DOI: 10.1002/chem.200700183

Infrared Spectrum and Structure of Thorimine ($HN{=}ThH_2$)

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Abstract: Laser-ablated thorium atoms react with ammonia to form thorimine ($NH{=}ThH_2$), the first actinide imine to be reported. This work underscores the high reactivity of thorium atoms, particularly for N−H bond activation, reveals a new type of multiple bond to actinide atoms, and shows that this bond is strong for thorium as a result of an important contribution from the f orbitals.

Keywords: density functional calculations · IR spectroscopy · matrix isolation · thorimine · thorium

Introduction

The characterization of multiple bonds between actinide (An) atoms and other elements is expanding rapidly from a small base, as new examples are discovered. Apart from the well-known uranyl ion, which contains U≡O triple bonds,[1,2] it has been realized only recently that actinide atoms can form multiple bonds to atoms of other elements. A few small molecules containing multiple bonds between actinide atoms and carbon, nitrogen, or oxygen atoms (for example, NUN, CUO, NUO, and $CH_2{=}ThH_2$) have been characterized in inert-gas matrices,[3–7] but these molecular species are not stable at room temperature. Very recently, imido analogues of the uranyl ion have been prepared, as have several large (24-membered) U−N rings.[8,9] Given the large number of atomic orbitals available on actinide atoms, the nature of the bonding in these systems is not immediately obvious. In particular, is the contribution of the 5f orbitals of thorium as negligible as its ground-state configuration ^3F ($7s^26d^2$) might suggest?

We report herein the synthesis and characterization of thorimine ($HN{=}ThH_2$) the first member of a new class of molecules containing multiple An−N bonds. This species is quite unlike organic imines.[10] Methylenimine is a reactive species produced by the photolysis of diazomethane and the pyrolysis of primary and secondary amines.[11,12] Vibrational spectra of $HN{=}CH_2$ isolated in a matrix and in the gas phase have been reported.[13] The planar structure of $HN{=}CH_2$ has been determined by microwave spectroscopy and computational analysis.[12,14] Furthermore, methylenimine has also been trapped as a unidentate ligand in rhenium complexes.[15]

Ti, Zr, and Hf imines have been produced by irradiation in matrix isolation experiments, and DFT calculations reveal nonplanar structures at the metal center with respect to nitrogen.[16,17] Previous multiconfiguration self-consistent field (MCSCF) studies of $HN{=}TiH_2$ reported linear H-N-Ti bonds and have suggested that strong back-donation of the nitrogen lone pair, into the empty metal d orbitals to create significant triple-bond character, was responsible.[18] Our calculations show that $HN{=}ThH_2$ has the same structure as Group 4 metal species that have been seen previously, and appreciable N≡Th triple-bond character, which has an important contribution from f-type orbitals.

Results and Discussion

Laser-ablated thorium atoms have been found to react with ammonia during condensation at $T=8$ K and 12 K in excess argon (ammonia concentrations of 0.1, 0.2, and 0.6 % employed) by using methods described previously.[19–22] Low ablation energy was employed to promote metal atoms as the reactive species and to minimize photochemistry. Infrared spectra are illustrated in Figure 1 for an experiment at 8 K; more efficient trapping of reactants and products can be achieved at this temperature than at 12 K. The major product exhibits five new absorptions at $\tilde{\nu}=1398.7$ (matrix site splittings at 1406.0 and 1414.1 cm^{-1}), at 1357.4 (matrix site bands at 1365.2 and 1374.8 cm^{-1}), at 793.4 (site splitting at 795.5 cm^{-1}), 552.2, and 498.4 cm^{-1} (labeled $HNThH_2$ in

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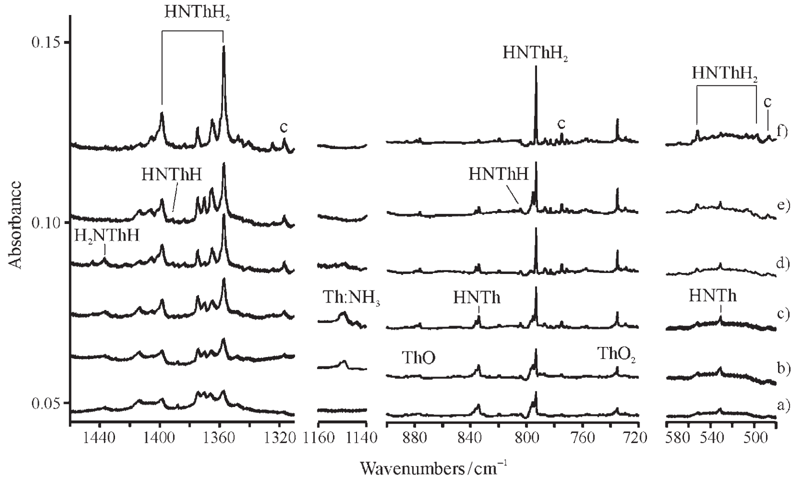

Figure 1. Infrared spectra of thorium and ammonia reaction products in solid argon at 8 K: a) after laser-ablated thorium atoms were co-deposited with 0.2 % NH_3 in argon for 60 min, b) after annealing to 15 K, c) after annealing to 20 K, d) after annealing to 25 K, e) after irradiation at $\lambda > 530$ nm for 20 min, and f) after second annealing to 25 K.

Figure 1). These absorptions increase simultaneously on sample annealing to 15, 20 and 25 K, then increase slightly after exposure to visible light irradiation ($\lambda > 530$ nm), and increase further after subsequent sample annealing at 25 K. In contrast, a very weak band at 1149.8 cm^{-1} (labeled Th:NH_3) increases on sample annealing to 15 and 20 K, decreases on sample annealing to 25 K, and disappears after exposure to visible light irradiation. Weak absorptions at 1445.3 and 1437.0 cm^{-1} (labeled H_2NThH) increase steadily upon sample annealing at 15, 20, and 25 K to undergo a similar decrease in absorption upon exposure to visible light irradiation. Additional weak absorptions at 834.3 and 530.9 cm^{-1} (labeled HNTh) decrease after sample annealing and exposure to visible light irradiation. Absorptions at 1391.5 and 804.3 cm^{-1} (labeled HNThH) increase slightly on early annealing but decrease on the final annealing at 25 K. A very weak absorption at 934.6 cm^{-1} (not shown) corresponds to the ThN diatomic molecule.[23,24] The same results could be reproduced by experiments that utilized visible light photolysis followed by annealing. UV light irradiation ($\lambda = 240$–380 nm) was found to reduce absorption of $HNThH_2$, and subsequent sample annealing at 25 K revealed that the absorption could be restored. Finally, weak absorptions were observed for the ThH_2 molecule, the NH_2 radical (not shown, $\tilde{\nu} = 1495.9$ cm^{-1}), and thorium oxides (produced by thorium reacting with trace oxygen impurities); these bands were stronger and required higher laser energy.[25–27] The observation of sharp, weak ThO_2 absorptions at 787.2 and 735.1 cm^{-1} confirms that these conditions favor the reaction of single thorium atoms. The ThH_2 molecule here arises from the reaction with ammonia as a hydrogen source. The NH_2 radical is probably formed by laser-plume photodissociation of ammonia, and the hydrogen atom liberated also contributes to the matrix chemistry.

Two Th and NH_3 samples were initially subjected to sample annealing to check for possible cold reactions in the solid argon matrix. The deposited sample was annealed to 20 K in the dark (the IR source of the spectrometer contains visible light, so this was blocked) and then spectra were recorded in 25 scan intervals to investigate the possibility of source photochemistry. The major site $HNThH_2$ absorptions increased by 50 % on annealing, but remained constant during recording of the spectra (256 scans). Consequently, we conclude that source photochemistry is not involved, and that Th and NH_3 react spontaneously in solid argon to form the major product.

Isotopic substitution was employed to identify the product absorptions. Enrichment of the reagent with ^{15}N in the vacuum apparatus produced unshifted bands in the $\tilde{\nu} = 1300$ and 1400 cm^{-1} regions and isotopic doublets for the absorptions near 800 cm^{-1} as shown in Figure 2 and for the lower product bands. Notably, the major new $HNThH_2$ absorptions increased by 30 % on sample annealing to 20 K, and by another 30 % on subsequent annealing to 25 K. Further annealing to 27 and 30 K caused a decrease in absorption. The top trace in Figure 2

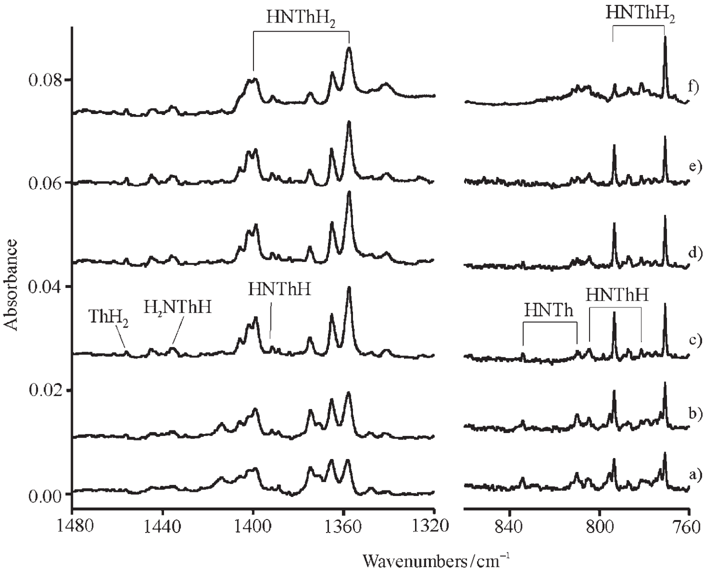

Figure 2. Infrared spectra of thorium and $^{14}NH_3$ and $^{15}NH_3$ reaction products in excess argon at 12 K: a) after laser-ablated thorium atoms co-deposited with a 0.1 % ammonia sample of (55 % nitrogen-15 enrichment) for 60 min, b) after annealing to 20 K, c) after annealing to 25 K, d) after annealing to 27 K, and e) after annealing to 30 K, f) spectrum after the thorium atoms have reacted with a 0.2 % ammonia sample (85 % nitrogen-15 enrichment) for 60 min and annealed to 25 K. The brackets in the 800 cm^{-1} region include both group nitrogen-14 and -15 counterparts.

shows the spectrum of the reagent that contains a high proportion of nitrogen-15, with the new shifted bands dominating the spectra. The introduction of ND_3 directly into the argon stream (to avoid exchange with the vacuum manifold) gave shifted absorptions at 1001.1 (splitting at 1003.6 cm^{-1}) and 971.6 cm^{-1} (splittings at 976.4 and 983.3 cm^{-1}), but a strong precursor absorption[19] at 763 cm^{-1} masked product absorption in this region.

The relative intensity of the three strongest absorptions of the matrix site, given above, do not change in response to change in ammonia concentration (from 0.6 to 0.2 to 0.1 %) or variation in ablation laser energy. Thus, we believe that these absorptions are due to the major product molecule in different local argon-matrix-trapping configurations. To investigate the matrix site splittings, three experiments were carried out by using krypton as the matrix host. The spectra from these experiments using 0.2 % $^{15}NH_3$ are shown in Figure 3. The strong bands redshift as expected, but the site absorption structure changes. The major bands redshift slightly and appear at $\tilde{\nu} = 1395.2$ (site splittings at 1396.5 and 1391.5 cm^{-1}) and 1351.8 cm^{-1} (site splittings at 1356.3 and 1348.1 cm^{-1}). As the sample employed here was mostly nitrogen-15 enriched, the major lower bands were observed at 766.2 cm^{-1} (site splitting at 765.0 cm^{-1} and the ^{14}N counterpart at 785.0 cm^{-1}), 546.7, and 504.6 cm^{-1}. The absorptions are sharper in solid krypton and the split bands are closer together than in solid argon. A weak ThO_2 band was observed at 732.5 cm^{-1}. These bands increase concurrently upon exposure to $\lambda > 470$ and > 320 nm irradiation. Annealing dynamics are different in solid krypton: annealing to 30 K alters the site structure, and increases the absorption of the new broad signals at 1376.0, 1332.4, and 1315.4 cm^{-1} as shown in Figure 3. Subsequent irradiation at $\lambda = 240$–380 nm decreases the broader absorptions, and increases one of the major site absorptions. A second annealing to 30 K reversed the alterations caused by UV irradiation. A final annealing to 35 K again increased the new broad bands at the expense of the major product bands. Annealing allows ammonia molecules to diffuse into the matrix, which is attested by the growth of ammonia cluster absorptions at the expense of ammonia monomer,[19] an effect that is more pronounced in the krypton matrix than in the argon matrix. Additional weak bands at 1423.3 and 1129.9 cm^{-1} increased on annealing, decreased on exposure to visible light irradiation, and increased on further annealings. This krypton-matrix experiment was repeated by using a 0.05 % sample to reveal that the major bands were still accompanied by the same site splittings, but the broader bands were weaker.

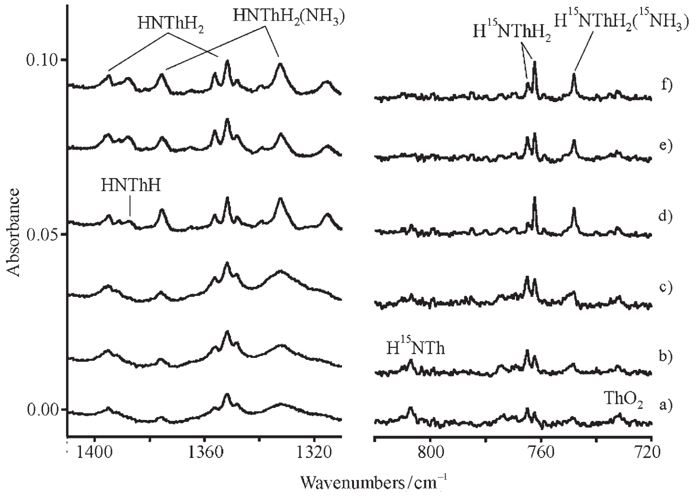

Figure 3. Infrared spectra of the thorium and ammonia reaction products in solid krypton at 12 K: a) after laser-ablated thorium atoms were co-deposited with 0.2 % NH_3 in the krypton sample for 40 min, b) after irradiation at $\lambda > 470$ nm for 20 min, c) after irradiation at $\lambda > 320$ nm for 20 min, d) after annealing to 30 K, e) after irradiation at $\lambda = 240$–380 nm for 20 min, and f) after second annealing to 30 K.

The new strong argon-matrix absorptions at 1398.7 and 1357.4 cm^{-1} are just below the thorium dihydride absorptions at 1480.1 and 1455.6 cm^{-1} from the reaction with hydrogen,[25] and they shift to 1001.1 and 971.6 cm^{-1} on ND_3 substitution (1.397 H/D ratio), which identifies Th–H stretching modes of a ThH_2 subunit. The small amount of hydrogen impurity in the deuterated precursor creates weak bands at 1384.3 and 989.5 cm^{-1} (in a 2:1 intensity ratio), which can be attributed to the ThHD subunit. The strong 793.4 cm^{-1} absorption shifts to 770.7 cm^{-1} after the addition of nitrogen-15, and the mixed-nitrogen-isotope ammonia sample reveals a doublet (Figure 2), which verifies the presence of a single nitrogen atom in the major new product species. A pure harmonic diatomic Th–N vibration would shift to 768.1 cm^{-1}, and the present shift is a fraction (22.7/25.3 = 0.90) of a pure Th–N stretching vibrational mode. Unfortunately, this region is obscured by the strong ND_3 absorption, so the deuterium shift could not be measured. Although the N–H stretching mode in the major product is too weak to be observed here, the H-N-Th bending modes produce weak absorptions at 552.2 and 498.4 cm^{-1} with small ^{15}N shifts (see calculations in Table 1), and this verifies the presence of a H-N-Th subunit. The low ablation energy employed and the sharp ThO_2 absorptions argue strongly for the dominance of single thorium atom reactions. Therefore, the spectroscopic data definitively identify a new molecule that contains a strong Th–N bond, an H-N-Th linkage, and a ThH_2 group.

A theoretical investigation including electron correlation on the activation of ammonia by second-row transition metal atoms found the reaction to be considerably more favourable than with methane, and the attraction of electron-deficient metal atoms to the lone pair was proposed.[28] Furthermore, a recent DFT study of methane activation by lanthanide and thorium metal atoms predicted that the thorium reaction should have a very small activation barrier ($E = 0.3$ kcal mol^{-1}).[29] Consequently, we expected the reaction of Th and ammonia to be favorable in solid noble gas matrices. Accordingly, we calculated the absorption signals of the $Th{:}NH_3$ complex (triplet ground state), the first insertion product H_2N–ThH (singlet ground state), and the rear-

Table 1. Comparison of observed (argon matrix) and calculated harmonic frequencies for the $HN{=}ThH_2$ thorimine.[a]

$HN{=}ThH_2$				$H^{15}N{=}ThH_2$		$DN{=}ThD_2$		Mode
CCSD	PW91	B3LYP	observed	B3LYP	observed	B3LYP	observed	description
3621(48)	3498(39)	3574.9(51)	–	3566.2	–	2623.6	–	a′ N−H stretch
1463(372)	1447(315)	1453.9(364)	1398.7	1453.7	1398.7	1033.6	1001.1	a′ ThH_2 stretch
1422(717)	1406(556)	1406.8(666)	1357.4	1406.8	1357.4	998.4	971.6	a″ ThH_2 stretch
821(278)	823(241)	825.9(283)	793.4	802.0	770.7	793.9	[b]	a′ N=Th stretch
575(196)	556(167)	568.5(187)	552.2	565.3	549.3	435.4	–	a′ H-N-Th bend
528(153)	520(146)	523.8(157)	498.4	520.9	495.2	402.1	–	a″ H-N-Th bend
500(145)	463(87)	477.2(113)	–	477.1	–	338.7	–	a′ ThH_2 bend
393(17)	371(9)	386.9(9)	–	386.4	–	278.3	–	a″ ThH_2 bend
380(155)	358(127)	369.4(145)	–	369.1	–	265.0	–	a′ $NThH_2$ def [c]

[a] All calculations used the TZP/SDD basis set. All frequencies are in cm^{-1}, and intensities are in $km\,mol^{-1}$. Description gives major coordinate. [b] Overlapped by precursor band. [c] def:deformation.

ranged $HN{=}ThH_2$ isomer reaction product (a singlet ground state) by using theoretical methods described recently.[30–34] The frequencies calculated for the rearranged isomer product, at the coupled-cluster single and double excitations method (CCSD) level of theory and by using the B3LYP and PW91 density functionals, are given in Table 1. The five new IR absorptions labeled $HNThH_2$ were compared with the calculated frequencies, and the agreement is appropriate considering the approximations involved; notably, the isotopic shifts are predicted with satisfying accuracy. By using the B3LYP method, the three strongest bands produced by the bond-stretching modes were calculated to be 3.9, 3.6, and 4.0 % higher than the experimental values, and the two bending modes were found to be 3.0 and 5.1 % higher, which is within the expected range of agreement.[35]

The argon matrix absorptions ($\tilde{\nu} = 1341.6$, 1317.0, 775.0, and 487.1 cm^{-1}, labeled c for the ammonia complex in Figure 1) and the krypton matrix bands ($\tilde{\nu} = 1376.0$, 1332.4, and 747.9 cm^{-1}(^{15}N)) clearly increase on annealing at the expense of isolated $HN{=}ThH_2$ absorptions and are favored at higher ammonia concentrations, which are appropriate for $HN{=}ThH_2(NH_3)$ complexes. We know that ammonia clusters increase on annealing the matrix samples,[19] and it is reasonable to expect unreacted ammonia to form heterodimers with the imine product. The most intense $HN{=}ThH_2$ absorptions (two Th−H and the Th=N stretching modes) are redshifted ($\Delta\tilde{\nu} = 19.2$, 19.4, and 14.3 cm^{-1}, in solid krypton) from the perturbation by ammonia. We suggest that the lone pair of the ammonia is attracted to the electron-deficient metal center to affect these shifts. Finally, the absorption of the weaker band (1317.0 cm^{-1}) in solid argon and the band in solid krypton (1315.4 cm^{-1}) increases at the highest annealing at the expense of the others, and this is likely due to a higher order complex with more than one ammonia ligand.

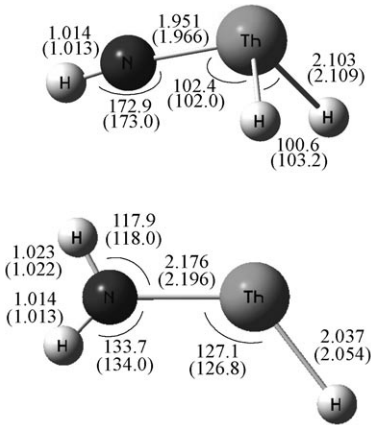

Figure 4. Structures (C_s) for $HN{=}ThH_2$ (top) and $NH_2{-}ThH$ (bottom) with bond lengths [Å] and angles [°] listed for B3LYP and (CCSD) calculations.

The structure calculated for $HN{=}ThH_2$ is shown in Figure 4 in which the bond lengths and angles obtained by using the B3LYP and CCSD methods are both given. The T1 diagnostic for the CCSD calculation is 0.024, which suggests that single-reference methods are adequate for this molecule.[36] The excellent agreement between the CCSD and the B3LYP parameters reinforces this application of the DFT method for these new actinide-metal-containing molecules. Note the almost linear H−N=Th angle and the short N=Th bond. If we take the B3LYP-calculated thorium-to-nitrogen bond lengths in ThN and HThN ($^2\Sigma$, 1.810 Å, 760 $N\,m^{-1}$ (force constant) and $^1A'$, 1.820 Å, 724 $N\,m^{-1}$, respectively) as prototype Th≡N triple bonds, then the longer bond in $HN{=}ThH_2$ (1.951 Å, 564 $N\,m^{-1}$) is in the Th=N double bond range, as the still longer Th−N single bond (2.176 Å, 287 $N\,m^{-1}$) has been calculated for $NH_2{-}ThH$. If the H−N=Th angle in $HN{=}ThH_2$ is fixed at 110.4°, as computed for $HN{=}CH_2$, the nitrogen lone pair is unavailable for bonding to Th: for this prototype Th=N double bond, we calculate the bond length to be 1.982 Å. From these calculations we can conclude that there is some polarized triple-bond character in thorimine $HN{=}ThH_2$, which is derived from nitrogen lone-pair donation to vacant Th orbitals. The calculated thorimine N=Th bond length is just 0.05 Å longer than the average triple-bond covalent radii reported in a recent compilation.[37] Our conclusions can be quantified by natural bond orbital (NBO) analysis:[30,38] The natural electron configuration of thorium is Th-[core] $7s^{0.42}5f^{0.28}6d^{0.73}\,7p^{0.02}$. The N−Th bonds are very strongly polarized, indeed, the Th contributions make up only 10–13 %, and the participation of d-type acceptor orbitals of Th is about twice as much as those of f-type orbitals. The N−Th bond in $HN{=}ThH_2$ is both short and strong: it is computed to be 0.165 Å shorter than the C=Th bond in $CH_2{=}ThH_2$ (2.116 Å), but part of this (0.061 Å by computation) is in response to the larger covalent radius of carbon relative to nitrogen, and its bond energy of 620 $kJ\,mol^{-1}$ is 150 $kJ\,mol^{-1}$

greater than that for C=Th in CH_2=ThH_2 and almost as high as the C=N bond energy in CH_2=NH (computed as $E = 671\ \mathrm{kJ\,mol^{-1}}$).

We find that the Th=N bond in HN=ThH_2 is longer (by 0.110 Å) and weaker ($\Delta E = 181\ \mathrm{kJ\,mol^{-1}}$) when the 5f orbitals are removed from the Th basis set. As the extra binding energy due to polarization functions is *much* smaller than this amount, for example, only 30 $\mathrm{kJ\,mol^{-1}}$ for the d-type orbitals on carbon in CH_2=NH, we conclude that Th 5f orbitals can and do make a significant contribution to the bonding of thorium, at least when Th is bonded to small atoms such as nitrogen. In addition, Küchle and co-workers have made similar observations for ThO when using wave-function based methods,[34b] and de Almeida and Cesar have proposed that the mixing of Th 5f orbitals into the valence shell enhances the ability of Th to activate methane.[29]

The agostic interaction in CH_2=ThH_2 is responsible for tilting one C−H bond closer to the Th center than the other (agostic angle H′CTh = 95.6°).[7] In HN=ThH_2, we have competition between an imine lone pair and a N−H bonded pair for interaction with the metal center, and we see from the structure in Figure 4 that the lone pair interaction dominates. This interaction between the nitrogen lone pair and the thorium vacant d/f orbital gives rise to partial N−Th triple-bond character.

We found evidence for the first and second higher energy Th:NH_3 and NH_2−ThH reaction products, whose calculated relative energies are shown in Figure 5. The band at 1149.8 $\mathrm{cm^{-1}}$ and its $^{15}NH_3$ counterpart at 1143.5 $\mathrm{cm^{-1}}$ are appropriate for Th:NH_3, as stronger bands have been observed at 1156.0 and 1158.8 $\mathrm{cm^{-1}}$ for the analogous Zr and Hf complexes.[17] The krypton matrix counterpart of Th:$^{15}NH_3$ was observed at $\tilde{\nu} = 1129.9\ \mathrm{cm^{-1}}$, which represents a reasonable matrix shift of 13.6 $\mathrm{cm^{-1}}$. The band at 1149.8 $\mathrm{cm^{-1}}$ gives way after exposure to visible light irradiation, as do the 1445.3 and 1437.3 $\mathrm{cm^{-1}}$ site-split bands that are attributed to the strongest absorption of the first NH_2−ThH product, which absorbs at 1423.3 $\mathrm{cm^{-1}}$ in solid krypton. Calculated frequencies for this molecule reveal one strong infrared absorption at 1491 $\mathrm{cm^{-1}}$ ($E = 367\ \mathrm{km\,mol^{-1}}$) which is $\Delta\tilde{\nu} = 84\ \mathrm{cm^{-1}}$ above the strongest absorption calculated for NH_2−ThH and in very good agreement with the observed matrix bands.[39] Figure 4 also shows the structure of the first insertion product, which is 16 $\mathrm{kcal\,mol^{-1}}$ (B3LYP) or 8 $\mathrm{kcal\,mol^{-1}}$ (CCSD(T)) higher in energy than the final HN=ThH_2 product.

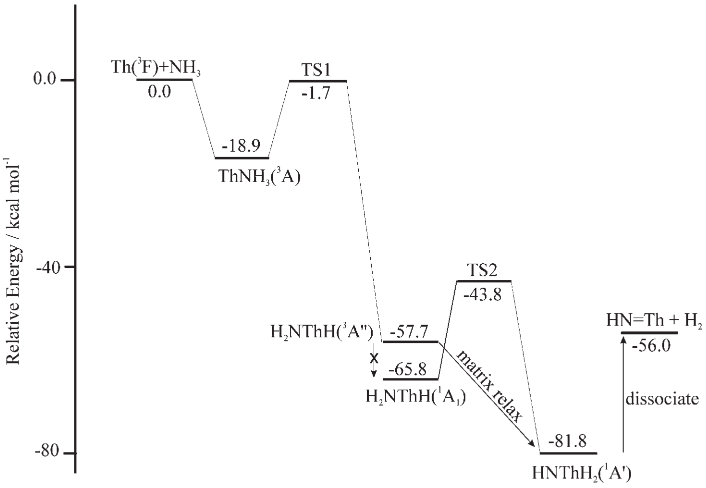

Figure 5. Relative energies [$\mathrm{kcal\,mol^{-1}}$] calculated for thorium and ammonia reaction products using the B3LYP method.

The activation of ammonia by thorium is so favorable that the reaction with atomic Th shown in Equation (1) proceeds directly on the triplet potential-energy surface to give the triplet Th:NH_3 complex and then the H_2N−ThH intermediate, which is in small part relaxed by the matrix to the singlet ground electronic state NH_2−ThH product [Eq. (2a)], but mostly undergoes α-hydrogen transfer, and relaxes to the lowest energy singlet thorimine product HN=ThH_2 [Eq. (2b)]. It is clear that hydrogen atom transfer is efficient in these species, which are energized by the substantial reaction exothermicity.

$$\mathrm{Th(^3F) + NH_3 \rightarrow Th:NH_3(^3A) \rightarrow H_2N{-}ThH(^3A'')} \quad (1)$$

$$\mathrm{H_2N{-}ThH(^3A'') \xrightarrow[\text{relax}]{\text{matrix}} NH_2{-}ThH(^1A_1)} \quad (2a)$$

$$\mathrm{H_2N{-}ThH(^3A'') \xrightarrow[\text{relax}]{\text{matrix}} HN{=}ThH_2(^1A')} \quad (2b)$$

Additionally, the 800 $\mathrm{cm^{-1}}$ region (Figure 2) reveals two weak isotopic nitrogen doublets that have large isotopic nitrogen shifts (834.3–810.0 $\mathrm{cm^{-1}}$ and 804.5–781.5 $\mathrm{cm^{-1}}$), which identify Th−N stretching modes of new molecules. The strongest absorptions for H−N=Th are predicted as 865.6 and 562.7 $\mathrm{cm^{-1}}$ at the harmonic B3LYP level, which are in good agreement with the pair of signals at 834.3 and 530.9 $\mathrm{cm^{-1}}$. Similarly, calculations for the HN=ThH radical reveal an intermediate Th=N stretching mode, in accord with the 804.5 $\mathrm{cm^{-1}}$ band, and a Th−H stretching mode between those for HN=ThH_2, in agreement with the 1391.7 $\mathrm{cm^{-1}}$ band. The HN=Th and HN=ThH intermediates are probably formed through photodissociation of HN=ThH_2 by the laser-plume emission from the Th surface during sample deposition.

Conclusion

The 40 to 50 % increase in HN=ThH_2 absorptions on annealing to 25 K (Figures 1, 2 and several other experiments) indicates a spontaneous reaction between Th and NH_3 in the cold argon matrix. Although an essentially spontaneous reaction was theoretically predicted for the Th and CH_4 reaction,[29] we found that visible light irradiation was necessary to initiate this reaction.[7] However, calculations indicate that NH_3 is more reactive than CH_4 with respect to activation by early transition metal atoms,[28] and our observations for Th and NH_3 are in line with this. Furthermore, we found that Th is more reactive than Hf with NH_3. Our experiments with Hf, and those of Zhou et al.,[17] reveal a $Hf{:}NH_3$ complex formed on annealing, which converts directly to $HN{=}HfH_2$ on exposure to visible light irradiation. Although the Th reactions with NH_3 are slightly more exothermic (Figure 5) than their Hf counterparts,[17] a similar $Th{:}NH_3$ complex is formed on annealing, but the band absorbance is less than the absorbance found for Zr and Hf. We suggest that the higher polarizability of Th compared with Hf (32.1 versus 16.2 $Å^3$)[40] enhances the reactivity of thorium towards polar species such as NH_3.

This work emphasizes the high reactivity of Th atoms, particularly N–H bond activation reactions, reveals a new type of multiple bond to actinide atoms, and shows that this bond is strong in the case of Th, owing to an important contribution from the f orbitals.

Acknowledgements

We gratefully acknowledge support for this research from the National Science Foundation (U.S.).

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Received: February 2, 2007