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Reactions of ThX₄ (X = F, Cl, Br, I) with Liquid Ammonia-Crystal Structures and a Theoretical Study of Ammine Thorium(IV) Halide Ammoniates

H. Lars Deubner,[a] Tim Graubner,[a] Florian Weigend,[a] Antti J. Karttunen,[b] and Florian Kraus*[a]

Reactions of thorium tetrahalides ThX₄ (X = Cl, Br, I) with liquid ammonia at room temperature lead to the formation of decaammine thorium(IV) halide ammoniates. Their different compositions [Th(NH₃)₁₀]X₄·nNH₃ were established by single crystal X-ray diffraction. While for the chloride the formation of a tetraammoniate is observed, the reaction of the bromide leads to an octaammoniate, whereas the iodide results in approximately a nonaammoniate. Additionally, the formation of the dinuclear Th complex compound [Th₂Cl₂(NH₃)₁₄(μ-O)]Cl₂·3NH₃ was observed when moisture was present within NH₃. As expected, the Th and the previously reported U compounds [An(NH₃)₁₀]Br₄·8NH₃ (Pbca, An=Th, U), [An(NH₃)₁₀]I₄·9NH₃ (P4/n), and [AnCl₂(NH₃)₁₀(μ-O)]Cl₂·3NH₃ (P1) are isotypic, respectively. Surprisingly, ThCl₄ formed the decaammine complex [Th(NH₃)₁₀]Cl₄·4NH₃ (P12₁/1/n), while UCl₄ formed the octaammine chlorido complex [UCl(NH₃)₁₂]Cl₂·3NH₃ (Pnma) in ammonia. Quantum-chemical gas-phase calculations were carried out to study the molecular structures and the energetics of the complex cations. In addition, the localized molecular orbitals (LMO) and Intrinsic Bonding Orbitals (IBO) were analyzed. However, the calculations could not explain the preferred formation of the [Th(NH₃)₁₀]I₄⁺ complex over the hypothetical cation [ThCl(NH₃)₄]⁺⁺ in general. The above-mentioned compounds are typically only stable up to a certain temperature under a certain ammonia equilibrium pressure and with rising the temperature the contained ammonia is typically given off step-wise and products of lower NH₃ content are obtained and may be even isolated and characterized. At higher temperatures and/or ammonia pressures, also ammonolysis reactions generally become faster, equilibria are shifted, and different products, such as amides, imides, or nitrides, may be obtained. Most of the research in the field of the early actinoids in liquid ammonia solution was conducted in the 60s and 70s of the last century. However, the analytical capabilities were not always convenient for the characterization of such types of compounds.[11-26] Nowadays, single crystal X-ray diffraction, especially at low temperatures, affords a suitable analytical method for the investigation of compounds that are often moisture as well as temperature sensitive. Recently, thorium compounds like [Th₂F₄O₆(NH₃)₁₂][NO₃]₈·19.6NH₃ and some uranium(III), (IV) and (V) compounds were described by us in the ammono system.[10,27] A review on the recent advances in the chemistry of uranium halides in anhydrous ammonia has been given.[10] The uranium tetrahalides UX₄ (X = F, Cl, Br, I) were reacted with liquid ammonia to form compounds like [UF₄(NH₃)₄]⁺⁻[NH₃],[28] [UCl(NH₃)₁₂]Cl₂·3NH₃, [UCl(NH₃)₁₀]Br₄·8NH₃, and [U(NH₃)₁₀]I₄·9NH₃ or [U(NH₃)₁₀]I₄·17.37(2)NH₃.[10] A novel synthesis method, which provides an easy access to crystalline, phase pure and solvent free thorium(IV) halides,[29] allowed us to investigate their respective reactions in anhydrous liquid ammonia. Here we present crystal structures of some ammoniates of the thorium tetrahalides obtained from the reaction with liquid ammonia and compare them to those obtained for the respective reactions of the uranium tetrahalides.

Introduction

While the aqueous chemistry of thorium and especially the chemistry of the thorium(IV) halides is quite well known and systematically studied, the chemistry of early actinoid compounds in solvents such as NH₃ or SO₂ remains little explored.[1-3] Liquid ammonia as a solvent, the so called ammono system,[4-6] is comparable to the aqueous system but becomes faster, equilibria are shifted, and different products, such as amides, imides, or nitrides, may be obtained. Most of the research in the field of the early actinoids in liquid ammonia solution was conducted in the 60s and 70s of the last century. However, the analytical capabilities were not always convenient for the characterization of such types of compounds.[11-26] Nowadays, single crystal X-ray diffraction, especially at low temperatures, affords a suitable analytical method for the investigation of compounds that are often moisture as well as temperature sensitive. Recently, thorium compounds like [Th₂F₄O₆(NH₃)₁₂][NO₃]₈·19.6NH₃ and some uranium(III), (IV) and (V) compounds were described by us in the ammono system.[10,27] A review on the recent advances in the chemistry of uranium halides in anhydrous ammonia has been given.[10] The uranium tetrahalides UX₄ (X = F, Cl, Br, I) were reacted with liquid ammonia to form compounds like [UF₄(NH₃)₄]⁺⁻[NH₃],[28] [UCl(NH₃)₁₂]Cl₂·3NH₃, [UCl(NH₃)₁₀]Br₄·8NH₃, and [U(NH₃)₁₀]I₄·9NH₃ or [U(NH₃)₁₀]I₄·17.37(2)NH₃.[10] A novel synthesis method, which provides an easy access to crystalline, phase pure and solvent free thorium(IV) halides,[29] allowed us to investigate their respective reactions in anhydrous liquid ammonia. Here we present crystal structures of some ammoniates of the thorium tetrahalides obtained from the reaction with liquid ammonia and compare them to those obtained for the respective reactions of the uranium tetrahalides.

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Results and Discussion

While the reaction of UF$_4$ with liquid ammonia, either at room temperature or at $-40^\circ$C, leads to the formation of emerald green crystals of [UF$_4$(NH$_3$)$_4$]·NH$_3$, the similar reaction with ThF$_4$ yields no crystals even after more than two years of crystallization time at room temperature. Much to our regret the solubility of ThF$_4$ seems to be too low under these conditions and harsher ammonothermal conditions must be explored. However, the other thorium tetrahalides react immediately with liquid ammonia. The reaction is visually directly observable as the volume of the solid tetrahalides increases immensely and already upon contact with gaseous NH$_3$. In case of ThI$_4$, its bright yellow color vanishes instantly, while the solution above the then colorless solid is also colorless. Colorless solutions are also observed for the reactions of ThCl$_4$ and ThBr$_4$ with NH$_3$.

An overview on the products of the reactions of AnX$_4$ (An=Th, U; X=F-I) with liquid ammonia is given in Scheme 1. From Scheme 1 we see that in several cases isotypic compounds for An=Th, U were obtained, except for the fluorides, as discussed above, and the chlorides, which will be discussed below. We assume that an amido and a chlorido complex with the composition [Th(NH$_3$)$_{10}$]Cl$_4$·4NH$_3$ should also exist, as these complexes exist for U(IV). Unfortunately, we have not been able to synthesize compounds containing these complexes as of yet.

Reaction of ThCl$_4$ with NH$_3$-Crystal Structure of [Th(NH$_3$)$_{10}$]Cl$_4$·4NH$_3$

The reaction of ThCl$_4$ with NH$_3$ was carried out at room temperature in a bomb tube and led to the formation of colorless crystals of decaammine thorium(IV) chloride ammonia (1/4), [Th(NH$_3$)$_{10}$]Cl$_4$·4NH$_3$. Surprisingly, this compound has a different constitution compared with [UCl(NH$_3$)$_8$]Cl$_3$·3NH$_3$, which was obtained when UCl$_4$ reacted with NH$_3$ under essentially similar conditions. So, it seems that U(IV) is chemically softer compared to Th(IV) in this system despite essentially similar ionic radii. [Th(NH$_3$)$_{10}$]Cl$_4$·4NH$_3$ crystallizes in the monoclinic space group $P1\overline{2}1/n$ (No. 14) with $a=9.18970(10)$, $b=14.65040(10)$, $c=17.4794(2)$ Å, $\beta=103.986(1)^\circ$, $V=2283.58(4)$ Å$^3$, and $Z=4$ at $T=100$ K. For crystallographic data and details of the structure determination see Table 2. The thorium atom is coordinated by ten ammine ligands (Figure 1) and its coordination polyhedron can be described best as a slightly distorted sphenocorona (Johnson solid J$_{86}$). Such a...
The atomic distances between the Th and the N atoms of the ammine ligands range from 2.614(3) to 2.722(3) Å and are in good agreement with those observed in uranium compounds like [UCl(NH3)8]Cl3 ·3NH3 and similar ones.\textsuperscript{10,27} The N–H–Cl hydrogen bonds between the ammine ligands and the chloride ions, the N–H–N hydrogen bonds between the ammine ligands and the ammonia molecules of crystallization, and the N–H–Cl hydrogen bonds between ammonia molecules

### Table 2. Selected crystallographic data and details of the structure determination of the thorium tetrahalide ammoniates and the oxygen bridged thorium complex. Pearson symbols are given without H atoms.

| Formula | [Th(NH3)10]Cl4 ·4NH3 | [Th(NH3)10]Br4 ·8NH3 | [Th(NH3)10]I4 ·8.5NH3 | [Th2Cl2(NH3)14(μ-O)]Cl4 ·3NH3 |
|---------|----------------------|----------------------|----------------------|----------------------------------|
| Molar mass/g·mol\(^{-1}\) | 1612.23 | 858.29 | 1046.25 | 982.35 |
| Space group (No.) | P12/1/n (14) | Pbca (61) | P4/n (85) | P1 (2) |
| a/Å | 9.1897(1) | 15.413(3) | 13.0000(18) | 8.9644(18) |
| b/Å | 14.6507(1) | 19.214(4) | 19.935(4) | 9.6808(19) |
| c/Å | 17.4794(2) | 19.935(4) | 9.6808(19) | 14.638(3) |
| α/° | 111.47(3) | 103.986(1) | 100.20(3) | 99.96(3) |
| β/° | 103.986(1) | 100.20(3) | 99.96(3) | 114.73(3) |
| γ/° | 99.96(3) | 100.20(3) | 99.96(3) | 114.73(3) |
| V/Å\(^3\) | 2283.58(4) | 5903(2) | 1636.1(6) | 1464.6(6) |
| Z | 4 | 8 | 2 | 2 |
| Pearson symbol (w/o H atoms) | mP\(_{76}\) | oP\(_{184}\) | tP\(_{48}\) | aP\(_{50}\) |
| \(\rho_{\text{calc.}}\) g·cm\(^{-3}\) | 3.178 | 3.131 | 3.138 | 3.122 |
| \(\mu\) mm\(^{-1}\) | 25.470 | 10.487 | 8.351 | 10.715 |
| Color | colorless | colorless | colorless | colorless |
| Crystal habitus | rod | block | plate | block |
| Crystal size/mm\(^3\) | 0.01·0.03·0.08 | 0.1·0.1·0.08 | 0.1·0.1·0.03 | 0.1·0.08·0.06 |
| T/K | 100(2) | 100(2) | 100(2) | 100(2) |
| λ/Å | 1.54178 (Cu-K\(_{\alpha}\)) | 0.71073 (Mo-K\(_{\alpha}\)) | 0.71073 (Mo-K\(_{\alpha}\)) | 0.71073 (Mo-K\(_{\alpha}\)) |
| No. of reflections | 40333 | 91248 | 21036 | 22739 |
| \(\theta\) range/° | 3.987–78.793 | 2.643–29.230 | 2.623–26.754 | 2.593–26.720 |
| Range of Miller indices | \(7 \leq h \leq 11\) | \(-21 \leq h \leq 21\) | \(-16 \leq h \leq 16\) | \(-11 \leq h \leq 11\) |
| | \(-18 \leq k \leq 18\) | \(-24 \leq k \leq 26\) | \(-16 \leq k \leq 16\) | \(-15 \leq k \leq 15\) |
| | \(-22 \leq l \leq 17\) | \(-27 \leq l \leq 27\) | \(-12 \leq l \leq 12\) | \(-18 \leq l \leq 18\) |
| Absorption correction | multi-scan | numerical | numerical | numerical |
| Completeness of the data set | 0.997 | 0.999 | 0.999 | 0.999 |
| No. of unique reflections | 4876 | 7962 | 1749 | 6198 |
| No. of parameters | 231 | 413 | 83 | 285 |
| No. of restraints | 12 | 0 | 0 | 0 |
| No. of constrains | 0 | 0 | 0 | 0 |
| S (all data) | 1.135 | 1.051 | 1.154 | 1.007 |
| R(F) (\(I \geq 2\sigma(I)\), all data) | 0.0197, 0.0208 | 0.0267, 0.0472 | 0.0260, 0.0301 | 0.0196, 0.0244 |
| wR(F) (\(I \geq 2\sigma(I)\), all data) | 0.0476, 0.0528 | 0.0414, 0.0457 | 0.0542, 0.0555 | 0.0413, 0.0425 |
| Extinction coefficient | 0.000195(14) | – | 0.00036(9) | – |
| \(\Delta P_{\text{max}}, \Delta P_{\text{min}}\) e·Å\(^{-3}\) | 1.245, 1.721 | 0.899, –0.770 | 1.608, –0.522 | 1.971, –1.496 |

Figure 1. Left: The [Th(NH3)10]\(^{4+}\) cation in [Th(NH3)10]Cl4 ·4NH3. Right: Illustration of the N–H–N and N–H–Cl hydrogen bonds (bond lengths in Å). The displacement ellipsoids are depicted at the 70% probability level at 100 K. Hydrogen atoms are displayed as spheres with arbitrary radii.
of crystallization and the chloride ions are shown in Figure 1 (right). The N–H–Cl hydrogen bond donor–acceptor distances (ammine–N–Cl) range from 3.331(3) to 3.671(3) Å and are also in agreement with the literature.\(^{[10]}\) The N–N distances range from 3.018(5) to 3.340(5) Å and for the ammonia molecules of crystallization and the chloride ions the distances lie between 3.417(5) and 3.747(4) Å. An overview of the hydrogen bond interactions in the decaammine complexes reported here is given in Table 1.

These hydrogen bonds for the different decaammine thorium(IV) halides are in good agreement with known N–H···X (X = Cl, Br, I) hydrogen bonds for example in \([\text{Co(NH}_3\text{)}_6\text{Cl}]_2\) (3.601 Å, \(T = 294\ K\), \([\text{Co(NH}_3\text{)}_6\text{Br(S}_2\text{O}_3\text{)}\cdot\text{H}_2\text{O}\) (3.509(4) to 3.539(3) Å, \(T = 295\ K\)) or \([\text{CoCO}_3(\text{NH}_3)_5\text{Br}\cdot\text{H}_2\text{O}\) (3.41 to 3.63 Å), or \([\text{Co(NH}_3\text{)}_6\text{I}_3\) (3.902 Å, \(T = 298\ K\)).\(^{[10,31-36]}\)

**Reaction of ThBr\(_4\) with NH\(_3\)-Crystal Structure of \([\text{Th(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot8\text{NH}_3\)**

The reaction of ThBr\(_4\) with liquid ammonia leads to decaamine thorium(IV) bromide–ammonia (1/8), \([\text{Th(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot8\text{NH}_3\) crystallizes in the orthorhombic space group Pbca (No. 61) with \(a = 15.413(3), b = 19.214(4), c = 19.935(4)\) Å, \(V = 5903(2)\) \(Å^3\), and \(Z = 8\) at \(T = 100\ K\). For crystallographic data and details of the structure determination see Table 2. In this compound the thorium atom is, like the U atom in the isotypic compound \([\text{U(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot9\text{NH}_3\), surrounded by ten ammonia ligands in the shape of a slightly distorted bicapped square antiprism. The \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\) cation is shown in Figure 2. The Th-N distances within the coordination polyhedron range from 2.607(3) to 2.784(3) Å, which is in good agreement with the isotypic uranium compound \([\text{U(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot9\text{NH}_3\) and the compounds discussed previously.\(^{[10]}\) It seems that compared to \([\text{U(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot9\text{NH}_3\) circa a half of a NH\(_3\) molecule of crystallization has been lost in \([\text{Th(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot8.5\text{NH}_3\) as the respective position is refined with a site occupancy factor of 0.57(4).\(^{[10]}\)

In the crystal structure of \([\text{Th(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot8.5\text{NH}_3\), each Th atom is surrounded cuboctahedron-like by twelve iodine atoms with three different Th-I atomic distances, two shorter and a longer one with 5.4205(8), 5.9488(9), and 6.8007(11) Å. These distances are of course much longer compared to those within Th\(_4\) and are non-bonding and the Th\(_{12}\) cuboctahedra are just invoked to explain the crystal structure. These Th\(_{12}\) cuboctahedra share rectangular faces stacking along the \(c\)-axis and forming one-dimensional infinite columns (Figure 3). These columns of cuboctahedra are interconnected further via iodine atoms and square channels are formed between them. Most of the ammonia molecules of crystallization are located in these channels and Figure 3 shows the resulting crystal structure.

![Figure 2. The \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\) cation in \([\text{Th(NH}_3\text{)}_{10}\text{]}\text{Br}_4\cdot8\text{NH}_3\). Left: The displacement ellipsoids are shown at the 70% probability level at 100 K. Hydrogen atoms are depicted as spheres with arbitrary radii. Right: The atoms are shown with arbitrary radii.](image2)
At $+40^\circ$C the reaction of ThCl$_4$ with liquid ammonia – which in this case has not been dried over Na metal – under autogenous pressure leads to the formation of colorless block-shaped crystals of [Th$_2$Cl$_2$(NH$_3$)$_7$($\mu$-O)]Cl$_4$·3NH$_3$. Thus, the O atom of the $\mu$-O bridged dinuclear Th complex stems from the moisture inside the liquid ammonia. The structure is isotypic to that of a uranium compound previously reported by us.\textsuperscript{[10]} [Th$_2$Cl$_2$(NH$_3$)$_7$($\mu$-O)]Cl$_4$·3NH$_3$ crystallizes in the triclinic space group $P1$ (No. 2) with $a=8.9644(18)$, $b=12.619(3)$, $c=14.638(3)$ Å, $\alpha=111.47(3)^\circ$, $\beta=100.20(3)^\circ$, $\gamma=99.96(3)^\circ$, $V=1464.6(6)$ Å$^3$, and $Z=2$ at $T=100$ K. For crystallographic data and details of the structure determination see Table 2. A section of the crystal structure is shown in Figure 4. Each thorium atom is coordinated by one chlorido and seven ammine ligands, while an oxygen atom acts as a $\mu$-bridging ligand. Thus, the coordination number of the Th atoms is nine and their coordination sphere can be described best as slightly distorted tricapped trigonal prisms sharing the $\mu$-O atom as a common corner.

The Th-N atomic distances in the tricapped trigonal prism range from 2.608(3) to 2.747(3) Å, what is in good agreement with the isotypic uranium compound [U$_2$Cl$_2$(NH$_3$)$_7$($\mu$-O)]Cl$_4$·3NH$_3$ and the compounds discussed earlier.\textsuperscript{[10]} The Th-Cl atomic distances within the cation are 2.8536(13) and 2.9019(15) Å for Th(1)-Cl(1) and Th(2)-Cl(2), respectively. This is comparable with distances in ThCl$_4$ (2.718 to 2.903 Å), [ThCl$_3$(NH$_3$)$_8$]Cl$_3$·3NH$_3$, as well as with the respective distances within the isotypic U compound. The Th-O atomic distance (Th(1)-O(1): 2.172(2) and Th(2)-O(1): 2.161(2) Å) is also comparable to the respective one within the isotypic uranium compound.\textsuperscript{[10]}

The hydrogen bond interactions are in good agreement with the compounds described above and summarized in Table 1.

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**Figure 3.** Left: The distorted cuboctahedron-like coordination sphere of thorium atoms by iodine atoms and the interconnection of two cuboctahedra. Right: The crystal structure of [Th(NH$_3$)$_3$]$^+$·8.5NH$_3$. The atoms are shown with arbitrary radii.

**Figure 4.** The [$\mu$-O(ThCl(NH$_3$)$_7$)]$^{3+}$ cation in [Th$_2$Cl$_2$(NH$_3$)$_7$($\mu$-O)]Cl$_4$·3NH$_3$. The displacement ellipsoids are displayed at the 70% probability level at 100 K. Hydrogen atoms are depicted as spheres with arbitrary radii.
Quantum-chemical calculations

As described above, we previously observed in a reaction of UCl$_4$ with liquid ammonia the formation of a [UCl(NH$_3$)$_8$]$^{3+}$ cation, while for the reactions of UBr$_4$ and UI$_4$ we obtained compounds containing the bicapped square antiprismatic complex cations [U(NH$_3$)$_8$]$_{4+}$. We attributed this difference to the chemical hardness of U(IV) and the respective halides according to Pearson principle.[37]

Hence we would expect Th(IV) to form an analogously constituted cation due to the similar effective ionic radii of U(IV) and Th(IV) for coordination number nine of 1.05 and 1.09 Å, respectively.[38] However, we did not observe a [ThCl(NH$_3$)$_8$]$^{3+}$ cation in the reaction of ThCl$_4$ with ammonia but a [Th(NH$_3$)$_8$]$_{4+}$ cation in a sphenerocorona-like shape.

To clarify this different behavior, we carried out density-functional (DFT-PBE0) calculations with Karlsruhe polarized triple zeta valence (TZVP) bases (combined with 60-electron effective core potentials for Th and U) for [An(NH$_3$)$_8$]$_{3+}$ and [AnCl(NH$_3$)$_8$]$_{3+}$ (An = Th, U). The conductor-like screening model (COSMO) was used to simulate the influence of the counterions. All optimized structures were confirmed as true local minima on the potential energy surface. For more details see the experimental section. The calculations for the [An(NH$_3$)$_8$]$_{3+}$ cations (An = Th, U) showed that no significant energy difference (<1 kJ/mol) between the sphenocorona-like (C$_2$) ammine ligand arrangement and the bicapped square antiprismatic (C$_s$) one was present. The point group of the latter is only C$_s$ as the H atoms of the NH$_3$ ligands lower the symmetry. The energy difference between the Th and U containing [AnCl(NH$_3$)$_8$]$_{3+}$ cations (at 0 K), calculated by the energy of the exchange reaction shown in equation 1, was 41 kJ/mol, with the Th species being more stable compared with the U species, respectively, which is not in line with the experimental observations.

\[ \text{ThCl(NH}_3\text{)}_8\text{]}^{3+} + \text{[U(NH}_3\text{)}_8\text{]}^{14+} \rightarrow \text{[UCl(NH}_3\text{)}_8\text{]}^{3+} + \text{[Th(NH}_3\text{)}_8\text{]}^{4+} \] (1)

However, when taking thermal contributions to the free enthalpy within the harmonic oscillator rigid rotor model into account, an essentially isoenergetic (−3 kJ/mol) situation is calculated for room temperature.

In order to estimate the preference for the formation of the chlorido complexes from the respective decaammine complexes, we calculated the reaction energies for the exchange reaction according to equation 2.

\[ \text{[An(NH}_3\text{)}_8\text{]}^{14+} + \text{Cl}^- \rightarrow \text{[AnCl(NH}_3\text{)}_8\text{]}^{3+} + 2 \text{NH}_3 \] (2)

For An = U the reaction is endoenergetic with +29 kJ/mol and for An = Th exoenergetic with −13 kJ/mol at 0 K. So, in contrast to the experimental findings, the decaammine complex would be energetically favored for U and the chlorido complex for Th. However, when again taking the thermal contributions to the free enthalpies into account, reaction 2 becomes slightly less exothermic with −7 kJ/mol for An = Th, while for An = U it turns into an exothermic reaction with −10 kJ/mol. The latter result of [UCl(NH$_3$)$_8$]$^{3+}$ formation is in line with our observation, while for An = Th it is not. The calculations within the conductor-like screening model of course do not explicitly account for the contribution of the lattice energies of the crystalline compounds to the stabilities and structures of the complex cations; in particular, they neglect hydrogen bonds and van der Waals interactions that certainly have a significant contribution to the lattice energies for the systems presented here.

To get an idea of the bonding situation and to see if different orbitals contribute to the An–Cl bond in the [AnCl(NH$_3$)$_8$]$_{3+}$ complexes, we studied the localized molecular orbitals (LMOs) for the respective cations. As expected, the U–Cl bond is quite ionic and the LMOs of the U–Cl σ-bond and one set of the degenerate π-backbonding is shown in Figure 5.

Based on a Mulliken population analysis, the contribution of the U atom to the U–Cl σ-bond is approximately 12% and circa 5% for the π-backbonding. The main orbital contributions of the U atom to the σ-bond originate from its 6d orbital with 56% and its 7s orbital with 32%. In contrast to this, the 5f orbital only contributes with 12%. The Cl atom shows 85% 3p and 15% 3s orbital contribution to the σ-bond. The average orbital contributions of the U atom for both π-backbonds are 41% by the 6d, 43% by the 5f, and 14% by the 7p orbital, respectively. The Cl atom provides 100% 3p orbital character to the π-backbonds.

In comparison, the Mulliken population analysis-based contributions of the Th atom to the Th–Cl σ-bond are essentially similar with approximately 12 and circa 5% for the π-backbonding. The figures showing the corresponding Th LMOs are available in the SI and look very similar to those of the U complex. The Th atom contributes 56% with its 6d orbital, 27% with its 7s orbital, and 17% with its 5f orbital to the Th–Cl σ-bond. The Cl atom contributes 86% with its 3p and 16% with its 3s orbital. The average orbital contributions of the Th atom to the π-backbonds are 35% from the 6d orbital, 50% from the 5f orbital, and 12% from the 7p orbital, respectively. The Cl atom donates its electron density with 100% via the 3p orbital to the π-backbonds. All values are given for comparison in Table 3 below.

The nature of the bond seems to be quite complex. It is dominated by the 6d and 7s orbitals for the An–Cl σ-bonds, while the contributions

| Table 3. Comparison of the An orbital contributions in % to the An–Cl bonds for LMO and IBO bonding analyses. * = alpha and beta spin components considered. # = average contribution for both π-backbonds. |
|---|---|---|---|---|---|
| Bonding analysis type | Bond | An | An orbital contribution to An–Cl bond | d orbital contribution to An–Cl bond | f orbital contribution to An–Cl bond |
| LMOs | α | U | 32* s | 56* | 12* |
| | | Th | 27 s | 56 | 17 |
| | π* | U | 14 p | 41* | 43* |
| | | Th | 12 p | 35 | 50 |
| | α | U | 21 s | 71 (dz$^2$) | 8 |
| | | Th | 18 s | 67 (dz$^2$) | 15 |
| IBOs | α | U | – | 67 | 33 |
| | π* | Th | – | 63 | 47 |
to the $\pi$-backbonds are mainly due to the 6d and 5f orbitals of the An atoms. This analysis shows that no significant differences of the involved orbitals of the An atoms are present. So, our bonding analysis cannot explain why the formation of the U complex is favored over the Th complex.

For comparison with the LMO analysis we carried out an Intrinsic Bonding Orbital (IBO) analysis for both complexes. A reference basis set (see the Supporting Information) for Th had to be derived to be able to conduct the IBO analysis. Unfortunately, the results of the IBO analysis for Th strongly depend on the atomic orbitals included in the reference basis set. A brief discussion is given in the SI. Here we discuss the IBO analysis with a reference basis set including f orbitals (labeled Th s$^2$d$^6$f$^1$ ($f$: t$_2$) in the SI), as they seem important with respect to the LMO analysis. Our calculations yield a Th atom contribution of circa 16% to the Th–Cl $\sigma$-bond and $\approx$ approximately 6% to the two $\pi$-backbonds. The larger the percentage within the IBO model, the more polarized the bond. For comparison, a gas-phase NaF molecule, in which the bond should be highly ionic, shows a contribution of the F atom of 96%. In the H$_2$ molecule, which has a purely covalent bond, the contribution of each atom is 50%.

The very ionic Th–Cl $\sigma$-bond is mainly dominated by the Th 6d orbital with 67% contribution, followed by the 7s orbital with 18% and the 5f orbital with 15%. Therefore, the IBO calculations show a slightly higher 6d contribution compared with the LMO analysis. The Cl atom contributes with 34% by its 3s and with 66% by its 3p orbital. In case of the two very ionic $\pi$-backbonds, the average Th 6d contribution is 63% and the 5f contribution is 47%. Compared with the LMO analysis there are no Th 7p orbitals involved in the $\pi$-backbonds, as these orbitals are not included in the IBO reference set. The Cl atom contributes 100% with its 3p orbitals, which is in agreement with the LMO analysis.

In case of the U complex an already tested and published reference basis set was used leading to similar results compared with the Th complex. The IBOs are shown in Figure 6.

The contribution of the U atom to the U–Cl $\sigma$-bond is circa 15% and circa 5% for the U–Cl $\pi$-backbonds. In case of the very ionic U–Cl $\sigma$-bond the contributing orbitals of the U atom are mainly its 6d orbital with 71% and its 7s orbital with 21%, whereas the 5f orbital contributes with only 8%. The Cl atom contributes with 68% by its 3p orbital and 32% by its 3s orbital. The 3s contribution is higher in comparison with the LMO analysis where it was only 15%. For the $\pi$-backbonds, the average contributions of the U atom are 67% from the 6d orbital and 33% from the 5f orbital, whereas the Cl atom contributes with 100% with its 3p orbital. All values are again compared in Table 3.

Comparing both analyses, only slight differences in the involved orbitals are obtained. In both bonding analyses, the percentages of contributions of the An atoms to the An–Cl $\sigma$-bonds and $\pi$-bonds are of almost the same value (Table 4). However, when comparing the contributing orbitals, the situation becomes complex. In both analyses and both for U and Th, the An–Cl $\sigma$-bond seems to be mainly formed by the 6d orbitals, with smaller contributions of the 7s and 5f orbitals. This result is to be expected for Th but less for U where f electron chemistry becomes usually more important. In case of the An–Cl $\pi$-backbonds the LMO and IBO analyses show that different orbitals are involved. LMO analysis clearly shows that the U 6d and 5f orbitals are the main acceptors for the Cl lone pairs and that the 7p orbitals are less involved with circa 14%. In the IBO analysis the 7p orbitals are not involved as they are not part of the reference basis set. The mainly contributing

Figure 5. The LMO representing the U–Cl $\sigma$-bond in the cation [UCl(NH$_3$)$_8$]$^{3+}$ (left) and one of the two LMOs representing the U–Cl $\pi$-backbonding (right). Cyan, green, blue, and white denote U, Cl, N, and H atoms, respectively. Isosurfaces are drawn at 0.03 a.u.
orbitals are 6d and 5f, the latter with a smaller contribution. When comparing the \( \text{An} \)−Cl \( \pi \)-backbond orbital contributions for the Th complex, the results are in case of the LMO analysis similar to those of the U complex, however, with a slightly higher 5f involvement.

Calculating the partial charges of the \( \text{An} \) atoms and the number of electrons for the d and f subshells for both complexes via both analyses shows no major differences, except for the total number of electrons, of course (Table 4). Comparing both complexes within one method shows similar f and d orbital occupations, essentially the same contributions to the \( \text{An} \)−Cl bonds, and similar partial charges of the \( \text{An} \) atoms within the complexes. Even when comparing the LMO with the IBO analyses there are no major differences, as the \( \text{An} \) contributions to the An−Cl bonds, partial charges and number of d/f electrons are quite close (Table 4).

The results of the LMO and IBO analyses show no major differences of the orbitals contributing to the An−Cl bonds (see Table 3), as well as no significant differences in partial charges (Table 4) of the \( \text{An} \) atoms. From our calculations, we also do not obtain significant differences of the \( \text{An} \)−Cl \( \sigma \)- and \( \pi \)-backbonds within the \([\text{AnCl(NH}_3]_8\]^{3+} \) cations \((\text{An}=\text{Th}, \text{Cl})\).

With respect to those results, it is peculiar that we obtained isotypic Th and U compounds in the reactions of \( \text{An} \)Br\(_4\) and \( \text{An} \)I\(_4\) with dry NH\(_3\) and of \( \text{An} \)Cl\(_4\) with moist NH\(_3\) \((\text{An}=\text{Th}, \text{U})\). The quantum-chemical calculations for the gas-phase cations could not resolve this issue. It may therefore be possible that for both \( \text{An} = \text{Th} \) and U the compounds \([\text{An(NH}_3]_{10}\]Cl\(_4\) \cdot 4\text{NH}_3\) and \([\text{AnCl(NH}_3]_8\]Cl\(_3\) \cdot 3\text{NH}_3\) exist and that their formation depends either strongly on the concentration of \( \text{An} \) species in solution, which we currently do not know, or that the compounds represent either the kinetic or the thermodynamic products of crystallization, which we presently do not know either.

Conclusion

We presented the reactions of the thorium tetrahalides ThX\(_4\) \((X=\text{Cl, Br, I})\) with liquid ammonia at room temperature and the crystal structures of the products \([\text{Th(NH}_3]_{10}\]Br\(_4\) \cdot 8\text{NH}_3\), \([\text{Th}-(\text{NH}_3]_{10}\]I\(_4\) \cdot 9\text{NH}_3\), and \([\text{Th}_2\text{Cl}_2(\text{NH}_3]_{14}(\mu\text{-O})\]Cl\(_2\) \cdot 3\text{NH}_3\) that are isotypic to their analogous U compounds, respectively. In the case of the chlorides we surprisingly did not obtain isotypic compounds, as ThCl\(_4\) formed with NH\(_3\) the decaammine
complex \([\text{Th(NH}_3\text{)}_{10}\text{Cl}_4 \cdot 4\text{NH}_3]\), while UCl_4 formed the octaammine chlorido complex \([\text{UCl(NH}_3\text{)}_8\text{Cl}_3 \cdot 3\text{NH}_3]\). We carried out quantum-chemical calculations to investigate this peculiarity. The calculations for the gas phase showed the formation of the \([\text{AnCl(NH}_3\text{)}_8\text{]}^{3+}\) (An = Th, U) complexes to be preferred over the \([\text{An(NH}_3\text{)}_9\text{]}^{4+}\) cations and therefore could not explain the observed formation of the decaamine complex. Even a detailed analysis of the bonding situation in both \([\text{AnCl(NH}_3\text{)}_8\text{]}^{3+}\) (An = Th, U) complexes using both the LMO and IBO approaches, could not help to explain the observed formation of the \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\) cation.

It is however possible that the concentration of An species in solution plays an important role. If the decaamine compounds \([\text{An(NH}_3\text{)}_9\text{]}^{4+}\text{Cl}_4 \cdot 4\text{NH}_3\) and the chlorido compounds \([\text{AnCl(NH}_3\text{)}_8\text{]}^{3+}\text{Cl}_3 \cdot 3\text{NH}_3\) exist for both actinoids and how they might be formed is still under investigation.

Experimental section

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (5.0, Praxair) using high vacuum glass lines and a glovebox (MBraun). Liquid ammonia was dried by storage over Na. The glass vessels were flame dried several times before utilization under vacuum. The thorium containing starting materials ThCl_4, ThBr_4, and ThI_4 were prepared according to the literature.\(^{29}\)

Work with thorium has been carried out in accordance with the German radiation protection law, section 8.

Synthesis of \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{Cl}_4 \cdot 4\text{NH}_3\)

30 mg of ThCl_4 (0.08 mmol) were reacted with liquid ammonia in a flame sealed glass ampoule (bomb tube made of borosilicate glass, 6 mm diameter with 1.5 mm wall thickness) at room temperature. Single crystals were isolated after 7 months of crystallization time.

Synthesis of \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{Br}_4 \cdot 8\text{NH}_3\)

30 mg of ThBr_4 (0.05 mmol) were reacted with liquid ammonia in a flame sealed glass ampoule (bomb tube made of borosilicate glass, 6 mm diameter with 1.5 mm wall thickness) at room temperature. Single crystals were isolated after 5 months of crystallization time.

Synthesis of \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{I}_4 \cdot 8.5\text{NH}_3\)

30 mg of ThI_4 (0.04 mmol) were reacted with liquid ammonia in a flame sealed glass ampoule (bomb tube made of borosilicate glass, 6 mm diameter with 1.5 mm wall thickness) at room temperature. Single crystals were isolated after 2 months of crystallization time.

Synthesis of \([\text{Th}_2\text{Cl}_2\text{N}[\text{H}_3\text{]}_{14}(\mu-\text{O})]\text{Cl}_4 \cdot 3\text{NH}_3\)

25 mg of ThCl_4 (0.07 mmol) were reacted with liquid ammonia that has not been dried over sodium in a flame sealed glass ampoule (bomb tube made of borosilicate glass, 6 mm diameter with 1.5 mm wall thickness) at room temperature. Single crystals were isolated after 8.5 months of crystallization time.

Single crystal X-ray diffraction

Single crystals were selected under nitrogen-cooled, pre-dried perfluorinated oil and mounted using a MiTeGen loop. Intensity data of a suitable crystal were recorded with an IPDS 2T or a STADI4VARI diffractometer (Stoe & Cie). The diffractometer was operated with Mo-K\(_\alpha\) radiation (0.71073 Å, graphite monochromator) or Cu-K\(_\alpha\) radiation (1.54178, graphite monochromator) and equipped with an image plate or a Dectris PILATUS 300 K detector, respectively. Evaluation, integration and reduction of the diffraction data was carried out using the X-Area software suite.\(^{41}\) Multi-scan or numerical absorption corrections were applied with the modules X-Shape, X-Red32, and LANA of the X-Area software suite. The structure was solved with dual-space methods (SHELXT-2014/5) and refined against \(F^2\) (SHELXL-2018/3).\(^{42,43}\) All atoms were refined with anisotropic displacement parameters, hydrogen atoms were either located from the difference Fourier map and refined isotropic using restraints and constraints were necessary, or using a riding model.

Computational Details

All calculations were carried out with the TURBOMOLE\(^{44,45}\) program suite using the PBE0\(^{46,47}\) hybrid density functional method (DFT-PBE0). Karlsruhe def2-TZVP\(^{46}\) basis sets were applied for hydrogen, nitrogen and chlorine. For thorium and uranium scalar relativistic effects were taken into account by using 60-electron effective core potentials,\(^{49}\) together with def-TZVP valence basis sets.\(^{50}\) Multi-pole-accelerated resolution-of-the-identity approximation (MA-RU) was used to speed up the DFT calculations\(^{51,53}\) and m4 integration grid was used for the numerical integration of the exchange-correlation part. The “conductor-like Screening Model” (COSMO) was applied to all structures to compensate the high charges.\(^{54}\) The geometry of the complexes were fully optimized within the constraints of their point group symmetries. Numerical harmonic frequency calculations were performed to check if the optimized structures are true local minima on the potential energy surface. The coordinates of the optimized structures are available from the Supporting Information. The Pipek-Mezey-LMO\(^{55}\) and IBO\(^{39}\) analyses were carried out with the Turbomole program proper. The thermal contributions to the free enthalpy were obtained within the harmonic oscillator rigid rotor model at room temperature, using the freeh module. The scaling factor of harmonic frequencies was set to 1. The published U\(^{46}\) reference basis set was used for the IBO analysis. For more details on the IBO reference basis set for Th, please see the SI. The reference basis set labeled s\(^2\)d\(^1\)f\(^1\) (f: t2) was used to obtain the IBO results reported in the main paper.

Deposition Numbers 2063667 (for \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{Cl}_4 \cdot 8.5\text{NH}_3\)), 2063668 (for \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{Cl}_4 \cdot 4\text{NH}_3\)), 2063669 (for \([\text{ThCl}_2\text{N}[\text{H}_3\text{]}_{14}(\mu-\text{O})]\text{Cl}_4 \cdot 3\text{NH}_3\)), and (2063670 for \([\text{Th(NH}_3\text{)}_{10}\text{]}^{4+}\text{Br}_4 \cdot 8\text{NH}_3\)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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