[UO$_3$(NH$_3$)$_5$]Br$_2$ · NH$_3$: Synthesis, Crystal Structure, and Speciation in Liquid Ammonia Solution by First-Principles Molecular Dynamics Simulations.†

Patrick Woidy,[a] Michael Bühl,[b,*] and Florian Kraus[c,*]

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Pentaammine dioxido uranium(VI) dibromide ammonia (1/1), [UO$_3$(NH$_3$)$_5$]Br$_2$ · NH$_3$, was synthesized in the form of yellow crystals by the reaction of uranyl bromide, UO$_2$Br$_2$, with dry liquid ammonia. The compound crystallizes orthorhombic in space group Cmcm and is isotypic to [UO$_3$(NH$_3$)$_5$]Cl$_2$ · NH$_3$ with $a = 13.2499(2)$, $b = 10.5536(1)$, $c = 8.9126(1)$ Å, $V = 1246.29(3)$ Å$^3$ and $Z = 4$ at 123 K. The UO$_3^{2+}$ cation is coordinated by five ammine ligands and the coordination polyhedron can be best described as pentagonal bipyramid. Car-Parrinello molecular dynamics simulations are reported for [UO$_3$(NH$_3$)$_5$]$^{2+}$ in the gas phase and in liquid NH$_3$ solution (using the BLYP density functional). According to free-energy simulations, solvation by ammonia has only a small effect on the uranyl-NH$_3$ bond strength.

1 Introduction

Fueled by continued industrial use and driven by advances in synthetic techniques, uranium chemistry has been blossoming of late.¹ One of the key elements in this development is the move from water to organic solvents, which has given access to a plethora of new uranium compounds with unusual oxidation states and new bonding motifs. However, one solvent that is quite common in inorganic synthesis has received relatively little attention so far in uranium chemistry, namely liquid ammonia. We have explored its use for preparative purposes and have added a number of uranium-ammonia compounds to the growing portfolio of uranyl(VI) and uranium(IV) complexes.²,³ We now report on a new compound that was isolated during our speciation studies, [UO$_2$(NH$_3$)$_5$]Br$_2$ · NH$_3$.

Liquid anhydrous ammonia is widely used in industry, mainly for refrigeration purposes. It has some attractive properties for use as a solvent, such as the possibility to work at low temperatures. Its polarity is between that of water, the traditional medium for uranyl(VI) chemistry, and that of inert organic solvents, which have led to the "renaissance" of uranium chemistry. It is thus conceivable that working in liquid ammonia can open up new avenues in uranium chemistry.

To understand the chemistry of uranium compounds in ammonia at an atomistic level and to help design new species and processes, e.g. for selective complexation and separation, first-principles modelling will be instrumental. For actinoid compounds in general, and uranyl complexes in particular, ab initio and density functional theory (DFT) calculations have a long history and are now well established.⁴ The vast majority of these studies attempt to model an aqueous environment, either by way of static optimisations and implicit solvation through polarisable continuum models (PCMs), or by explicit inclusion of the solvent in a dynamic ensemble. In the latter spirit, we have been using Car-Parrinello molecular dynamics (CPMD) simulations to model a number of uranyl complexes in aqueous solution.²,⁶,⁷ Using this method, together with a special numerical technique (pointwise thermodynamic integration, PTI), several thermodynamic and kinetic parameters of uranyl hydrate, [UO$_2$(H$_2$O)$_5$]$^{2+}$, have been reproduced with an accuracy of ca. ±2.5 kcal/mol. We have also reported the first CPMD simulations of uranyl complexes in a non-aqueous solvent (acetonitrile).⁵ We now apply this approach to the prototypical uranyl complex in ammonia, [UO$_2$(NH$_3$)$_5$]$^{2+}$. Special attention is called to the effect of the ammonia medium on the uranyl-NH$_3$ bond strength, as compared to that of an aqueous environment on the corresponding uranyl-water affinity in uranyl hydrate.

2 Experimental and Computational details

All experiments were carried out excluding humidity and air in an atmosphere of dried and purified argon (Westfalen AG) using a high-vacuum glass line or a glove box (MBraun). Liquid ammonia (Westfalen AG) was dried and stored over sodium (VWR) in a special high-vacuum glass line. All vessels used for reactions with liquid ammonia were made of borosilicate glass and flame-dried before use.

Synthesis and crystallization
UBr$_3$ was oxidized in anhydrous ammonia by bubbling O$_2$
through the solution which leads to formation of dissolved and solvated UO₂Br₂ besides Br₂ at -78 °C. The latter oxidizes ammonia under formation of N₂ and NH₃Br. Pure, anhydrous UO₂Br₂ was obtained by evaporation of the solvent at -34 °C and further heating to approximately 100 °C under a high vacuum (ca. 10⁻⁶ mbar) where further NH₃ and the NH₃Br are pumped off. 0.25 g (0.58 mmol) UO₂Br₂ were placed in a reaction flask under argon atmosphere. After cooling to -78 °C approximately 10 mL liquid ammonia were condensed on top of the red powder of UO₂Br₂, resulting in a clear yellow solution and a solid residue. Yellow single crystals of the title compound were obtained from storage at -40 °C after ten days. A suitable single crystal was selected under perfluoroether oil using the MiteGen system. As the compound is an ammoniate it is unstable upon warming above approximately -30 °C. The crystals burst due to the rising ammonia vapour pressure. Further analysis of the compound can therefore not be undertaken.

Structure Solution and Refinement

The structure was solved by using Direct Methods implemented in Shelxs and refined on F² using Shelxtl. The atoms (except for the hydrogen atoms) were located from the difference Fourier map. All atoms were refined anisotropically. The hydrogen atoms were added by using a riding model. The crystal structure does not show any features where special refinement procedures had to be applied. The residual electron densities are close to the uranium atom.

CPMD Simulations

Initial simulations were performed for a solution of [UO₂(NH₃)₃]Br in liquid NH₃. To facilitate comparison with previous work on aqueous uranyl, essentially the same methodology was used, namely CPMD / BLYP simulations using Troullier-Martins pseudopotentials, periodic boundary conditions with a plane-wave basis set (80 Ry cut-off), a fictitious electronic mass of 600 a.u., a time step of 0.121 fs and the mass of D instead of H. The complex was immersed in a cubic box with box size of 13.22 Å filled with 37 NH₃ molecules, corresponding to a density of 0.71 (this value was arrived at by taking the number of solvent water molecules in our previous simulation of aqueous UO₂Br₂ and scaling the density of the solvent from 1.0 to 0.61, the density of liquid NH₃ at 20 °C). The starting structure was built from a well-equilibrated solution of [UO₂(H₂O)₃]⁺ in water, changing O to N, deleting the appropriate number of solvent molecules and adding the missing H atoms. The system was first equilibrated in the NVE ensemble for 2 ps maintaining a temperature of 273 ± 50 K using velocity rescaling, then propagated freely for another 7 ps, at the end of which the temperature had equilibrated to 283 ± 13 K. Analogous simulations have been performed for in [UO₂(NH₃)₃]Br⁺ in the gas phase, starting from the fully optimised minimum (the latter denoted CP-opt); these simulations have been run for 3 ps, after which the temperature has equilibrated to 317 ± 41 K. For the free-energy PTI simulations the distance r between U and one N atom of a bound ammonia ligand was taken as reaction coordinate and elongated in steps of 0.2 Å until the resulting free-energy profile levelled off (see Supporting Information for further details). These computations were performed with the CPMD program.

The BLYP functional was chosen because of its good performance for the properties of liquid NH₃. Because the simulations were performed at constant volume, Helmholtz rather than Gibbs free energies are obtained, but in condensed phase the difference between both is very small. No further dissection of the free energies into enthalpic and entropic contributions (which would require, in principle, simulations at different temperatures) was attempted.

Selected nonperiodic geometry optimisations were performed at BLYP, and B3LYP levels, employing the small-core Stuttgart-Dresden relativistic ECP together with its valence basis set on U [17] (from which the most diffuse s-,p-,d-, and f-functions were omitted, affording a [7s6p5d3f] contraction), standard 6-311G+(d,p) basis [19] for all other elements, and an ultrafine integration grid (99 radial shells with 590 angular points per shell), denoted SDD. The minimum character of each stationary point was verified by computation of the harmonic vibrational frequencies, which were all real. Selected structures were reoptimised in a polarisable continuum (IEF-PCM, see supporting information for details and references) and subject to natural population and natural bond orbital analysis. These computations were performed with the Gaussian suite of programs.

3 Results and discussion

3.1 Structures

Yellow crystals of pentaamine dioxido uranium(VI) dibromide ammonia (1/1), [UO₂(NH₃)₅]Br₂ · NH₃, were prepared from the reaction of UO₂Br₂ with dry liquid ammonia according to equation 1.

\[ \text{UO}_2\text{Br}_2 + 6 \text{NH}_3 \rightarrow [\text{UO}_2(\text{NH}_3)_5]\text{Br}_2 \cdot \text{NH}_3 \] (1)

![Figure 1: The pentaamine dioxido uranium(VI) dication of the title compound. Displacement ellipsoids are shown at the 70 % probability level at 123 K. H atoms omitted. [Symmetry codes: (i) x, y, z + 1/2; (ii) −x + 1, y, z + 1/2.]]
The title compound crystallizes in the orthorhombic space group Cmcm (No. 63) isotypic to the previously reported [UO₂(NH₃)₃]Cl₂·NH₃.² The uranium atom occupies the 4c position, and the oxygen atom O1 the 8f position forming with its symmetry equivalent the uranyl cation. The [UO₂]²⁺ cation is coordinated by five ammine ligands (N1, N2 and N3 and their symmetry equivalents). A projection of the discrete pentammine dioxido uranium(VI) cation, [UO₂(NH₃)₅]²⁺, is shown in Figure 1. The ammonia molecule of crystallization occupies the 4c and the bromide anion the 8e position. The U–O distance of the almost linear uranyl cation (O–U–O angle of 179.1(2)°) is 1.771(3)Å. Comparable distances were reported for the alkali metal uranyl nitrates M[UO₂(NO₃)₂] with M= K,²³,²⁴ Rb,²⁵,²⁶ and Cs²⁷ of 1.746 to 1.795Å. The U–N distances of the title compound are observed in a range from 2.522(3) to 2.577(3) Å. The U–N distances of the isotypic compound [UO₂(NH₃)₅](Cl₂·NH₃) (2.505(2) to 2.554(3) Å) or the compound [UO₂F₂(NH₃)₆]·2 NH₃ (2.526(4) to 2.567(3) Å) differ only slightly from the U–N distances reported here.²

In [UF₄(NH₃)₅]∙NH₃ longer U–N distances of 2.618(5) Å were reported due to the higher coordination number.³ The closest U–Br distances are observed with 4.9480(3) Å, which is marginally shorter compared to the isotypic chloride (4.9554(3) Å). The compound shows N–H…Br and N–H…N hydrogen bonding, but caution is advised for its discussion as the N atoms reside on special positions (N(1) on m2m, N(2, 3) on ..m). Therefore only the H atoms on N(2) and N(3) could be located properly. The hydrogen atoms bound to the N(2) atom form N–H…Br hydrogen with H…Br distances in the range of 2.67 to 2.99 Å, and N–H…Br angles from 124.5 to 172.3°. The H atoms on N(3) form two N–H…Br hydrogen bonds with H…Br distances of 2.59 and 2.76 Å, and angles of 177.0 and 139.4°, respectively. The third H atom on N(3) forms a N–H…N hydrogen bond with a H…N distance of 2.24 Å and an N–H…N angle of 159.2°. These hydrogen bond parameters are comparable to the ones previously reported.² The unit cell of the title compound [UO₂(NH₃)₅]Br₂·NH₃ is shown in Figure 2, crystallographic details are available from Table 1.

![Figure 2: The unit cell of the title compound. Displacement ellipsoids are shown at the 70 % probability level at 123 K. H atoms omitted.](image)

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<th>Table 1. Crystallographic details of the title compound. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen (Germany), <a href="http://www.fiz-karlsruhe.de/icsd.html">http://www.fiz-karlsruhe.de/icsd.html</a>, on quoting the depository number CSD- 429046.</th>
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Subsequently we studied the pristine [UO₂(NH₃)₅]²⁺ cation of the title compound computationally. The observed five-coordination mode remained stable in vacuo and in ammonia solution (i.e. no spontaneous dissociation or association of ligands occurred). The resulting structural parameters are collected in Table 2.

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<th>Table 2. Optimised or mean simulated bond distances in [UO₂(NH₃)₅]²⁺ (in Å).</th>
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<td><strong>Level</strong>³⁴</td>
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³⁴CPMD: mean values during 2 ps of unconstrained MD (BLYP level, standard deviation in parentheses) in the gas phase (g) or liquid ammonia solution (l); BLYP, B3LYP: optimised parameters using the respective functional (SDD/6-311+G**basis) in the gas phase (g) or a polarisable continuum (PCM). ²²Mean values. ³⁵This work.
On going from the gas phase into solution, the U-N distance is computed to decrease notably, by ca. -7 pm (compare CPMD(g) and CPMD(l) values in Table 2). A similar decrease (-6 pm) had been observed for the U-O(water) bond in the pentahydrate upon solvation.\(^{12}\) A slightly smaller, but still notable contraction of ca. -4 pm is obtained upon immersion in a polarisable continuum (compare BLYP(g) and BLYP(PCM) values in Table 2). The simulated mean U-N distance in solution, 2.62 Å, is notably elongated compared to that found experimentally in the title compound in the solid\(^{28}\) (2.522(3) to 2.577(3) Å). It is likely that the BLYP functional employed in the CPMD simulations (which is used for its good description of liquid water and NH\(_3\))\(^{13}\) inherently overestimates this distance, as frequently found for metal-ligand distances in general.\(^{29}\) A slight decrease is found on going to a hybrid functional (compare BLYP(g) and B3LYP(g), or BLYP(PCM) and B3LYP(PCM) data in Table 2), but using this in the MD simulations would be too expensive.

The structure of [UO\(_2\)(NH\(_3\))\(_5\)]\(^{2+}\) in liquid NH\(_3\) was further characterised in terms of the U-N pair correlation (or radial distribution) function displayed in Figure 3. The width of the first maximum between 2.4 and 3.0 Å illustrates the soft binding mode of the ammonia ligands, which is also reflected in the large standard deviations of the averaged distances in Table 1 (numbers in parentheses).

There is clear indication of a second solvation shell, manifest in a broad maximum of the U-N pair correlation function between ca. 4 Å and 5.5 Å (maximum value \(g_{UN} \approx 2.1\)). Integration of the pair correlation function between 3.9 Å and 5.75 Å (where \(g_{UN}\) assumes the lowest value in this area) affords a mean number of 12 ammonia molecules within this second solvation sphere\(^{11}\).

### 3.2 Uranyl-NH\(_3\) Bond Strength

In gaseous [UO\(_2\)(H\(_2\)O)\(_3\)]\(^{2+}\) one water ligand is unbound at the BLYP level, i.e. a “4+1” structure with a water molecule H-bonded to [UO\(_2\)(H\(_2\)O)\(_3\)]\(^{2+}\) in the second hydration shell is more stable by -2.2 kcal/mol, and it is only in aqueous solution that the regular five-coordination is preferred (Figure 4a).\(^{12}\) In contrast, all five ammonia ligands in [UO\(_2\)(NH\(_3\))\(_5\)]\(^{2+}\) are bound in the gas phase already. This is found in static geometry optimisations, where [UO\(_2\)(NH\(_3\))\(_4\)]\(^{2+}\)NH\(_3\) is higher in energy than [UO\(_2\)(NH\(_3\))\(_3\)]\(^{2+}\) (by \(\Delta E = 6.4, 5.3\), and 8.2 kcal/mol at the CP-opt, BLYP(g) and B3LYP(g) levels, respectively). The same is apparent upon tracing the free-energy pathway for NH\(_3\) dissociation using constrained MD and thermodynamic integration, where the dissociation is endergonic (by \(\Delta A = 5.3\) kcal/mol, see the dotted pathway in Figure 4b).

That uranyl intrinsically (in the gas phase) binds NH\(_3\) stronger than water is borne out by direct assessment via:

\[
[UO_2(NH_3)_5]^{2+} + 5 H_2O \rightarrow [UO_2(H_2O)_3]^{2+} + 5 NH_3,
\]

for which \(\Delta E = +21.9\) kcal/mol is computed at the BLYP (g) level [+20.9 kcal/mol at B3LYP(g)]. An even stronger intrinsic preference of N-donor ligands over water had been noted previously for acetonitrile.\(^{33}\)

Solvation stabilises the five-coordinate ground state of [UO\(_2\)(NH\(_3\))\(_5\)]\(^{2+}\), so that the free energy of dissociation is increased to \(\Delta A = 9.1\) kcal/mol in liquid NH\(_3\) (passing over a shallow barrier of \(\Delta A' = 10.9\) kcal/mol). This finding is in line with the decrease of the mean U-N bond upon solvation discussed above.

The absolute computed uranyl-ligand bond strengths in the respective solvents are thus indicated to be surprisingly...
similar for water and ammonia (both ca. 9 kcal/mol). The relative solvation effects (with respect to the gas phase) are predicted to be quantitatively different, however: the higher coordination number is favoured in solution by ca. 11 kcal/mol and by ca. 4 kcal/mol for water and ammonia, respectively (compare Figure 4a and 4b). The apparent reduction of solvation effects on uranyl-ligand bond strengths in ammonia may be good news for continuum solvation models, because the accuracy of these models tends to deteriorate with increasing strength of specific solute-solvent interactions. Detailed performance studies of such PCM methods are beyond the scope of the present investigation, however.

According to natural population analysis, the bonding between U and N in \([\text{UO}_2(\text{NH}_3)_6]^2+\) is largely ionic, but with significant covalent character: the Wiberg bond index (WBI),\(^\text{33}\) which approaches values close to 1 for fully covalent single bonds, is 0.44 between U and N (BLYP/PCM level), and a natural bond orbital (NBO) analysis finds five localised U-N NBOs, which are however highly polarised toward N (12% contribution from U with comparable shares from s, p, d, and f orbitals). These bonds provide a means for charge transfer to the metal, as reflected in a natural charge of +0.69 for the \(\text{UO}_2\) moiety, as opposed to +2 for bare \([\text{UO}_2]^2+\). The U-OH\(_2\) bond in \([\text{UO}_2(\text{H}_2\text{O})_3]^2+\) is computed to have a slightly higher ionic character (U-O WBI of 0.43 and natural charge of +0.81 on \(\text{UO}_2\) at the same level).

The NH\(_3\) dissociation in Figure 4b is a possible mechanism for ligand/solvent exchange in \([\text{UO}_2(\text{NH}_3)_5]\text{Br}_2\cdot\text{NH}_3\), an alternative associative pathway via a six-coordinate intermediate or transition state needs to be studied (in analogy with the aquo complex, where such an associative interchange is preferred).\(^\text{35}\)

4 Conclusions

In summary, we have structurally characterised a new member of the family of pentaamine uranyl complexes, \([\text{UO}_2(\text{NH}_3)_5]\text{Br}_2\cdot\text{NH}_3\), which can be readily prepared in liquid ammonia. We have further characterised the structure of the pristine cation, \([\text{UO}_2(\text{NH}_3)_5]^2+\), in the same solvent through the first DFT/BLYP-based CPMD simulations of this system. According to free-energy simulations the uranyl-NH\(_3\) bond strength in ammonia is similar to that of the uranyl-water bond in aqueous \([\text{UO}_2(\text{H}_2\text{O})_4]^2+\), ca. 9 kcal/mol. However, the effect of the solvent on this property is markedly weaker for ammonia than for water. This effect is still noticeable in ammonia, though (reinforcement of the bond strength by 4 kcal/mol with respect to the gas phase). Thus, uranyl chemistry in this solvent may indeed be different from that in water or in truly inert organic solvents.

Our findings open up numerous opportunities for joint experimental and computational studies to explore and design new uranium chemistry. The renaissance of this chemistry may not be approaching its end just yet.

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Notes and references


6 For more recent applications of this technique see e.g.: (a) M. Bühl, I. Grenthe, Dalton Trans., 2011, 40, 11192-11199; (b) M. Bühl, N. Sieffert, G. Wipff, Dalton Trans., 2014, 43, 1129-1137.


9 (a) G. M. Sheldrick, SHELXS-97, Göttingen (Germany), 1997; (b) G. M. Sheldrick, SHELXL-97, Göttingen (Germany), 1997.


14 We did not explore more sophisticated reaction coordinates such as coordination numbers. Using a simple distance as constraint could introduce some bias, but the concomitant error is probably smaller than that from the other approximations involved. For proton transfers, for instance, free energies within 4 kJ/mol had been obtained using either a simple X-H distance as coordinate or the coordination number about H, e.g. for water: (a) M. Sprik, *Chem. Phys.*, 2000, **258**, 139-150; or for histidine: (b) I. Ivanov, M. Klein, *J. Am. Chem. Soc.*, 2002, **124**, 13380-13381.


18 This small-core ECP has been shown to reproduce all-electron scalar relativistic results very well, see: S. O. Odoh, G. Schreckenbach, *J. Phys. Chem. A*, 2010, **114**, 1957-1963.


22 M. J. Frisch, et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009 (see SI for full references).


28 Part of this discrepancy could also stem from the presence of the counteranions in the crystal, although in view of the similarity of the U-N distance with different coligands and counterions discussed above, this does not seem to be the overriding factor.


30 For DFT computations see: (a) M. Bühl, N. Sieffert, A. Chaumont, Georges Wipff, *Inorg. Chem.*, 2011, **50**, 299–308; (b) M. Bühl, N. Sieffert, A. Chaumont, Georges Wipff, *Inorg. Chem.*, 2012, **51**, 1943–1952; these findings are consistent with with experiments using electrospray ionization and ion-cyclotron resonance, where [UO₃(MeCN)₃]²⁻ species (n = 1–4) readily take up water or acetonitrile, but the complex with n = 5 does not (i.e. water does not displace acetonitrile in the gas phase); (c) Van Stipdonk, M. J.; Chien, W.; Bulleigh, K.; Wu, Q.; Groenewold, G. S. *J. Phys. Chem. A* 2006, **110**, 959-970; also gas-phase vibrational spectroscopy of [UOₓ(XIS)ₓ]²⁻ species (X = anionic ligand) showed a more pronounced redshift of the v₇ asymmetric UO₂ stretch (indicative of a stronger donor/acceptor) interaction for S = NH₃ than S = H₂O; (d) G. S. Groenewold, A. K. Gianotto, M. E. McIlwain, M. J. Van Stipdonk, M. Kullman, D. T. Moore, N. Polfer, J. Oomens, I. Infante, L. Visscher, B. Siboulet, W. A. de Jong, *J. Phys. Chem. A* 2008, **112**, 508–521.
