The reactions of TiCl₃, and of UF₄ with TiCl₃ in liquid ammonia: unusual coordination spheres in [Ti(NH₃)₈]Cl₃·6NH₃ and [UF(NH₃)₈]Cl₃·3.5NH₃

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TiCl₃ and NH₃ form octaammine titanium(III) chloride ammonia (1/6), [Ti(NH₃)₈]Cl₃·6NH₃, which is the first structurally characterized octaammine complex of a transition metal. An excess of TiCl₃ reacts with UF₄ in liquid NH₃ and forms octaammine fluorido uranium(IV) chloride ammonia (1/3.5), [UF(NH₃)₈]Cl₃·3.5NH₃. It shows a distorted threefold-capped trigonal-prismatic coordination sphere around U(IV).

In the recent decades uranium chemistry experienced a renaissance, as more “non-nuclear” uses of uranium compounds, for example, in small molecule activation, or catalysis were investigated. Also, the workup of radioactive wastes and actinoid containing nuclear fuels, the selective extraction of actinoids, as well as the understanding of their geological fate in the environment after an accident, requires a profound knowledge of actinoid species in solution. Single crystal X-ray structures would be of aid for the assessment of potential structural motifs in the solution chemistry of the actinoids. However, structural information from single crystal X-ray diffraction was often not available asolation and oxolation reactions occur with actinoids in aqueous solutions. These were believed to lead to “ill-defined structures and chemistry” and thus it remained crystallographically unexplored. The structural chemistry of actinoid complexes obtained from aqueous solutions is therefore rather poorly understood. Liquid ammonia is a solvent system similar to water, and it may serve as a model system to obtain crystalline actinoid species which are otherwise difficult or impossible to isolate from aqueous media. Liquid ammonia shows a much lower autoprotolysis and has a broader pH range which may allow easier access to products coming from protonation and deprotonation reactions. The literature on the coordination chemistry of uranium with only simple, inorganic, monodentate ligands, with the exception of the aqua ligand, is very scarce compared to the magnitude of literature of multidentate-binding organic ligands. Uranium compounds may feature various coordination numbers, often from six to eight, but also higher in the case of multidentate ligands, and even coordination numbers of twelve or more, for example in the borohydrides, are known.

A coordination number of nine for monodentate ligands is, however, rare and has, to the best of our knowledge, been reported only for the threefold capped trigonal prismatic cations of Ba³⁺, La³⁺, Sm³⁺, trivalent actinoids⁶ and for uranium compounds with DMSO, DMF, or acetonitrile as ligands. Our compound seems to be a rare example of such a threefold-capped trigonal-prismatic coordination sphere where only simple inorganic ligands are present on the uranium atom. We have previously investigated the reactions of UF₄ and UF₃ with anhydrous ammonia. In our attempts to identify usable fluoride ion acceptors for the liquid ammonia system, and in order to expand the chemistry of UF₄, we report herein the usage of titanium(III) chloride as a fluoride ion acceptor in anhydrous ammonia besides the unusual coordination spheres of U(IV) and Ti(III) in the resulting compounds.

The coordination chemistry of titanium has been extensively reviewed. Titanium(III)-complexes of the formula types TiL₆⁺, TiX₆L₄⁺ or TiX₅L₃⁺ show an octahedron-like coordination. In aqueous solution the hexaqua-cation [Ti(H₂O)₆]³⁺ is known. In a reaction of TiI₃ in liquid ammonia at room temperature, only a byproduct with the composition [(NH₃)₅Ti–O–Ti(NH₃)₅]I₄·NH₃ (octahedral coordination) was observed. A square-antiprismatic coordination sphere for titanium has been reported for multidentate ligands, such as bidentate binding oxalate, and tridentate binding C₁₆H₁₈N₄O₇⁺ and in the Ti₃Br₄ and Ti₃Mn₈P₁₂ (Ti(n)) compounds. For monodentate ligands, a Ti atom was observed in a metal–organic-framework compound which was coordinated by seven H₂O ligands and one hydroxide anion in a distorted square-antiprismatic manner. Octaammine complexes of other metal cations are also quite rare, and structural proof is only available in the case of the twofold capped trigonal prismatic cations [M(NH₃)₆]³⁺ (M = Ca, Sr, and Ba) and the square-antiprismatic cation [Yb(NH₃)₁₄]⁺⁺⁺ during the synthesis of TiX₃·6NH₃ (X = Cl and Br) colorless-greyish compounds with the composition of TiBr₃·8NH₃ and TiCl₃·7NH₃ have been observed without the

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The chlorine atoms Cl(1) and Cl(2) occupy the crystallographic sites 4g and 2f, respectively. With a Ti ⋅ ⋅ ⋅ Cl-distance of 4.1374(4) and 4.7104(2) Å there is no direct cation–anion contact. The chloride anions act as acceptors for N–H ⋅ ⋅ ⋅ Cl-hydrogen bonds, for details see the ESI†. The unit cell of the [Ti(NH3)6]Cl3·6NH3 compound is shown in Fig. 2. It is interesting to note that the compound presented here shows a Ti:N-ratio of 1:14, which has not been reported previously. Schläfer and coworkers report that TiCl3·6NH3 is obtained when ammonia is carefully pumped off from the reaction mixture of TiCl3 in liquid ammonia at –54 °C for five to six weeks.36 In our case we obtained the crystals of [Ti(NH3)6]Cl3·6NH3 under autogenous pressure at –40 °C. As Schläfer and coworkers have obtained “only” TiCl3·6NH3, it is plausible to assume that [Ti(NH3)6]Cl3·6NH3 can be converted to yield the respective compound. The decomposition of TiCl3·6NH3 has been studied in the temperature range from –40 to +450 °C.41 At room temperature TiCl3·6NH3 as well as TiCl3·5NH3 were both reported to be stable.43 TiCl3·6NH3 decomposes to TiCl3·5NH3 at +7 °C.44 The crystals of [Ti(NH3)6]Cl3·6NH3 burst upon warming to temperatures higher than approximately –40 °C without autogenous pressure present. At room temperature TiCl3·5NH3 was obtained as evidenced by elemental analysis (calc.: N: 29.26%; H: 6.32%, det.: 29.83%, 6.231%).

Aqueous solutions of Ti[m] are known to be violet/blue. Typically they show small extinction coefficients as the electronic d–d transition is forbidden. [Ti(NH3)6]3+ crystallizes in colorless crystals of [Ti(NH3)6]Cl3·6NH3, suggesting that it might show interesting electronic differences in comparison to the known Ti[m] compounds. Because the compound is not stable above ca. –40 °C, we could not obtain a UV/VIS spectrum. Instead, we investigated the spectroscopic properties of [Ti(NH3)6]3+ using ab initio quantum chemical methods high level coupled cluster calculations at the CC2/def2-TZVPP level of theory; for further computational details, see Experimental section. We first investigated the well-known Ti[m] complex [Ti(H2O)6]3+ as a reference case. A broad absorption band in the region around 500 nm has been reported in the most recent experimental UV/VIS spectrum, in agreement with computational results obtained with the

Fig. 1 Depiction of the [Ti(NH3)6]3+ cation of [Ti(NH3)6]Cl3·6NH3. Displacement ellipsoids are shown at the 70% probability level at 123 K. H-atoms are isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 = x, y, z; #2 = 1/2-x, 1/2+y, 1/2-z; #3 = –x, –y, –z+1/2. Selected atomic distances [Å]: Ti(1)–N(1): 2.3115(12), Ti(1)–N(2): 2.3063(12), Ti(1)–N(3): 2.2902(12), Ti(1)–N(4): 2.2752(13).

Fig. 2 The unit cell of the [Ti(NH3)6]Cl3·6NH3 compound. Displacement ellipsoids are shown at the 70% probability level at 123 K. H-atoms are isotropic with arbitrary radii.
DFT-B3LYP method. The UV/VIS results predicted here are in good agreement with the experiment, showing an absorption band centered at 490 nm. The transition strength is very low (0.2 × 10⁻⁶ a.u.), as expected for a forbidden d-d transition. In the case of the [Ti(NH₃)₈]³⁺ complex, the predicted absorption wavelength is noticeably red-shifted to 711 nm. Therefore, the [Ti(NH₃)₈]³⁺ complex should absorb in the red regime of the spectrum, suggesting a pale blue complementary color that might be rather difficult to observe properly, e.g. from crystals in cooled perfluoro-ether oil. Also for [Ti(NH₃)₈]³⁺, the transition strength of the absorption is very small (0.2 × 10⁻⁷ a.u.). A comparison between the frontier orbitals of [Ti(H₂O)₆]³⁺ and [Ti(NH₃)₈]³⁺ shows that in both cases the HOMO is the Ti dₓ₂₋₅ orbital, which is also in line with the previous results for [Ti(H₂O)₆]³⁺. The other four d orbitals are ordered in two practically degenerate pairs. For [Ti(NH₃)₈]³⁺, the lower-lying pair of d orbitals is composed of dₓ₂₋₅ and dₓᵧ, but the 711 nm absorption involves the higher-energy dₓ₂ and dₓᵧ orbitals. This energy ordering for the square antiprismatic [Ti(NH₃)₈]³⁺ ion is reversed in comparison to the octahedral [Ti(H₂O)₆]³⁺ complex. The square antiprismatic configuration of [Ti(NH₃)₈]³⁺ is non-centrosymmetric, but the dₓᵧ → (dₓᵧ/dₓᵧ) transition is still symmetry forbidden.

By comparing the radii/charge-ratios of Ti(m) and U(n) for various coordination numbers (for C.N. 6: 0.14 and 0.17, respectively), and in view of our experiment Ti(m) should be a slightly harder Lewis-acid and therefore prefer the bonding to “harder” F⁻-anions over “softer” ammine ligands. When UF₄ is reacted with TiCl₃ in liquid ammonia solution, the reaction may be described by eqn (1):

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2\text{UF}_4(\text{am}) + 2\text{TiCl}_3(\text{am}) + 23\text{NH}_3 \rightarrow 2\text{[UF(NH}_3)_8]\text{Cl}_3 \cdot 3.5\text{NH}_3 + 2\text{“TiF}_3“(\text{am})
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The identity of the resulting titanium(III) compound could not be established besides numerous attempts and is therefore referred to as “TiF₃”. It is obtained in the form of a greyish precipitate of variable N, H, and F content, and is X-ray amorphous. Its IR spectrum shows that besides bound NH₃ molecules, NH₃⁻ and possibly NH₂⁻ anions may also be present. The [UF(NH₃)₈]Cl₃·3.5NH₃ compound is obtained in the form of green crystals. The composition has been elucidated using single-crystal X-ray analysis (details in Table S1, ESI†). The atoms of the asymmetric unit of [UF(NH₃)₈]Cl₃·3.5NH₃ occupy only two crystallographic sites: the atoms U(1), F(1), N(1) to N(10), N(12), and Cl(1) to Cl(3) reside on the 8f position and the nitrogen atom N(11) occupies the 4e position. The uranium atom is coordinated by one fluoride atom and eight ammine ligands (N(1–8)) forming the octaammine fluoroide uranium(n) cation [UF(NH₃)₈]³⁺, shown in Fig. 3. The coordination polyhedron may be best described as a distorted, trifold-capped trigonal prism. The trigonal faces, which are formally formed by the atoms N(1), N(2), F(1) and N(4), N(5), N(7), respectively, are not parallel to each other but deviate by 5.24(8)°. The centers of these faces are 1.872(1) and 1.648(1) Å away from the U atom, respectively. The tetragonal planes show angles of 63.27(3), 58.37(4) and 58.38(4)° towards each other. They are capped by the ammine ligands N(6), N(8), and N(3) with distances of 1.755(2), 1.734(2), and 1.671(2) Å, to these planes, respectively. The nitrogen atoms of the tetragonal face deviate only by ±0.049(1) Å from the respective least-squares-planes.

The U–N distances are observed in the range between 2.559(1) and 2.630(1) Å. They are comparable with distances reported for the [UF₄(NH₃)₄]⁻NH₃ compound with 2.618(3) Å, where the U–atom is only eightfold coordinated. Despite the coordination number of nine, the U–F-distance is quite short with 2.117(1) Å compared to the respective distances reported for the [UF₄(NH₃)₄]⁻NH₃ (2.188(4) Å) and (N₅H₅)(NH₄)[UF₄(NH₃)] (2.200(2) to 2.336(2) Å) compounds, where the coordination number is only eight. For the [UO₂F₂(NH₃)₃]₂²⁻NH₃ compound longer U–F-distances ranging from 2.217(2) to 2.241(2) Å have been observed. So, the uranium(n) cation seems to exert a strong pull towards the F⁻ anion. Selected atomic distances and angles of the crystal structure are available from Table S4 (ESI†) and the caption of Fig. 3. The short N···Cl, N···F and N···N distances are indicative of the presence of the respective hydrogen bonds, for details see the ESI†. Fig. 4 shows the unit cell of the compound. Upon warming to room temperature an X-ray amorphous powder is obtained, the IR spectrum of which shows the presence of ammine ligands. As the compound cannot be
As we could characterize such a U(II) species with ligands similar to aqua ligands, we expect that this result is important for actinoid speciation in aqueous solutions as well.

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Tungsten(VI)-chloride seems to be a fluoride ion acceptor usable for the liquid ammonia system. It is able to subtract three fluoride ions from UF\textsubscript{4} and green crystals of [UF(NH\textsubscript{3})\textsubscript{8}]Cl\textsubscript{3} have been characterized, however with organic ligands such as dimethylformamide, acetonitrile, and dimethylsulfoxide.\textsuperscript{16–19}

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Notes and references


