Rudel, Stefan S.; Karttunen, Antti J.; Kraus, Florian

\[ \text{Rb}_2\{\text{U(NH}_2\text{)}_6\} \text{, a Rubidium Hexaamidouranate(IV) obtained from the Reaction of U}_3\text{ with RbNH}_2 \text{ in Anhydrous Ammonia} \]

Published in:
Zeitschrift fur Anorganische und Allgemeine Chemie

DOI:
10.1002/zaac.202000086

Published: 31/07/2020

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Rudel, S. S., Karttunen, A. J., & Kraus, F. (2020). Rb₂[U(NH₂)₆], a Rubidium Hexaamidouranate(IV) obtained from the Reaction of U₃ with RbNH₂ in Anhydrous Ammonia. Zeitschrift fur Anorganische und Allgemeine Chemie, 646(14), 1023-1029. https://doi.org/10.1002/zaac.202000086

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Rb₂[U(NH₂)₆], a Rubidium Hexaamidouranate(IV) obtained from the Reaction of UI₃ with RbNH₂ in Anhydrous Ammonia

Stefan S. Rudel,[a] Antti J. Karttunen,[b] and Florian Kraus*[a]

Dedicated to Professor Dr. Juri Grin on the Occasion of his 65th Birthday

Abstract. The pyrophoric compound Rb₂[U(NH₂)₆] was obtained as a grey to black powder from the reaction of more than three equivalents of RbNH₂ with UI₃ in anhydrous liquid ammonia. During the process, Uᵢ₁ is oxidized to Uᵢ₄ and ammonia is reduced under evolution of H₂. Rb₂[U(NH₂)₆] crystallizes in the cubic crystal system, space group Fm₃m, with the lattice parameter a = 9.7870(12) Å, V = 937.4(2) Å³, Z = 4 at T = 293 K. It is isotypic to K₂PtCl₆. The compound contains the unprecedented hexaamidouranate(IV) anion [U(NH₂)₆]²⁻.

Introduction

Our investigations on the reactions of uranium halides with anhydrous liquid ammonia and dissolved amides[1–3] were driven by the desire to obtain uranium nitrides such as UN under comparably mild conditions. Similar research efforts had been undertaken in the past for the low-temperature synthesis of uranium as well as plutonium nitrides.[4,5] The peculiarity that UI₃ is able to act as a reducing agent for Rb⁺ was recently briefly reported by us.[3] We were now able to identify one of the reaction products as rubidium hexaamidouranate(IV), Rb₂[U(NH₂)₆]. The existence of such a compound was not totally unexpected, as we were able to obtain K₂[Zr(NH₂)₆] from comparable conditions in the past.[6]

Results and Discussion

Choosing UI₃ and RbNH₂ dissolved in anhydrous liquid ammonia as starting materials for the synthesis of uranium nitrides is reasonable. UI₃ and RbNH₂, as well as the side product RbI are well soluble and therefore easily filtered off from the insoluble uranium nitrides. Previous reports that employed other alkali metal amides claimed that UN would directly precipitate.[4] When we carried out the reactions with up to three equivalents of RbNH₂, we obtained a brown precipitate that was amorphous to X-rays. However, the brown precipitate could be annealed to obtain microcrystalline UN.[3] When more than three equivalents of RbNH₂ were used, the initially formed brown precipitate reacted to form a blue solution that was accompanied by a strong evolution of gas and the formation of a grey precipitate (Figure 1 left).

Figure 1. A photograph of a reaction of UI₃ with six equivalents of RbNH₂ in anhydrous ammonia. The reaction takes place at –78 °C. The blue color of the solvated electrons, the gas evolution and the formation of a grey precipitate is clearly seen (left). The right side shows a green compound, probably [U(NH₃)₉]I₃·₁₃NH₃ or a higher ammoniate, that is converted to a brown compound (probably UN or U(NH₂)₃), and finally to the grey/black Rb₂[U(NH₂)₆].

The observed blue color is absolutely typical for solvated electrons in anhydrous ammonia and the strong gas evolution is due to the formation of H₂ from the reduction of ammonia by the solvated electrons. Both phenomena are well known from solutions containing only alkali metals or the other metals that are soluble in ammonia.[7–13] However, a catalyst must be present that lowers the kinetic barrier towards amide formation and H₂ evolution as otherwise solutions of these metals can be kinetically stable for years.[14–16]

We may conclude that Uᵢ₁ acted as a reducing agent under these conditions and produced solvated electrons which obvi-
ously induced H₂ formation immediately. Therefore, U⁴⁺ is formed. We would like to point out that such a reductive behavior is also known for solutions of Eu⁴⁺ or Yb⁴⁺ in ammonia. The solutions become blue due to solvated electrons upon addition of, for example, a suitable alkali metal compound such as KI.[17–19] A reduction of potassium amide by UBr₃ was suspected by Bergstrom.[19] The reaction of Ui₃ with RbNH₂ in ammonia can be described by Equation (1), however, we will comment in more detail below.

\[
\text{U}_i + 5 \text{RbNH}_2 + \text{NH}_3 \rightarrow \text{Rb}_2[\text{U(NH}_2)_6]\ + \frac{1}{2} \text{H}_2 + 3 \text{RbI} \tag{1}
\]

After filtration and removal of excess of the solvent NH₃, a solid, grey to black product is obtained which shows sharp reflections of RbI and a second crystalline phase in its powder X-ray diffraction pattern. Additionally, the reflection positions of the second phase are in very good agreement with those of K₂[PtCl₆] (see Figure S1, Supporting Information),[20] to which the aforementioned K₂[Zr(NH₂)₆] is structurally related as well.[6] So, the lattice parameters of the second crystalline phase besides RbI are very similar to those of K₂[PtCl₆]. The diffraction pattern could therefore be indexed in the cubic crystal system, a LeBail refinement (Figure S2, Supporting Information) lead to the lattice parameter \(a = 9.796(1) \text{ Å} \), \(V = 940.1(1) \text{ Å}^3 \) at \(T = 293 \text{ K} \). For comparison, the lattice parameters of K₂[PtCl₆] at room temperature were reported with \(a = 9.756 \text{ Å} \), \(V = 928.6 \text{ Å}^3 \).[20] Due to the relative similarity of the reflection intensities, we assume that the indexed powder X-ray diffraction pattern of the second phase is due to the formation of the microcrystalline compound Rb₂[U(NH₂)₆] which crystallizes in the K₂[PtCl₆] structure type. So, except for four weak reflections at circa 10, 28, 29, and 47° 2θ, the recorded diffraction pattern could be nicely described using the two crystalline phases RbI and Rb₂[U(NH₂)₆].

Applying the space group and the atomic coordinates of K₂[PtCl₆] and replacing the respective atoms by Rb, U, and N atoms only, a Rietveld refinement was carried out (Figure 2). The Rb, U, and N atoms could only be refined isotropic but hydrogen atoms could not be located, as may have been expected. The quantum chemical calculations (see below) indicated space group \(\text{R}3\) for the title compound, as otherwise the two f-electrons of the U atom could not have been localized. Eventually, spin-orbit coupling might enable calculations in the higher cubic symmetry. We attempted a Rietveld refinement in space group \(\text{R}3\). However, it did not lead to a significant change of the structure model. Thus, the higher symmetry space group is chosen for Rb₂[U(NH₂)₆]. See Table 1 for selected crystallographic data and details of the structure determination and Table 2 for atomic coordinates and equivalent isotropic displacement parameters. The crystal structure of Rb₂[U(NH₂)₆] is shown in Figure 3.

The Rietveld refinement leads to a U–N distance of 2.274(15) Å within the [U(NH₂)₆]²⁻ anion. In the amido complex compound [U(NH₂)(NH₃)₈]Br₃·3NH₃,[3] the U–N amido distance was observed with 2.207(3) Å, while the U–N ammine distances ranged from circa 2.5 to 2.9 Å. Due to the lower coordination number of six in the [U(NH₂)₆]²⁻ complex, we would expect the U–N amido bond to be shorter than the one in the [U(NH₂)(NH₃)₈]³⁺ complex, where the coordination

![Figure 2](image-url)
Table 1. Selected crystallographic data and details of the structure determination of Rb$_2$[U(NH$_2$)$_6$] from Rietveld refinement.

| Property                      | Value                        |
|-------------------------------|------------------------------|
| Formula                       | H$_2$N$_6$Rb$_2$U            |
| Molar mass /g·mol$^{-1}$       | 505.10                       |
| Space group (no.)             | Fm$ar{3}$m (225)           |
| a /Å                          | 9.7870(12)                   |
| V /Å$^3$                      | 937.4(2)                     |
| Z                             | cF$^{84}$ (with H atoms, cF$^{36}$ without) |
|ρ$_{\text{calc.d.}}$ /g·cm$^{-3}$ | 3.484                        |
| Color of the powder           | grey to black                |
| T /K                          | 293                          |
| λ /Å                          | 1.54060 (Cu-K$_\alpha$)     |
| 2θ$_{\text{min, max, step}}$ /° | 5.155, 90.085, 0.015        |
| No. of data points            | 5663                         |
| No. of parameters             | 18                           |
| No. of restraints             | 0                            |
| No. of constraints            | 0                            |
| Peak shape function           | Pseudo-Voigt                 |
| Background                    | manual                       |
| S                             | 2.03                         |
| R$_p$                         | 11.94, 9.05                  |
| R$_w$(a)                      | 2.50                         |
| Δρ$_{\text{max, min}}$ /e·Å$^{-3}$ | 0.62, -0.63                 |

(a) Background-corrected R factors.

Figure 3. Crystal structure of Rb$_2$[U(NH$_2$)$_6$]. Rb atoms are shown in dark green, U atoms in bright green, all atoms isotropic with arbitrary radii. [U(NH$_2$)$_6$]$^{2-}$ coordination polyhedra are shown as bright green octahedra.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U$_{iso}$ for Rb[U(NH$_2$)$_6$].

| Atom | Position | x      | y  | z      | U$_{iso}$ /Å$^2$ |
|------|----------|--------|----|--------|-----------------|
| U    | 4a       | 0      | 0  | 0      | 0.0436(7)       |
| Rb   | 8c       | ¼      | ¼  | ¼      | 0.0656(16)      |
| N    | 24e      | 0.2323(15) | 0 | 0      | 0.067(6)        |

number is nine. This expectation is fulfilled; however, such a comparison is not straightforward as bond lengths between central atom and ligands in an anionic complex are naturally longer than in a cationic complex of same coordination number and oxidation state of the central atom. In the complex [U(N$_2$)$_4$] with coordination number eight, a U–N distance of 2.314(3) Å has been observed\cite{21} This is slightly longer than the U–N distance in [U(NH$_2$)$_6$]$^{2-}$, as the coordination number is larger. A dimethylamido complex of U$^{IV}$ of the composition [U(NMe$_2$)$_4$]$_3$ has been structurally characterized as a trigonal, centrosymmetric, linear complex where each U atom carries six NMe$_2$ ligands\cite{22} The terminally bound NMe$_2$ ligands show U–N distances of 2.25 Å, thus circa 0.02 Å shorter than in the title compound. As the steric demand of the NH$_2$– ligand is less compared to that of the NMe$_2$– ligand, a shorter distance would be expected for our case. However, the observed difference is likely due to the comparison of data obtained from powder and single-crystal X-ray diffraction and should therefore not be overstressed. Near-perfect octahedral hexakis(organo)amido complexes of U$^{IV}$ and U$^{VI}$ have been reported with U–N bond lengths of 2.217(2) to 2.292(6) Å and 2.178(6) to 2.208(5) Å, respectively\cite{23-25} The U$^{VI}$–N bonds are thus shorter than the U$^{IV}$–N bonds, and thus U$^{IV}$–N bonds should be a little longer. This is fulfilled in our case with 2.274(15) Å. In comparison with quantum chemical calculations for the solid-state compound as well as for the isolated [U(NH$_2$)$_6$]$^{2-}$ anion (both see below), where the U–N distance is calculated to 2.35–2.36 Å, the observed bond length agrees well. The next nearest Rb···U distance in Rb$_2$[U(NH$_2$)$_6$] is 4.2379(6) Å, which is a plausible value as the metal cations are separated far enough, as expected.

For the formation of the title compound we assume a formal or maybe even an intermediate formation of uranium triamide U(NH$_2$)$_3$ for the reactions of U$_3$ with up to three equivalents of RbNH$_2$ [Equation (2)].

$$\text{U}_3 + 3 \text{RbNH}_2 \rightarrow \text{U}(\text{NH}_2)_3 + 3 \text{RbI}$$ (2)

We expect, in analogy to oxo- and olation reactions in the aqueous system, that U(NH$_2$)$_3$ is easily converted, that is, it “ages”, into uranium nitride, UN, see Equation (3):

$$\text{U}(\text{NH}_2)_3 \rightarrow \text{UN} + 2 \text{NH}_3$$ (3)

This ageing reaction would also be a plausible pathway for the formation of UN from the reaction of uranium tetraiodide, U$_4$, with Na or K dissolved in ammonia, as reported by Cleve-land and co-workers\cite{4} If U$^{IV}$ is first reduced to a soluble U$^{III}$ species is unclear. The reaction according to Equation (3) seems to be favored over the formation of other complex amides, as besides the brown precipitate that could be annealed to UN only crystals of [U(NH$_2$)$_3$]$_2$I$_3$·13NH$_3$ were obtained when up to three equivalents of RbNH$_2$ were used. So far, we have not observed the formation of complex amides of U$^{III}$, such as [U(NH$_2$)$_x$I$_y$]$^{2-}$ with $x$ = 1 to 3 or amidoammine com-
plexes of $\text{U}^{\text{III}}$. When more than three equivalents of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ are used, then the low solubility of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ and its lattice energy could act as an additional driving force for the reduction of ammonia and the oxidation of $\text{U}^{\text{III}}$, see Equation (4) and Equation (5):

$$\text{U(NH}_2\text{)}_3 + 2 \text{RbNH}_2 + \text{NH}_3 \rightarrow \text{Rb}_2[\text{U(NH}_2\text{)}_6] \downarrow + \frac{1}{2} \text{H}_2 \quad (4)$$

$$\text{U}_3 + 5 \text{RbNH}_2 + \text{NH}_3 \rightarrow 3 \text{Rb} \downarrow + \frac{1}{2} \text{H}_2 \quad (5)$$

Why and how the reactions really proceed is beyond our capabilities.

Tschirne and Naumann suggested the formation of $[\text{U(NH}_2\text{)}_4\text{]}_2^-$ from the reaction of $\text{UCl}_4$ and $\text{NaNH}_2$. $[\text{U(NH}_2\text{)}_4\text{]}_2^-$ was said to decompose already at low temperatures. If $[\text{U(NH}_2\text{)}_4\text{]}_2^-$ is really formed, then it is unclear as to why the formation of a hexaamidouranate(IV) complex, $[\text{U(NH}_2\text{)}_6\text{]}^{2-}$, was not reported. It is possible that either their reaction conditions were not suitable, or that an intermediate of trivalent uranium is essential for the formation of the $\text{U}^{\text{IV}}$ complex. Both we deem possible. The pyrophoric behavior and the tendency to detonate upon air contact make it plausible that we have obtained the complex amide $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ as Schmitz-Dumont has reported thorium amido complexes that were pyrophoric and exploded vigorously upon air contact, as well. They reported thermal decomposition reactions according to the following Equation (6), Equation (7), Equation (8), and Equation (9). [26]

$$\text{K}[\text{Th(NH)}_2(\text{NH}_2)] \rightarrow \text{K}[\text{Th(NH)}_2(\text{NH}_2)] + \text{NH}_3 \quad (6)$$

$$\text{K}_2[\text{Th}_2(\text{NH})_3(\text{NH}_2)] \rightarrow 2 \text{K}[\text{Th(NH)}_2(\text{NH}_2)] + \text{NH}_3 \quad (7)$$

$$2 \text{K}[\text{Th(NH)}_2(\text{NH}_2)] \rightarrow \text{K}_2[\text{Th}_2(\text{NH})_3] + \text{NH}_3 \quad (8)$$

$$3 \text{K}[\text{Th(NH)}_2(\text{NH}_2)] \rightarrow 2 \text{K}_2\text{ThN}_5 + 5 \text{NH}_3 \quad (9)$$

The obtained nitride $\text{K}_3\text{ThN}_5$ still reacted explosively with air. When the compound was heated even further, elemental potassium was released. [Equation (10)]. [26]

$$\text{K}_3\text{ThN}_5 \rightarrow 3 \text{ThN} + 3 \text{K} + \text{N}_2 \quad (10)$$

It is known that the heavier alkali metal amides can be decomposed above their melting points into the elements. [15] The vigorous reaction of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ in air could therefore be not only due to exothermic protolysis, hydrolysis and oxidation reactions, but may also be due to a thermal decomposition induced by reaction heat. The latter we assume due to an observation where $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ reacted explosively with an extremely small amount of air due to a capillary leak in a glass apparatus. Due to its high lattice energy $\text{UN}$ would form as an additional product, among $\text{N}_2$, $\text{Rb}$, and $\text{H}_2$. The latter two would also react strongly exothermically with (moist) air. In analogy to the report of Schmitz-Dumont, a hypothetical decomposition reaction can be formulated [Equation (11)].

$$2 \text{Rb}_2[\text{U(NH}_2\text{)}_6] \rightarrow 4 \text{Rb} + 2 \text{UN} + 5 \text{N}_2 + 6 \text{H}_2 \quad (11)$$

Our efforts to shed light on the thermal decomposition of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ and its reactions with (moist) air, as well as attempts to synthesize other complex amidouranates(IV) are ongoing.

One may argue that instead of the $\text{U}^{\text{IV}}$ compound $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$, the $\text{U}^{\text{VI}}$ amido imido complex $\text{Rb}_2[\text{U(NH}_2\text{)}_4(\text{NH}_2)]_2$ could have been obtained. While the discrimination in the X-ray diffraction experiment would be difficult as hydrogen atoms could not be located and the molecular anions could be disordered showing an average $\text{U}–\text{N}$ distance that would lie in between $\text{U}–\text{N}_{\text{amido}}$ and $\text{U}–\text{N}_{\text{imido}}$ distances, chemical reasoning excludes such $\text{U}^{\text{VI}}$ compounds. $\text{U}^{\text{IV}}$ is the most stable oxidation state in cold liquid ammonia and uranium cations in higher oxidation states are immediately reduced by ammonia to $\text{U}^{\text{IV}}$ or form only metastable compounds that are reduced over time. This of course is different for very high temperatures of several hundred °C, where ammonia can oxidize uranium to $\text{UN}_2$. See for example the works on the ammonolyses of uranium halides, [27–34] the works on uranium(IV) amides, [3] and our own works on both topics. [3] In this light, it seems highly unlikely for uranium to be oxidized by ammonia to an oxidation state which is usually unstable towards reduction – especially in a solution of strongly reducing solvated electrons.

We also investigated the structure and electronic properties of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ using quantum chemical calculations. We started the calculations using the subgroup $\text{Fm}$ (no. 202) which enables an ordered structural model for the hydrogen atoms of the amide ligands. However, in this space group the calculations always converged into a metallic ground state regardless of the initial f-orbital occupation of the $\text{U}^{\text{IV}}$ atom. Such behavior suggests that the wavelength breaks the crystallographic symmetry. Lowering the symmetry further to subgroup $\text{R}^3$ (no. 148) resulted in an insulating ground state with two f-electrons localized at the U atom ($\alpha$-spin bandgap 3.7 eV).

The optimized crystal structure of $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$ is given in the Supporting information. Harmonic frequency calculations showed the structure to be a true local minimum. The lattice parameter differs from the experimental value by −1.4%. The unit cell angles of the trigonal primitive cell are 60.26°, deviating by 0.4% from the perfect 60° angle in the original primitive cell of the face-centered cubic unit cell. The $\text{U}–\text{N}$ distance in the optimized structure is 2.36 Å, which is slightly longer in comparison to the $\text{U}–\text{N}$ distance of 2.274(15) Å obtained from the Rietveld refinement.

We also investigated a hypothetical $[\text{U(NH}_2\text{)}_4(\text{NH}_2)]^{2-}$ anion at the DFT-PBE0/def2–TZVP level of theory (the anionic charge was countered by a COSMO solvent field). Similar to $\text{Rb}_2[\text{U(NH}_2\text{)}_6]$, the symmetry of the molecular anion had to be reduced from $T_h$ to $D_{2h}$ to obtain the correct electronic state with two f-electrons localized at the U atom. In line with the solid-state calculation, the structure is a true local minimum, the HOMO–LUMO gap is 3 eV, and the optimized $\text{U}–\text{N}$ distance is 2.35 Å, which is close to the value of 2.274(15) Å. We structurally optimized also the $\text{U}^{\text{VI}}$ amido imido complex $[\text{U(NH}_2\text{)}_4(\text{NH}_2)]^{2-}$, in order to get an impression on the $\text{U}–\text{N}$
distances. The point group symmetry of this molecular anion is $C_{2h}$. The U–N$_{amido}$ distances are 2.34 Å and those of U–N$_{amide}$ are 1.93 Å, respectively. In quantum chemical solid-state calculations of Rb$_2$[U(NH$_2$)$_4$(NH)$_2$], the symmetry had to be lowered to the monoclinic crystal system ($C2/m$) in order to obtain a true local minimum structure. Then, however, all Rb···Rb and U···U distances completely disagree with the ones observed in Rb$_2$[U(NH$_2$)$_3$]. So, also from this purely theoretical point of view, the presence of such a U$^{IV}$ species is unlikely.

Conclusions

When more than three equivalents of RbNH$_2$ were reacted with UI$_3$ dissolved in anhydrous liquid ammonia, the typical color of solvated electrons was observed visually. The solvated electrons triggered ammonia reduction under evolution of hydrogen. UI$_3$ was oxidized to U$^{IV}$ and precipitated as a grey to black powder of highly pyrophoric rubidium hexaamidouranate(IV), Rb$_2$[U(NH$_2$)$_6$]. As evidenced from its powder X-ray diffraction pattern, the compound crystallizes in the K$_2$PtCl$_6$ structure type. Within the [U(NH$_2$)$_6$]$^{2-}$ anion, a U–N distance of 2.274(15) Å was determined from Rietveld refinement. Quantum chemical calculations for the solid-state compound as well as for the isolated [U(NH$_2$)$_6$]$^{2-}$ anion, where the U–N distance is calculated to 2.35–2.36 Å, agree well.

Experimental Section

Caution! Rb$_2$[U(NH$_2$)$_6$] turned out to be very sensitive towards air and several explosions occurred (really a dirty bomb…).

All work was carried out trying to exclude 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 under fine vacuum several times before utilization.

Synthesis of UI$_3$: UI$_3$ was prepared according to the literature.$^{[35]}$

Synthesis of RbNH$_2$: Rb was reacted with an excess of ammonia in the presence of a catalyst (trace of rust) at −78 °C and slowly warming to the boiling point.$^{[15]}$ After removal of the excess of NH$_3$, pure RbNH$_2$ was obtained as evidenced by powder X-ray diffraction.

Reaction of UI$_3$ with 5 Equivalents of RbNH$_2$: 31.1 mg (0.050 mmol, 1 equiv.) of UI$_3$ and 27.8 mg (0.274 mmol, 5 equiv.) of RbNH$_2$ were reacted in a flame-dried Schlenk tube with approximately 10 mL of liquid ammonia. The reaction mixture became brown and turned then blue due to solvated electrons. The solvated electrons triggered ammonia reduction under evolution of hydrogen. UI$_3$ was oxidized to U$^{IV}$ and precipitated as a grey-black powder. The precipitate formed during a strong evolution of gas. After filtration through the fritt and washing three times with ammonia, a colorless powder was obtained from which UI$_3$ crystallized after removal of NH$_3$. Samples for powder X-ray diffraction were obtained from both sides of the H-tube. Residual grey-black powder exploded with a sharp bang when brought from the glovebox to air.

To obtain single crystals and purify the grey-black powder of Rb$_2$[U(NH$_2$)$_6$] further by thoroughly removing RbI, a Soxhlet-like extractor for liquid ammonia was charged.$^{[16,37]}$ When evacuating the extractor for flame-sealing, the grey-black powder detonated with an orange flash destroying the extractor as soon as the powder on the fritt was swirled by the pumped-off argon (that due to a pinhole in the glassware contained some air, presumably).

Reaction of UI$_3$ with 8 Equivalents of RbNH$_2$: 224 mg (0.362 mmol, 1 equiv.) of UI$_3$ and 307.4 mg (3.029 mmol, 8 equiv.) of RbNH$_2$ were placed together with glass coated stirring bars into the separate tubes of an H-shaped reaction vessel. Both sides were filled with circa 10 mL of liquid ammonia each. The RbNH$_2$ solution was poured via the fritt to the UI$_3$-side of the H-tube. The mixture became immediately blue and a black precipitate formed during a strong evolution of gas. After filtration through the fritt and washing three times with ammonia, a colorless filtrate was obtained from which RbI crystallized after removal of NH$_3$. The precipitate of the H-tube 110 mg of an almost black powder – which appeared darker than in the synthesis described with six equivalents of RbNH$_2$ – were obtained. Unfortunately, the black powder appeared amorphous to X-rays but contained still a trace of RbI.

Powder X-ray Diffraction: The sample was filled into a borosilicate glass capillary with a diameter of 0.3 mm. The powder X-ray pattern was recorded with a StadiMP diffractometer (Stoe & Cie) in Debye–Scherzer setup. The diffractometer was equipped with a Cu-K$_{α1}$ radiation (1.5406 Å, germanium monochromator) and equipped with a MYTHEN 1 K detector. The diffraction pattern was indexed using the WinXPOW suite.$^{[38]}$ The extraction of integrated intensities a Le Bail decomposition was performed with the JANA2006 software.$^{[39]}$ In order to solve the structure the analogy to the K$_2$PtCl$_6$ structure...
type was used. Finally, a Rietveld refinement of the obtained structure model was performed with the JANA2006 software. In the course of this refinement, the reflection profiles were fitted with a pseudo-Voigt function. In addition to the profile parameters, a zero-shift parameter and a manual background were refined. The peak asymmetry was refined using a four-term Berar-Baldinozzi correction. A cylindrical absorption correction was applied. All atoms, except for the hydrogen atoms, which could not be located, were refined with isotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the deposition number CCDC-1993022 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Quantum Chemical Calculations: The solid-state quantum chemical calculations were carried out with the CRYSTAL17 program package.[40] PBE0 hybrid density functional method and Gaussian-type basis sets of triple-zeta-valence + polarization quality were used (split-valence + polarization for Rb).[41] The basis sets for H, N, and Rb have been previously derived from the molecular Karlsruhe def2 basis sets.[42–44] The basis set for U was a slightly modified version of the basis set used previously in the literature (details and full basis set listing in the Supporting Information).[45] The reciprocal space was sampled using a \(4 \times 4 \times 4\) Monkhorst-Pack-type \(k\)-point grid.[46] For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, and 16 were used. We carried out spin-polarized calculations as the UIV species possesses two unpaired \(f\)-electrons. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. The harmonic vibrational frequencies were obtained by using the computational schemes implemented in CRYSTAL.[47,48] Molecular calculations on \(\text{U}(\text{NH}_2)_6\)\(^+\) anion were carried out with TURBOMOLE program package at the DFT-PBE0/def2-TZVP level of theory (def-TZVP for U).[49,50] The anionic charge was countered using the BOMOLE program package at the DFT-PBE0/def2-TZVP level of chemically optimized structures.

The supporting information contains powder X-ray patterns, the computational schemes implemented in CRYSTAL.[47,48] Molecular models were calculated on \([\text{U}(\text{NH}_2)_6\]\(^–\) anion were carried out with TURBOMOLE program package at the DFT-PBE0/def2-TZVP level of theory (def-TZVP for U).[49,50] The anionic charge was countered using the BOMOLE program package at the DFT-PBE0/def2-TZVP level of chemically optimized structures.

Supporting Information (see footnote on the first page of this article): The supporting information contains powder X-ray patterns, the uranium basis set in CRYSTAL17 input format, and the quantum-chemically optimized structures.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for generous funding and Dr. Ivlev, Marburg, for helpful discussions. Computational resources were provided by CSC, the Finnish IT Center for Science. Open access funding enabled and organized by Projekt DEAL.

Keywords: Uranium; Amides; Liquid ammonia; Alkali metals; Ammonia reduction

References

[1] F. Kraus, BioInorganic React. Mech. 2012, 8, 29–39.
[2] F. Kraus, S. A. Baer, Chem. Eur. J. 2009, 15, 8269–8274.
[3] S. S. Rudel, S. A. Baer, P. Woidy, T. G. Müller, H. L. Deubner, B. Scheibe, F. Kraus, Z. Kristallgie, Cryst. Mater. 2018, 233, 817–844.
[4] J. M. Cleveland, G. H. Bryan, C. R. Heiple, R. J. Sironen, Nucl. Chem. 1975, 25, 541–545.
[5] G. Tschirne, D. Naumann, Z. Anorg. Allg. Chem. 1967, 354, 50–55.
[6] F. Kraus, S. A. Baer, A. J. Kartunnen, Z. Anorg. Allg. Chem. 2011, 637, 1122–1130.
[7] O. Ruff, J. Zedner, Ber. Dtsch. Chem. Ges. 1908, 41, 1948–1960.
[8] E. J. Kirschke, W. L. Jolly, Inorg. Chem. 1967, 6, 855–862.
[9] V. Doetsch, J. Jander, U. Engelhardt, C. Lafrenz, J. Fischer, H. Nagel, W. Renz, G. Türk, T. von Volkman, G. Weber, Chemistry in Anhydrous Liquid Ammonia - Part I - Anorganische Und Allgemeine Chemie in Flüssigem Ammoniak, Friedr. Vieweg & Sohn, Braunschweig, 1966.
[10] M. Gold, W. L. Jolly, Inorg. Chem. 1962, 1, 818–827.
[11] W. L. Jolly, Adv. Chem. Ser. 1965, 50, 27–35.
[12] W. L. Jolly, in Progress in Inorganic Chemistry (Ed.: F. A. Cotton), John Wiley & Sons, Inc., 1959, pp. 235–281.
[13] L. A. Seaman, S. Fortier, G. Wu, T. W. Hayton, Inorg. Chem. 2007, 63, 2641–2643.
[14] R. Juza, Angew. Chem. 1964, 76, 290–300.
[15] G. W. Watt, G. D. Barnett, L. Vaska, Ind. Eng. Chem. 1954, 46, 1022–1024.
[16] J. C. Warf, W. L. Korst, J. Phys. Chem. 1956, 60, 1590–1591.
[17] J. C. Warf, V. Gutmann, J. Inorg. Nucl. Chem. 1971, 33, 1583–1587.
[18] F. W. Bergstrom, J. Am. Chem. Soc. 1925, 47, 2317–2323.
[19] R. J. Williams, D. R. Dillin, W. O. Milligan, Acta Crystallogr., Sect. B 1973, 29, 1369–1372.
[20] G. Nocton, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. 2008, 47, 3040–3042.
[21] J. C. Berthet, M. Ephritikhine, Coord. Chem. Rev. 1998, 178–180, 83–116.
[22] K. Mayer, D. J. Minidola, T. A. Baker, W. M. Davis, C. C. Cummins, Angew. Chem. Int. Ed. 2000, 39, 3063–3066.
[23] L. A. Seaman, G. Wu, N. Edelstein, W. W. Lukens, N. Magnani, T. W. Hayton, J. Am. Chem. Soc. 2012, 134, 4931–4940.
[24] L. A. Seaman, S. Fortier, G. Wu, T. W. Hayton, Inorg. Chem. 2011, 50, 636–646.
[25] O. Schmitz-Dumont, F. Raabe, Z. Anorg. Allg. Chem. 1954, 277, 297–314.
[26] G. Beck, Z. Anorg. Allg. Chem. 1932, 206, 416–424.
[27] P. Spacu, Z. Anorg. Allg. Chem. 1936, 230, 181–186.
[28] J. Selbin, M. Schobert, J. D. Ortego, J. Inorg. Nucl. Chem. 1966, 28, 1385–1395.
[29] H. J. Berthold, H. Knecht, Z. Anorg. Allg. Chem. 1968, 356, 151–162.
[30] H. J. Berthold, H. Knecht, Z. Anorg. Allg. Chem. 1969, 366, 249–264.
[31] H. J. Berthold, H. Knecht, Angew. Chem. 1965, 77, 453–453.
[32] W. Burk, D. Naumann, Z. Anorg. Allg. Chem. 1966, 344, 306–315.
[33] W. Burk, Z. Chem. 1969, 9, 233–234.
[34] S. S. Rudel, H. L. Deubner, B. Scheibe, M. Conrad, F. Kraus, Z. Anorg. Allg. Chem. 2011, 644, 323–329.
[35] E. Zintl, O. Kohn, Ber. Dtsch. Chem. Ges. 1928, 61, 189–199.
[36] A. Stock, B. Hoffmann, Ber. Dtsch. Chem. Ges. 1903, 36, 895–900.
[37] STOE WinXPOW, STOE & Cie GmbH, Darmstadt, Germany, 2015.
[38] V. Petičček, M. Dušek, L. Palatinus, Z. Kristallogr., Cryst. Mater. 2014, 229, 345–352.
[39] R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalieri, L. Mascio, M. Rénat, S. Casassa, J. Baima, S. Salustro, et al., Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, e1360.
[40] C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158–6170.
[42] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[43] A. J. Karttunen, T. Tynell, M. Karppinen, *J. Phys. Chem. C* **2015**, *119*, 13105–13114.
[44] B. Scheibe, S. I. Ivlev, A. J. Karttunen, F. Kraus, *Eur. J. Inorg. Chem.* **2020**, DOI 10.1002/ejc.202000106.
[45] B. Scheibe, S. Lippert, S. S. Rudel, M. R. Buchner, O. Burghaus, C. Pietzonka, M. Koch, A. J. Karttunen, F. Kraus, *Chem. Eur. J.* **2016**, *22*, 12145–12153.
[46] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.
[47] F. Pascale, C. M. Zicovich-Wilson, F. López Gejo, B. Civalleri, R. Orlando, R. Dovesi, *J. Comput. Chem.* **2004**, *25*, 888–897.
[48] C. M. Zicovich-Wilson, F. Pascale, C. Roetti, V. R. Saunders, R. Orlando, R. Dovesi, *J. Comput. Chem.* **2004**, *25*, 1873–1881.
[49] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.
[50] University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, TURBOMOLE, TURBOMOLE GmbH, Karlsruhe, **2017**.
[51] A. Klamt, G. Schürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, *799–805.*

Received: February 21, 2020
Published Online: April 16, 2020