70° above the equatorial plane. A third N_3 group (N16–N18) points at an angle of 63° steeply

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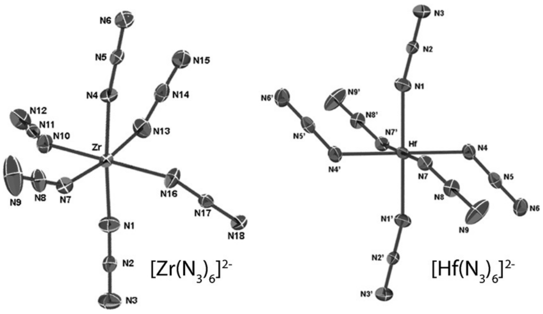


Figure 1. ORTEP drawing of the anions in the crystal structures of $[PPh_4]_2[Zr(N_3)_6]$ and $[PPh_4]_2[Hf(N_3)_6]$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Zr–N1 2.132(1), Zr–N4 2.137(1), Zr–N7 2.136(1), Hf–N1 2.118(2), Hf–N4 2.160(2); Zr-N1-N2 165.9(1), Zr-N4-N5 168.3(1), Hf-N1-N2 164.4(1).

below the equatorial plane while the fourth azido group (N10–N12) points at an angle of only 10° slightly below this plane. A similar arrangement of the azido ligands is also found for the hexaazido anions $[In(N_3)_6]^{3-}$ and $[Tl(N_3)_6]^{3-}$.[8] The Zr–N distances range from 2.132(2) Å to 2.178(3) Å and are significantly shorter than the ones found for $[ZrCl_4(N_3)_2]^{2-}$ (2.20(1) Å)[3d] but are in good agreement with typical Zr–N bond lengths reported in the literature.[9] The most interesting feature of the $[Zr(N_3)_6]^{2-}$ structure, however, is the fact that the axial azido ligands exhibit a significantly enlarged average Zr-N-N bond angle of 167.1(2)° while the four equatorial ligands (140.9(2)°) show bond angles that are typical for covalent azides.[1a,4,6,7,10] The average N–N distances of 1.149(3) Å for the terminal bond and 1.193(3) Å for the internal bond are in good agreement with the bond lengths previously reported for similar hexaazido anions.[1a,4,6,7,10] The N-Zr-N bond angles are 86.51(5)–95.49(5)° and 172.69(6)–175.58(6)°.

The hafnium azide $[PPh_4]_2[Hf(N_3)_6]$ crystallizes in space group $P\bar{1}$ with well-separated $[PPh_4]^+$ and $[Hf(N_3)_6]^{2-}$ ions. The closest intermolecular Hf···N distance is 6.677(3) Å and the shortest cation–anion distance is 3.267(3) Å. The $[Hf(N_3)_6]^{2-}$ anion exhibits a pseudo-octahedral ligand arrangement around the central hafnium atom (Figure 1). The ligand arrangement in the $[Hf(N_3)_6]^{2-}$ anion is different from that in $[Zr(N_3)_6]^{2-}$ but is similar to the one in the related titanium species $[Ti(N_3)_6]^{2-}$.[4] Both consist of asymmetric MN_9 units (M = Ti, Hf) with three covalently bonded azido groups to give a trigonal pyramidal coordination environment around the central metal atom. The remaining azido groups are generated by symmetry (symmetry operation $-x+2$, $-y+1$, $-z$). The anion shows a ligand arrangement similar to other hexaazido anions such as $[V(N_3)_6]^-$,[11] $[Se(N_3)_6]^{2-}$,[12] $[Ti(N_3)_6]^{2-}$,[4] and $[Mn(N_3)_6]^{2-}$[1a] but different from the $[Zr(N_3)_6]^{2-}$ anion. Similar to the related zirconium anion, a noticeable difference in bond lengths and angles is observed between the axial and equatorial azido ligands of the $[Hf(N_3)_6]^{2-}$ anion. With an Hf–N_{axial} distance of 2.118(2) Å, the two axial azido groups are closer to the metal than the equatorial N_3 ligands with an average Hf–N_{eq} distance of 2.161(2) Å. The average Hf–N distance of 2.147(3) Å is in good agreement with typical Hf–N bond lengths reported in the literature.[13] The M-N-N angles in $[Hf(N_3)_6]^{2-}$ show a similar pattern as the related zirconium anion $[Zr(N_3)_6]^{2-}$. The four equatorial azido ligands exhibit Hf-N-N angles of 128.2(1)° and 133.7(1)°, typical for covalent metal azides, while the axial N_3 ligands coordinate more linear with Hf-N-N angles of 164.5(1)°. A difference between the axial and equatorial azido ligands is also observed in the N–N distances. While the equatorial N_3 groups exhibit a shorter terminal N–N distance of 1.151(2) Å (average) and a longer internal distance of 1.208(2) Å (average) typical for covalent azides, the N–N distances of the axial ligands are more similar (1.188(2) Å and 1.150(2) Å). This indicates a higher ionic character for the axial N_3 ligands than for the equatorial ones and could explain the more linear arrangement of these groups.

For the neutral azides $[M(N_3)_4]$, as well as for the anions $[M(N_3)_5]^-$ and $[M(N_3)_6]^{2-}$ (M = Ti, Zr, Hf) quantum mechanical calculations were carried out at the B3LYP//DZVP2(N)/aug-cc-pVDZ-PP and SVWN//DZVP2(N)/aug-cc-pVDZ-PP density functional theory (DFT) levels of theory as well as the correlated molecular orbital theory MP2/aug-cc-pVDZ(-PP) level. The obtained structures and the list of calculated vibrational frequencies are given in the Supporting Information. The local DFT functional was included as it often gives better geometries for transition metal compounds than the hybrid functional B3LYP.

Previous quantum chemical calculations using the B3LYP exchange-correlation functional with various basis sets predicted the Group 4 tetraazides $[M(N_3)_4]$ (M = Ti, Zr, Hf) to exhibit a unique linear M-N-N coordination of the metal.[5] These findings are validated by our independent calculations with the local functional and at the MP2 level. DFT with the B3LYP and SVWN5 functionals as well as MP2 predict for $[Ti(N_3)_4]$, $[Zr(N_3)_4]$ and $[Hf(N_3)_4]$ a minimum-energy structure of T_d symmetry (Figure 2) with a linear M-N-N ligand arrangement. Our calculated Ti–N distances of 1.874 Å (B3LYP), 1.855 Å (SVWN) and 1.881 Å (MP2) for $[Ti(N_3)_4]$ are in good agreement with the value from previous MP2 predictions of 1.880 Å.[5] The calculated Hf–N distances of 2.007 Å (B3LYP) and 1.986 Å (SVWN) are shorter than the value predicted previously (2.030 Å) but the MP2 value of 2.025 Å is quite similar.[5] For $[Zr(N_3)_4]$, the calculated Zr–N distance of 2.031 Å at the B3LYP level is in good agreement with the previously predicted value (2.023 Å)[5] whereas the SVWN5 value of 2.010 Å is marginally shorter and the MP2 value of 2.046 Å is slightly longer.

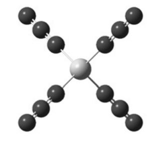
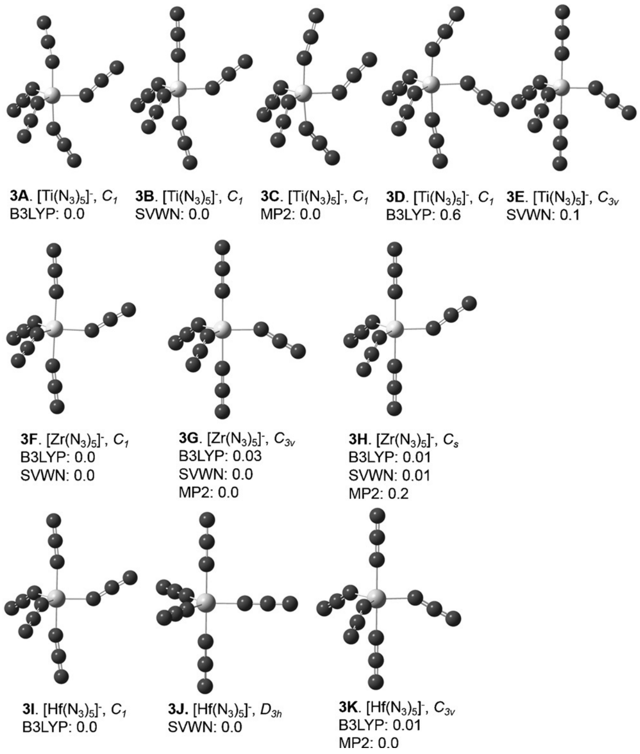

$[M(N_3)_4]$, M = Ti, Zr, Hf, T_d

Figure 2. Optimized structures of the neutral metal tetraazides at the B3LYP, SVWN, and MP2 levels.

For $[M(N_3)_5]^-$, different structures based on a pseudo-trigonal bipyramidal ligand arrangement (Figure 3) were predicted at the B3LYP, SVWN, and MP2 levels. As a limiting case, we take the D_{3h} structure with a linear arrangement of all five azido ligands. All of the structures differ only in the relative arrangement of the azido ligands and are within 8.0 kcal mol^{-1} of the higher energy D_{3h} limit with the highest value is for M = Ti. This is in good agreement with previous results that there are only subtle energy differences of less



3A. $[Ti(N_3)_5]^-$, C_1 B3LYP: 0.0
3B. $[Ti(N_3)_5]^-$, C_1 SVWN: 0.0
3C. $[Ti(N_3)_5]^-$, C_1 MP2: 0.0
3D. $[Ti(N_3)_5]^-$, C_1 B3LYP: 0.6
3E. $[Ti(N_3)_5]^-$, C_{3v} SVWN: 0.1
3F. $[Zr(N_3)_5]^-$, C_1 B3LYP: 0.0 SVWN: 0.0
3G. $[Zr(N_3)_5]^-$, C_{3v} B3LYP: 0.03 SVWN: 0.0 MP2: 0.0
3H. $[Zr(N_3)_5]^-$, C_s B3LYP: 0.01 SVWN: 0.01 MP2: 0.2
3I. $[Hf(N_3)_5]^-$, C_1 B3LYP: 0.0
3J. $[Hf(N_3)_5]^-$, D_{3h} SVWN: 0.0
3K. $[Hf(N_3)_5]^-$, C_{3v} B3LYP: 0.01 MP2: 0.0

Figure 3. Optimized structures of the pentaazido anions $[M(N_3)_5]^-$ and the energy differences [kcal mol^{-1}] at the B3LYP, SVWN, and MP2 levels.

than 5 kcal mol^{-1} between various orientations of the azido ligands in metal polyazides.[14] As a result, polyazido compounds may adopt several structures with only small energy differences among them.[15] For the $[Ti(N_3)_5]^-$ anion, each method predicts slightly different minima (**3A**–**3C**) that differ mainly in the orientation of the axial ligands. While the B3LYP functional predict Ti-N-N angles of 148–170° for the axial ligands (**3A**), the SVWN functional predicts a more linear coordination of the metal by the axial ligands (**3B**). The predicted minimum energy structure at the MP2 level (**3C**) exhibits Ti-N-N angles of 142° and 156° for the axial ligands. A C_{3v} structure (**3E**) with all three equatorial ligands pointing towards the same side of the equatorial plane is a minimum and just 0.1 kcal mol^{-1} higher in energy at the SVWN level. At the B3LYP level, the C_{3v} structure is 0.9 kcal mol^{-1} higher in energy but not a minimum with two small imaginary frequencies. Thus, at the B3LYP level the C_{3v} structure distorts to a C_1 structure (**3D**) which is 0.6 kcal mol^{-1} higher in energy than the minimum energy structure. At the MP2 level, the C_{3v} structure (**3E**) is 6.3 kcal mol^{-1} higher in energy and not a minimum exhibiting ten imaginary frequencies. The limiting structure with D_{3h} symmetry is 1.5 kcal mol^{-1} higher in energy at the SVWN level (five imaginary frequencies), 4.7 kcal mol^{-1} higher at the B3LYP level (ten imaginary frequencies), and 8.0 kcal mol^{-1} higher at the MP2 level (seven imaginary frequencies) as compared to the minimum energy structure. The minimum energy structure of the $[Zr(N_3)_5]^-$ anion at the SVWN and B3LYP levels (**3F**) is of C_1 symmetry with Zr-N-N angles of the axial ligands close to linearity (B3LYP: 171° and 174° and SVWN 178°). A C_{3v} symmetry structure is predicted to be the minimum at the MP2 level (**3G**). At all three levels of calculation, a C_s symmetry structure (**3H**) is also predicted to be a minimum. For both B3LYP and SVWN, the three minimum energy structures for $[Zr(N_3)_5]^-$ are essentially isoenergetic. The optimized MP2 C_s structure (**3H**) is just 0.2 kcal mol^{-1} higher in energy than the C_{3v} structure (**3G**). The limiting D_{3h} symmetry structure with a linear arrangement for all five azido ligands is only 0.1 kcal mol^{-1} higher in energy at the SVWN level (three imaginary frequencies), 0.6 kcal mol^{-1} higher at the B3LYP level (four imaginary frequencies) and 1.4 kcal mol^{-1} at the MP2 level (five imaginary frequencies). The B3LYP minimum energy structure of the $[Hf(N_3)_5]^-$ anion exhibits C_1 symmetry (**3I**). The Hf-N-N angles of 171° and 174° for the axial ligands are predicted to be the same as for $[Zr(N_3)_5]^-$ (**3F**). At the SVWN level, the $[Hf(N_3)_5]^-$ anion is predicted to have D_{3h} symmetry (**3J**). At the MP2 level, the lowest energy structure is predicted to be of C_{3v} symmetry (**3K**). At the B3LYP level, this structure is isoenergetic with the C_1 structure (**3I**). The D_{3h} structure (**3J**) is 0.5 kcal mol^{-1} higher in energy at the B3LYP level (three imaginary frequencies) and 0.9 kcal mol^{-1} higher in energy than the lowest energy structure with five imaginary frequencies at the MP2 level. Thus, the azide structure becomes more fluxional with a heavier metal center, allowing for linear M-N-N-N moieties.

The hexaazido anions would be expected to be even more fluxional and this is indeed what we predict. Only $[Ti(N_3)_6]^{2-}$ is predicted not to have O_h symmetry or have an O_h symmetry structure that is close in energy to the minimum energy structure. Thus, for M = Ti, the O_h structure (**4C**) is predicted to be higher in energy by 3.9 kcal mol^{-1} (B3LYP, 12 imaginary frequencies), 0.5 kcal mol^{-1} (SVWN, nine imaginary frequencies) and 2.9 kcal mol^{-1} (MP2, 12 imaginary frequencies) than the C_1 minimum structure (**4A**). The O_h structure (**4C**) is predicted to be a minimum at the SVWN and MP2 levels for $[M(N_3)_6]^{2-}$ with M = Zr and Hf. There is distortion from the O_h structure at the B3LYP level (six very small imaginary frequencies for both M = Zr and Hf due to the grid) but this distorted structure (**4B**) is essentially isoenergetic with the O_h structure. The average angles for the Ti-N-N moieties are 144° at the B3LYP level, 155° at the SVWN and 141° at the MP2 level. For M = Zr, the average angle is 167° and for M = Hf 166° at the B3LYP level. The arrangements of the azido ligands in the predicted minimum energy structures of the three $[M(N_3)_6]^{2-}$ anions (Figure 4) are different than observed in the crystal structures.[4] It is also interesting to note that the M-N-N angles in the predicted C_1 structures of the $[Zr(N_3)_6]^{2-}$ and $[Hf(N_3)_6]^{2-}$ anions agree very well with the experimental angles of about 165° for the axial azido ligands in the crystal structures while the experimental angles of the equatorial N_3 groups (about 140°) are not found in the predicted structures. However, the calculations show that the azido groups are very fluxional with different configurations separated by less than 3.9 kcal mol^{-1} for Ti and very small energy values for M = Zr and Hf, indicating that solid-state and packing effects easily influence the actual orientation of the azido groups in the crystal.[15] It should be kept in mind that the theoretical

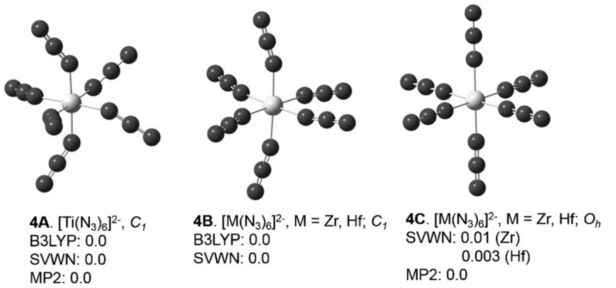


Figure 4. Optimized structures of the hexaazido anions $[M(N_3)_6]^{2-}$ and the energy differences [kcal mol^{-1}] at the B3LYP, SVWN, and MP2 levels.

predictions are for the free ions at 0 K and that the experimental structures will always be dominated by crystal packing effects. The average B3LYP Ti–N distance of 2.0376 Å for the predicted C_1 structure of $[Ti(N_3)_6]^{2-}$ is slightly larger than the experimental value of 2.023(2) Å[4] while the predicted B3LYP Ti–N distance of the O_h structure of 2.0148 Å is slightly shorter. The Zr–N distance of 2.1667 Å (B3LYP) for the O_h $[Zr(N_3)_6]^{2-}$ structure is only slightly shorter than the average Zr–N distance for the C_1 structure (2.1693 Å). Both distances fall within the range of the experimental distances from the X-ray crystal structure. The average Hf–N distances at the B3LYP level of 2.1431 Å for the O_h structure and 2.1459 Å for the C_1 isomer are in good agreement with the average experimental value of 2.147(2) Å from the crystal structure.

The energetics of the azide addition reactions with various titanium, zirconium, and hafnium azide species in the gas phase and in acetonitrile solution were calculated at the B3LYP level as well as the MP2 level with augmented correlation consistent basis sets since the MP2 method accounts better for weak interactions than most DFT functionals do. The results of these calculations are summarized in the Supporting Information (Table S17). The solvent calculations were done at the B3LYP level in acetonitrile with the solvent treated by a self-consistent reaction field approach. The addition of N_3^- to $[M(N_3)_4]$ and formation of the $[M(N_3)_5]^-$ anion is an exothermic process for M = Ti, Zr, and Hf in both gas phase and acetonitrile solution. At the B3LYP level, the addition of another N_3^- to $[M(N_3)_5]^-$ to form the dianion $[M(N_3)_6]^{2-}$ is calculated to be exothermic in acetonitrile solution but not in the gas phase. At the MP2 level, the addition of N_3^- to $[Zr(N_3)_5]^-$ and $[Hf(N_3)_5]^-$ is exothermic in both, the gas phase and acetonitrile solution while the addition to $[Ti(N_3)_5]^-$ is calculated to be endothermic in the gas phase but exothermic in solution.

In conclusion, the first binary zirconium and hafnium polyazides $[PPh_4]_2[M(N_3)_6]$ (M = Zr, Hf) were prepared from the corresponding metal fluorides $[MF_4]$ and two equivalents of $[PPh_4][N_3]$ by fluoride–azide exchange with Me_3SiN_3. Both azido salts were fully characterized by their X-ray crystal structures, vibrational and NMR spectra, and decomposition temperatures. The species $[M(N_3)_4]$, $[M(N_3)_5]^-$, and $[M(N_3)_6]^{2-}$ (M = Ti, Zr, Hf) were studied by quantum chemical calculations at the density functional theory level. Most predicted minimum energy structures exhibit linear or almost linear M-N-N arrangements around the metal while in the crystal structures of the $[M(N_3)_6]^{2-}$ anions M-N-N angles of 167.1(2)° and 164.5(1)° are found only for the axial azido ligands. The remaining four equatorial azido ligands exhibit M-N-N angles of about 140° that are typical for covalent metal azides.

Experimental Section

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. The use of appropriate safety precautions is mandatory.[16]

Further experimental details are given in the Supporting Information.

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Keywords: azides · computational chemistry · hafnium · structure elucidation · zirconium

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