

Review

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Fluorine chemistry meets liquid ammonia

Abstract: Chemistry of metal and non-metal fluorides in liquid ammonia is often severely hampered, due to the low solubility of inorganic fluorides. This can be overcome by applying either strongly oxidizing fluorides, appropriate fluoride ion acceptors, or by the reduction or conversion of fluorides using solvated electrons. The article summarizes the state-of-the-art of the chemistry of inorganic fluorides in liquid ammonia, with special emphasis on compounds of beryllium, silver and uranium.

Keywords: beryllium; inorganic fluorides; liquid ammonia; silver; uranium.

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Introduction

The knowledge about reactions of fluorides in liquid ammonia is very limited. In 1898, Kraus and Franklin commented on the solubility of metal fluorides in ammonia that “the fluorides are insoluble” (Franklin and Kraus, 1898). Due to the high lattice energies of many fluorides and to the resulting low solubilities, reactions of fluorides in ammonia remained largely unexplored. Fluorides like NH_4F , alkali and alkaline earth metal fluorides, many transition metal fluorides, rare earth and actinide fluorides are insoluble in liquid ammonia (Jander et al., 1966; Dougal et al., 1988; Lagowski, 2007). Exceptions are AgF , LiF , NaF , BeF_2 , BF_3 , SiF_4 , and UF_6 (Jander et al., 1966). Biltz and coworkers obtained the ammoniates of some of the insoluble fluorides by extracting hydrates of the fluorides with liquid ammonia. This way, they obtained the ammoniates of AlF_3 , GaF_3 , InF_3 , MnF_2 , FeF_2 , CoF_2 , NiF_2 , AgF , and ZnF_2 and characterized them by tensiometric (vapour pressure and gas volume) measurements or by elemental analysis (Biltz et al., 1927). Patil and Secco carried out thermal analysis on ammoniates of bivalent metal fluorides (Patil and

Secco, 1972). X-ray structural studies were carried out and compounds like $[\text{BF}_3(\text{NH}_3)]$, $[\text{SiF}_4(\text{NH}_3)_2]$, $[\text{Zr}(\text{NH}_3)_4\text{F}_4]$, $[\text{Hf}(\text{NH}_3)_4\text{F}_4]$, $[\text{Ga}(\text{NH}_3)_3\text{F}_3]$, and $[\text{Ga}(\text{NH}_3)_2\text{F}_3]$ were characterized (Plitzko and Meyer, 1996; Plitzko et al., 1997; Roos and Meyer, 1999; Göbbels et al., 2002). Ammoniates like $[\text{Sn}(\text{NH}_3)_4]\text{F}_2$ have been considered as precursors for nitride fluorides (Woodward et al., 1998), of which only MNF ($M = \text{Ti}, \text{Zr}, \text{Hf}, \text{U}$) (Juza and Sievers, 1968; Yoshihara et al., 1969; Jung and Juza, 1973a,b), M_2NF ($M = \text{Mg}, \text{Sr}$) (Andersson, 1970; Wagner, 2002; Brogan et al., 2012), one iron (Menil et al., 1975), and some rare earth metal (Tanguy et al., 1971, 1972; Pezat et al., 1976; Vecher et al., 1984; Vogt et al., 1989) and zinc nitride fluorides (Marchand and Lang, 1971) are known. Only two anionic nitride fluorides, $[\text{TcNF}_4]^-$ and $[\text{ReNF}_4]^-$, have been described (Baldas et al., 1997; Voigt et al., 1998). Recently the first quaternary nitride fluoride $\text{Ce}_2\text{MnN}_3\text{F}_{2-\delta}$ was obtained by direct fluorination of Ce_2MnN_3 (Headspith et al., 2009). Nitrides such as Li_3N , Be_3N_2 , BN , Si_3N_4 , TiN and VN react with F_2 , if at all, only under formation of N_2 and the pure fluoride (Schumb and O'Malley, 1964). Nitride fluorides, however, are an interesting class of compounds and should – due to the analogy $\text{N}^{3-} + \text{F}^- \approx 2\text{O}^{2-}$ – feature properties similar to oxides (Headspith and Francesconi, 2009).

The information about amide and imide fluorides is also very limited. The existence of amide and imide fluorides of boron has been shown by mass spectroscopy (Göbbels et al., 2002) and the crystalline amide fluorides $\text{Ga}(\text{NH}_3)(\text{NH}_2)\text{F}_2$ and $\text{Sn}(\text{NH}_2)_2\text{F}_2$ were obtained in solid-state reactions (Weber et al., 1998; Roos and Meyer, 1999b).

The number of reactions of fluorides with liquid or gaseous ammonia is very small compared to the corresponding reactions of the other halides, pseudo halides, Zintl anions and related compounds. In some reviews of “liquid ammonia chemistry” the fluorides are not mentioned at all (Dougal et al., 1988; Lagowski 2007). However, the reactions of BF_3 , SiF_4 and SF_4 with NH_3 have been investigated in great detail (Gay-Lussac and Thenard, 1809; Davy, 1812; Brown and Johnson, 1945; Cohen et al., 1966; Plitzko and Meyer, 1996; Göbbels et al., 2002; Kraus and Baer, 2010).

Mixed anionic compounds of other halides with nitrogen-containing anions are much more common. These compounds have very different physical and chemical properties compared to the fluorides (Jung and Juza, 1973b).

Recently we have shown that if appropriate reaction conditions are employed, liquid ammonia is a much better solvent for inorganic fluorides than expected (Meng 2008; Kraus and Baer, 2009, 2010, 2011a,b; Kraus et al., 2009a,b, 2011, 2012; Baer and Kraus, 2010). Subsequently we investigated the chemistry of inorganic fluorides in liquid ammonia solution in more detail.

Discussion

For successful fluorine chemistry in liquid ammonia, the solvation problem has to be “solved”. Biltz and Rahlfs used the extraction of fluoride hydrates with liquid ammonia (Biltz and Rahlfs, 1927). These hydrates dissolve reasonably well in liquid ammonia, because they have lower lattice energies compared to those of the anhydrous fluorides, and water dissolves excellently in liquid ammonia. By this method, they synthesized several ammoniates of fluorides (Biltz et al., 1913; Biltz, 1914a,b, 1925a,b; Biltz and Stollenwerk, 1920, 1921; Biltz and Hüttig, 1921; Biltz and Fischer, 1922, 1923; Biltz and Hansen, 1923; Biltz and Messerknecht, 1923, 1925; Biltz and Mau, 1925; Biltz and Wein, 1925).

We came up with three different approaches in order to perform fluorine chemistry in liquid ammonia:

1. Usage of compounds with atoms in high oxidation states.
2. Usage of strong fluoride ion acceptors.
3. Usage of ammonia-soluble metals for the conversion of fluorides.

Usage of compounds with atoms in high oxidation states

The employment of elemental fluorine or other strong fluorooxidants (ClF_3) in general leads to high oxidation states. If metal fluorides with elements in a high oxidation state are brought into contact with liquid ammonia at low temperatures, the NH_3 molecule is oxidized and nitrogen is produced. At the same time, the metal fluoride is reduced and dissolved in NH_3 . This method of “dissolving insoluble fluorides” has been called the “reactive fluoride route” (Meng and Kraus, 2008). As the liquid ammonia solvent system shows some similarities to the aqueous system, one may think that a correlation of redox potentials should exist. The redox potentials available for oxidizers refer,

as usual, to the aqueous system. However, due to differences in solvation enthalpies of the two solvent systems, standard potentials do differ, leading to pronounced differences. For example, Cu and Cu(II) should spontaneously form Cu(I) in liquid ammonia; in water, disproportionation is thermodynamically favored. However, pure thermodynamic reasoning is also improper; NH_3 has a very narrow window of electrochemical stability of only 0.04 V, but it is kinetically very stable, as large overpotentials can be present (Jander et al., 1966). So, redox potentials may only serve as an aid for the choice of proper systems, but other effects have to be taken into account, which must be established experimentally.

Two new compounds containing cesium fluoride have been obtained as side-products from the reactions of Cs_2CuF_6 and Cs_2KDYF_6 , which are both strong oxidizers, with liquid ammonia. To the best of our knowledge, no redox potentials have been determined for compounds containing Cu(IV). Cs_2CuF_6 reacts under the formation of the blue compound $[\text{Cu}(\text{NH}_3)_5]\text{F}_2 \cdot \text{NH}_3$, and the colorless ammoniate $\text{Cs}_3\text{F}_3(\text{NH}_3)_4$ (Figure 1) (Baer and Kraus, 2010). The latter is also obtained from the reaction of BeF_2 with CsNH_2 in liquid ammonia. $\text{Cs}_3\text{F}_3(\text{NH}_3)_4$ represents the first ammoniate of the “insoluble” alkali metal fluorides. The reaction of Cs_2KDYF_6 leads to colorless crystals of NH_4CsF_2 (Figure 1) (Baer and Kraus, 2010), which could not be obtained from solutions of NH_4F and CsF in liquid ammonia, or from aqueous solutions.

Chemistry of silver in high oxidation states

Silver compounds with the element in the higher oxidation states Ag(II) or even Ag(III) are accessible via fluorine chemistry. These highly oxidized silver cations are strong oxidizing agents, and thus the “insoluble fluorides” (Franklin and Kraus, 1898) are expected to react with ammonia, and the resulting Ag(I) cations should be solvated. It is well known that Ag^+ cations can easily be converted into the diammine silver(I) complex with aqueous ammonia. We prepared compounds with the compositions $\text{Ag}_3\text{M}_2\text{F}_{14}$ ($M=\text{Zr}, \text{Hf}$), AgF_2 and AgF and reacted them with liquid ammonia. The intense colors of the silver(II) compounds vanished immediately upon contact with ammonia, and the evolution of nitrogen was observed. From these reactions, we obtained compounds like $[\text{Ag}(\text{NH}_3)_2]\text{F} \cdot 2\text{NH}_3$ (Figure 2), $\text{N}_2\text{H}_7\text{F}$ (Figure 3), $[\text{MF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$ (isotypic to the uranium compound, see Figure 4), and $[\text{Ag}(\text{NH}_3)_3(\mu\text{-NH}_3)\text{Ag}(\text{NH}_3)_4][\text{MF}_6]$ ($M=\text{Zr}, \text{Hf}$) (Figure 3) (Meng and Kraus, 2008; Kraus et al., 2009a). As an example, the reduction of AgF_2 is given in Eq. (1):



AgF_2 is reduced to Ag(I) , thereby forming the first structurally characterized halide salt of the well-known diammine silver(I) cation as an ammoniate. Nitrogen and $\text{N}_2\text{H}_7\text{F}$ are produced as byproducts.

Chemistry of uranium in high oxidation states

From the available literature, it has become obvious that those reactions of uranium which have been explored, are mainly

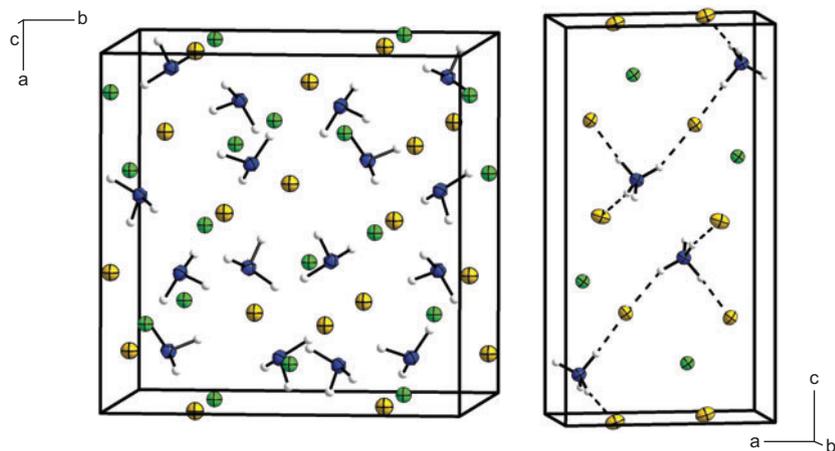


Figure 1 The unit cells of $\text{Cs}_3\text{F}_3(\text{NH}_3)_4$ and NH_4CsF_2 . Displacement parameters at 70% at -150°C .

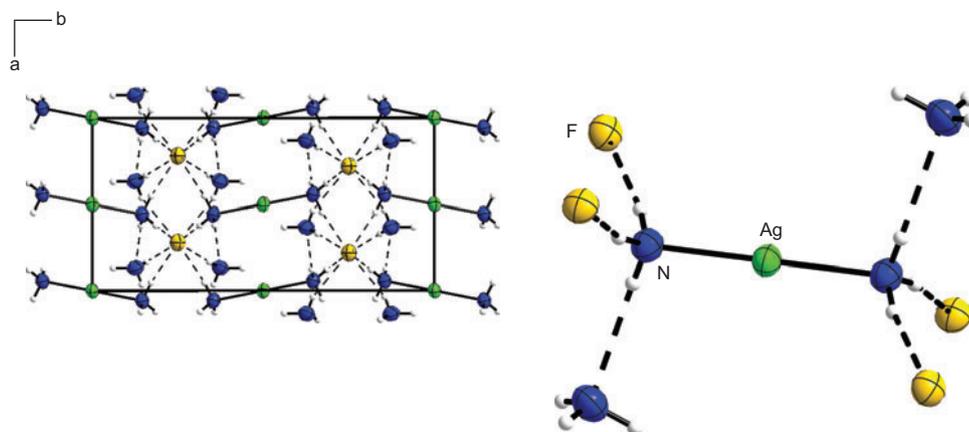


Figure 2 The unit cell of $[\text{Ag}(\text{NH}_3)_2]\text{F}\cdot 2\text{NH}_3$ and the hydrogen bonding of the $[\text{Ag}(\text{NH}_3)_2]^+$ cation to adjacent fluoride ions and ammonia molecules. Displacement parameters at 70% at -150°C .

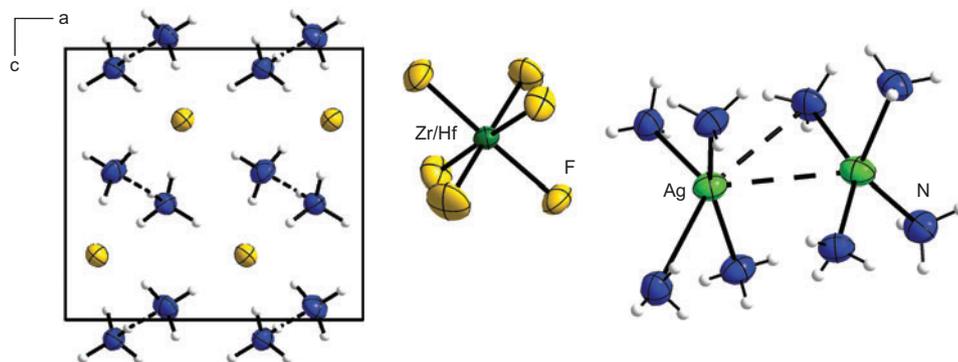


Figure 3 The unit cell of $[\text{N}_2\text{H}_7]\text{F}$ and the molecular structures of $[\text{Ag}(\text{NH}_3)_3(\mu\text{-NH}_3)\text{Ag}(\text{NH}_3)_4][\text{MF}_6]$ ($M=\text{Zr, Hf}$). Displacement parameters at 70% at -150°C .

relevant for mining, purification and isotope separation. However, in the last couple of years, uranium chemistry has been revisited, especially in the field of organometallic chemistry. Molecular uranium compounds are used for the catalytic activation of nitrogen and carbon dioxide (Ephritikhine, 2006; Bart and Meyer, 2008; Fox et al., 2008); organometallic hexakisamido complexes of uranium have been prepared (Meyer and Minidola, 2000; Meyer et al., 2000), as well as organometallic imido complexes, (Berthet et al., 2008) and rings of uranium with alternating nitride and azide bridges (Evans et al., 2005). Recently, an organometallic nitrido cluster of uranium was isolated (Nocton et al., 2008a,b). More uncommon oxidation states of uranium, like U(V), have been stabilized using appropriate ligands (Graves and Kiplinger, 2009), and we have focused on purely inorganic systems considering the choice of ligands and the solvents used.

Berthold and coworkers investigated some ammonolysis reactions of uranium halides and were able to prepare an imide chloride of uranium (Berthold and Knecht, 1965a,b,c,d, 1966a,b, 1969; Berthold and Delliehausen, 1966; Berthold et al., 1966; Berthold and Hein, 1969). At the same time, Burk considered the formation of amide halides in reactions of UCl_3 and UBr_3 with ammonia as unlikely; UCl_4 and UBr_4 , however, form a series of mixed anionic compounds, and also the pure nitrides could be obtained (Burk and Naumann, 1966, 1969; Burk, 1967, 1969). Both Berthold and Burk used temperatures between 20 and 1000°C for their experiments. The reactions of uranium halides with organo-substituted amides like $[\text{N}(\text{SiMe}_3)_2]^-$ led to uranium amide complexes (Drozdzyński, 2005). However, information on the reactions with pure amides remained elusive. In reactions of uranium tetrafluoride, Berthold and coworkers obtained emerald-green crystals (Berthold and Delliehausen, 1966b), however, Burk did not observe any reaction with UF_3 or UF_4 in NH_3 (Burk, 1969). We confirmed the existence of the emerald-green crystals and elucidated their composition and structure to be $[\text{UF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$ (Figure 4) (Kraus and Baer, 2009).

At high temperatures, Berthold and coworkers obtained crystalline amide and imide fluorides of U(III), which were said to crystallize in the fluorite-type structure

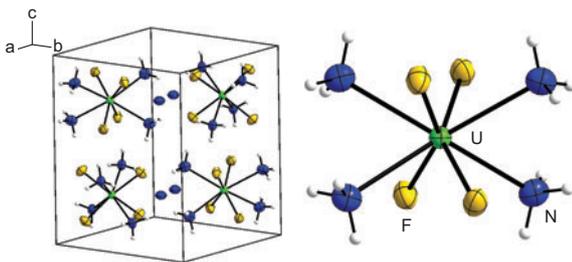


Figure 4 The unit cell of $[\text{UF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$ and molecular structure of $[\text{UF}_4(\text{NH}_3)_4]$. Displacement parameters at 70% at -150°C .

(Berthold and Hein, 1969). Juza and coworkers were able to obtain the mixed anionic compounds UNCl , UNBr and UNI from the tetrahalide and ammonia at high temperatures (Juza and Meyer, 1969). Molecular NUF_3 was observed spectroscopically at 4 K (Andrews et al., 2008). These results prompted us to attempt the synthesis of such compounds in liquid ammonia at low temperatures.

Redox reactions of uranium compounds in liquid ammonia seem to be limited. Galkin and coworkers observed the reduction of UF_6 by NH_3 leading to a uranium(V) compound (Galkin et al., 1960). In our own studies, we found that this reduction leads to a uranium(IV) compound, namely $(\text{NH}_4)_2(\text{N}_2\text{H}_7)[\text{UF}_7(\text{NH}_3)]$ (Figure 5) (Kraus and Baer, 2009).

It is interesting to note that Kline and Kerschner used silver(I) acetate in liquid NH_3 for the oxidation of a green uranium(IV) to a yellow U(VI) compound under deposition of Ag (Kline and Kerschner, 1966). We, however, were not able to reproduce this result.

Depleted uranium hexafluoride $^{238}\text{UF}_6$ is available worldwide in enormous amounts; the production of 1 ton of enriched uranium (3–5% ^{235}U) for nuclear power stations leads to about 7 tons of depleted uranium. However, the long-term storage of UF_6 is problematic due to its corrosivity. Thus, the conversion into less-reactive substances would be desirable. UF_6 reacts with NH_3 already at -78°C . The products of this reaction have only been characterized by elemental analysis (Galkin et al., 1960). We studied the reaction of UF_6 with liquid NH_3 in more detail and characterized all reaction products, which are N_2 , emerald green $[\text{UF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$, and signal green $(\text{NH}_4)_2(\text{N}_2\text{H}_7)[\text{UF}_7(\text{NH}_3)]$ (see above) (Kraus, 2009).

Usage of strong fluoride ion acceptors

Fluoride ion abstraction in liquid ammonia may afford amide, imide and nitride fluorides and may very well also

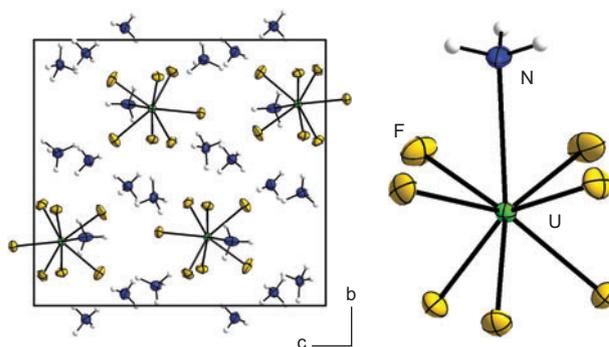


Figure 5 The unit cell of $(\text{NH}_4)_2(\text{N}_2\text{H}_7)[\text{UF}_7(\text{NH}_3)]$ and the molecular structure of the $[\text{UF}_7(\text{NH}_3)]^{3-}$ anion. Displacement parameters at 70% at -150°C .

lead to pure nitrides as the final products. Since the abundantly used strong fluoride ion acceptors SbF_5 and AsF_5 cannot be used in liquid ammonia (due to decomposition to yet unidentified orange products), we set out to explore other fluoride ion acceptors such as BF_3 and SiF_4 . We also studied Be^{2+} and UO_2^{2+} as fluoride ion acceptors which are much easier to handle compared to BF_3 and SiF_4 .

Fluoride ion acceptors based on beryllium

Compared to its neighbors in the periodic table of elements, the chemistry of beryllium is poorly developed (Metz et al., 2006; Dehnicke and Neumüller, 2008), and the sheer number of theoretical studies published on beryllium chemistry is by far larger than the number of experimental investigations. However, the chemistry of beryllium in aqueous solutions (Schmidt and Schmidbaur, 1998; Holleman and Wiberg, 2007) in glasses and in organic solvents is very well explored (Schmidbaur et al., 1991; Han and Parkin, 1993; Ruhlandt-Senge et al., 1993; Sohrin et al., 1993; Dressel et al., 2003; Puchta et al., 2005; Neumüller et al., 2008; Puchta and van Eldik, 2008a,b,c; Puchta et al., 2009a,b) and comprehensive studies in the field of beryllium chemistry have been performed and summarized in a review by Dehnicke (Dehnicke and Neumüller, 2008). However, reactions of beryllium compounds with and in liquid ammonia have not been greatly investigated.

Beryllium is insoluble in liquid ammonia (Jander et al., 1966). The addition of NH_4Cl or electrolysis leads to faintly bluish solutions. In 1927, Bergstrom reacted Be with NH_4Cl in liquid ammonia and obtained two products of the composition $\text{BeCl}_2 \cdot 2\text{NH}_3$ and $\text{BeCl}_2 \cdot 4\text{NH}_3$ which were stable at ambient temperature. The same products had been obtained in 1913 by Mieleitner and Steinmetz from BeCl_2 and NH_3 (Mieleitner and Steinmetz, 1913; Bergstrom, 1928). $\text{BeCl}_2 \cdot 4\text{NH}_3$ presumably contains the tetraammine beryllium cation for which, to our knowledge, no structural evidence is available so far, although it is mentioned in many text books on inorganic chemistry (Cotton et al., 1999; Holleman and Wiberg, 2007). A ^9Be NMR spectrum of BeCl_2 has been recorded in liquid ammonia, and the signal has been assigned to the $\text{Be}(\text{NH}_3)_4^{2+}$ cation, (Kovar and Morgan, 1970). We could, however, show that the reported signal was due to the oxygen-containing species $[\text{Be}_3(\mu\text{-OH})_3(\text{NH}_3)_6]^{3+}$ (Kraus, 2012). IR analyses gave evidence of the existence of $[\text{Be}(\text{NH}_3)_4]^{2+}$ (Grigor'ev et al., 1969; Sipachev et al., 1969), but these findings were heavily doubted (Schmidt and Müller, 1976). In tensiometric measurements, Biltz and coworkers have found adducts of two, four, six and twelve molecules of ammonia (Biltz and Messerknecht, 1925).

According to a Guinier photograph, $\text{Be}(\text{NH}_3)_4\text{Cl}_2$ should be isotopic to K_2BeCl_4 (Semenenko, 1965) – a finding which we were not able to reproduce (Kraus et al., 2012).

Finally, we succeeded in the synthesis and unambiguous characterization of the tetraammine beryllium cation in the compound $[\text{Be}(\text{NH}_3)_4]\text{Cl}_4 \cdot 17\text{NH}_3$ (Figure 6) (Kraus et al., 2012). This, which was characterized by single-crystal X-ray analysis, IR and NMR spectroscopy, should be a very versatile fluoride ion acceptor in liquid ammonia.

Reactions of beryllium fluorides in ammonia have been studied even less than those of the other halides or pseudohalides: Grigor'ev and coworkers reported that BeF_2 reacts with liquid ammonia under formation of $[\text{Be}(\text{NH}_3)_4][\text{BeF}_4]$ (Grigor'ev et al., 1967), but we have shown that this reaction leads to $[\text{BeF}_2(\text{NH}_3)_2]$ (Figure 7). The compound was characterized by X-ray structural analyses on single crystals, IR and Raman spectroscopy and by thermogravimetric analyses (Kraus et al., 2009b; Kraus et al., 2012).

With BeF_2 as a fluoride ion acceptor from UF_4 in liquid ammonia, $[\text{N}_2\text{H}_7][\text{BeF}_3(\text{NH}_3)]$ was obtained as a product (see below) (Kraus et al., 2012), which was probably formed via the reactions in Eqs. (2)–(4).

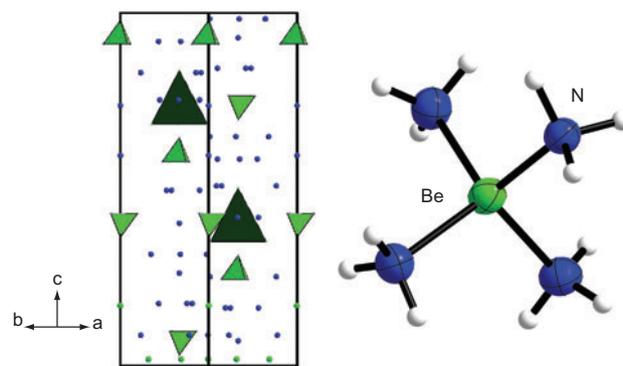


Figure 6 Left: The unit cell of $[\text{Be}(\text{NH}_3)_4]\text{Cl}_4 \cdot 17\text{NH}_3$. $[\text{Be}(\text{NH}_3)_4]^{2+}$ cations are depicted as small tetrahedra, $[\text{Cl}_4(\text{NH}_3)_4]^{4-}$ anions are shown as large tetrahedra. Right: Molecular structure of the tetraammine beryllium dication. Displacement parameters at 70% at -150°C .

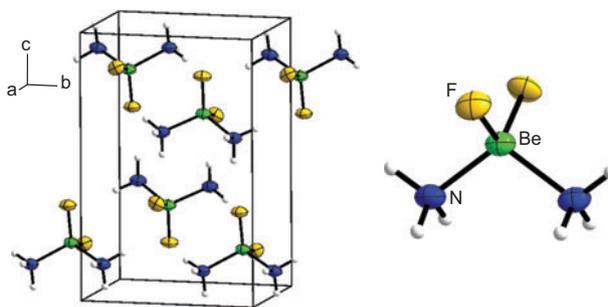
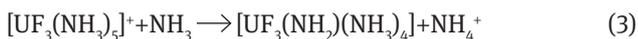


Figure 7 The unit cell of $[\text{BeF}_2(\text{NH}_3)_2]$ and its molecular structure. Displacement parameters at 70% at -150°C .



It is possible that the amide fluoride $[\text{UF}_3(\text{NH}_2)(\text{NH}_3)_4]$ is produced in solution, although it could not be isolated. Probably this amide either condensates or reacts with further BeF_2 following the routes shown in Eqs. (5) and (6).

Deprotonation of the ammine ligand



Deprotonation of the amide ligand



So, further reactions can take place which may finally lead to $[\text{U}(\text{NH}_2)_4(\text{NH}_3)_4]$, to oligonuclear complexes or to polymers. Upon deprotonation of the amide, imides and nitrile fluorides like $[\text{UFN}(\text{NH}_3)_6]$ may become available and the removal of NH_3 should lead to pure UNF.

Fluoride ion acceptors based on uranium – uranyl fluoride and chloride

Uranyl fluoride is a well known and explored compound, as it was suggested it might serve as a nuclear fuel (Myers, 1990). Its solubility in water and organic solvents and its phase diagrams have been determined, and its properties in nuclear power generation have been evaluated (Knacke

et al., 1969a,b; Myers, 1990). It is interesting to note that only some complex fluorides of the uranyl cation $M_3\text{UO}_2\text{F}_5$ or $M_3(\text{UO}_2)_2\text{F}_7$ are known (Olsson, 1930), of which the physical properties have been determined.

The UO_2^{2+} cation is said to abstract a fluoride ion from BF_4^- (John et al., 2004). However, no compounds with BF_3 (or SiF_4) are known (Ahrlund and Larsson, 1954). In aqueous solution, UO_2^{2+} accepts a maximum of four fluoride anions, leading to the formation of $\text{UO}_2\text{F}_4^{2-}$ (Johnson and Kraus, 1952; Johnson et al., 1954; Ahrlund et al., 1956). Compounds with SbF_5 are known with compositions of $\text{UO}_2\text{F}_2 \cdot n\text{SbF}_5$ ($n=2, 3, 4$). However, they have not been characterized in detail (Fawcett et al., 1982; Holloway et al., 1982). This fluoride ion affinity of UO_2^{2+} might be of great importance for the synthesis of new compounds in liquid ammonia.

Ammoniates of UO_2Cl_2 are known (von Unruh, 1909; Peters, 1912; Spacu, 1936), but those of uranyl fluorides have not been published so far. In 1909, von Unruh provided evidence for the compounds $\text{UO}_2\text{F}_2 \cdot n(\text{NH}_3)$ ($n=2, 3, 4$) by vapor pressure measurements (von Unruh, 1909). Only two hydrazine adducts of UO_2F_2 are known which are convertible to UF_4 at higher temperatures (Sahoo and Satapathy, 1964).

Recently, we obtained $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]_2 \cdot 2\text{NH}_3$, which was formed in the reaction of uranyl fluoride in liquid ammonia, the structure of which is shown in Figure 8.

Uranyl chloride UO_2Cl_2 reacts with liquid ammonia to give $[\text{UO}_2(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{NH}_3$ (Figure 9), and the fluoride-acceptor-properties of the $[\text{UO}_2(\text{NH}_3)_5]^{2+}$ are currently under investigation (Kraus et al., 2012; Woidy et al., 2012).

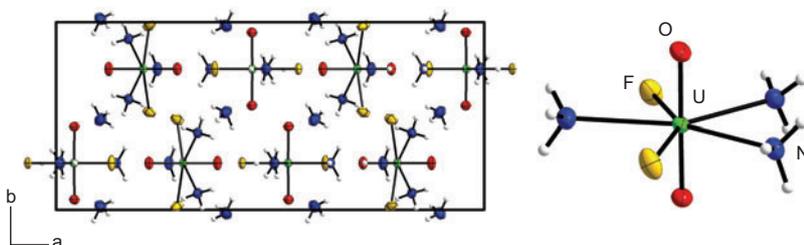


Figure 8 The unit cell of $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]_2 \cdot 2\text{NH}_3$ and molecular structure of $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]_2$. Displacement parameters at 70% at -150°C .

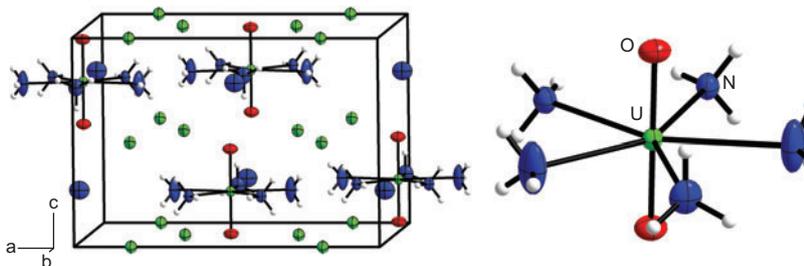


Figure 9 The unit cell of $[\text{UO}_2(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{NH}_3$ and molecular structure of $[\text{UO}_2(\text{NH}_3)_5]^{2+}$. Displacement parameters at 70% at -150°C .

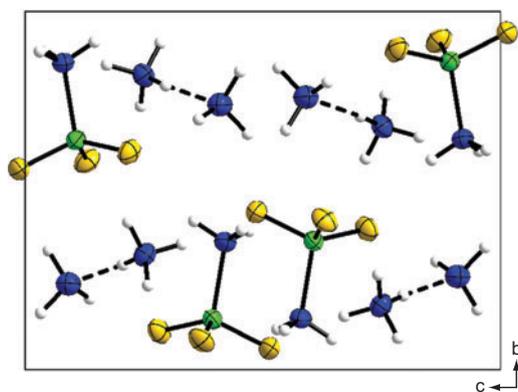


Figure 10 Depiction of the unit cell of $(\text{N}_2\text{H}_7)[\text{BeF}_3(\text{NH}_3)]$. Thermal displacement parameters c at 70% at -150°C .

Reactions with fluoride ion acceptors in liquid ammonia

Silicon atoms of certain silanes are well known as fluoride ion acceptors. Uranium hexafluoride was co-condensated by Jacob with $\text{Si}(\text{OCH}_3)_4$ yielding $\text{U}(\text{OCH}_3)_6$ and $\text{SiF}(\text{OCH}_3)_3$ (Jacob, 1982). The reaction is driven by the thermodynamic stability of the Si – F bond. To the best of our knowledge, Be^{2+} has not been used as an acceptor for fluoride ions, at least not in liquid ammonia, and the same is true for the uranyl cation which is said to be the strongest fluoride ion acceptor.

In the reaction of UF_4 with BeF_2 , we found $[\text{N}_2\text{H}_7][\text{BeF}_3(\text{NH}_3)]$ as a product (Figure 10). This result shows that BeF_2 indeed acts as a fluoride ion acceptor in liquid ammonia and confirms our postulate (Kraus et al., 2012).

The usage of fluoride ion acceptors opens a novel synthesis route toward ammine fluorides in liquid ammonia, since the formation of nitrogen containing fluorides should be quite simple this way. If a fluoride ion is, e.g., abstracted from $[\text{UF}_4(\text{NH}_3)_4]$, it is very likely that the resulting $[\text{UF}_3(\text{NH}_3)_4]^+$ cation is deprotonated, leading to an amide fluoride.

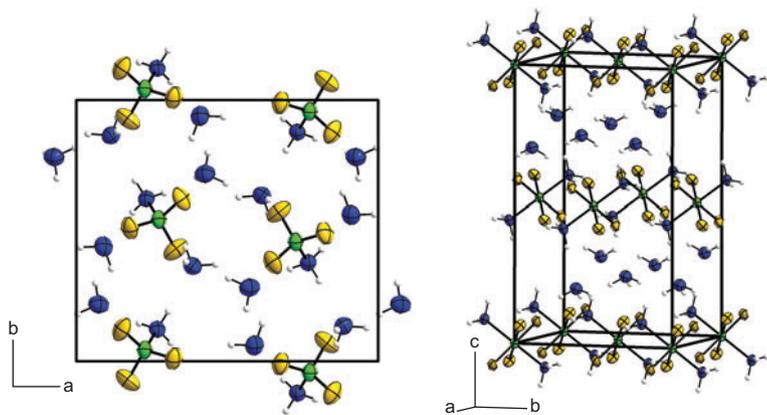


Figure 11 The unit cells of $[\text{BF}_3(\text{NH}_2)] \cdot 3\text{NH}_3$ and $[\text{SiF}_4(\text{NH}_2)_2] \cdot 2\text{NH}_3$. Displacement parameters at 70% at -150°C .

It is interesting to note that TaF_5 does not seem to be an appropriate fluoride ion acceptor in liquid ammonia. In a reaction of $\text{Sr}(\text{TaF}_6)_2$ with liquid NH_3 , we obtained $[\text{TaF}_5(\text{NH}_3)_3]$ and SrF_2 as the only products (F. Kraus, unpublished results).

From the reaction of BF_3 and SiF_4 in liquid ammonia, we obtained the low-temperature ammoniates of the long-known compounds $[\text{BF}_3(\text{NH}_3)]$ and $[\text{SiF}_4(\text{NH}_3)_2]$ (Figure 11) (Kraus and Baer, 2010), and the usage of these two compounds as fluoride ion acceptors in NH_3 is under investigation.

Usage of ammonia-soluble metals for the conversion of fluorides

It is well known that metal fluorides can be reduced at higher temperatures to the respective elements using an alkali or alkaline earth metal. By this method, e.g., depleted uranium metal can be obtained in chunks up to 500 kg. If, however, metal fluorides are reacted with, for example, alkali metals dissolved in liquid ammonia, the reactions rarely lead to the respective elements, but yield mostly grayish or greenish residues which have not been characterized yet (Jander et al., 1966).

It is possible that these residues are low-valent metal fluorides with oligonuclear or polymeric structures, and thus this process could turn out to be a very simple way to obtain these otherwise hardly accessible compounds. It is also possible that the residues contain amides, imides or nitrides. Thus, the reactions of metal fluorides with metals dissolved in ammonia are well worth exploring. It is known that Li, Na, K, Rb, Cs, Ca, Sr, Ba, Eu, and Yb dissolve in ammonia (Jander et al., 1966). The solutions are intensively blue, bronze or golden in color, depending on the concentration of the metal. It has been reported that by electrochemical reduction of beryllium compounds in

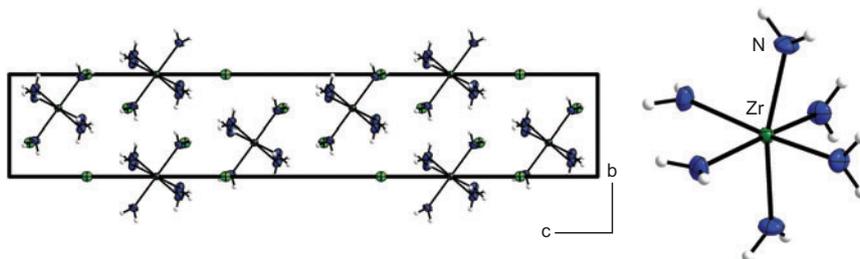


Figure 12 The unit cell of $K_2[Zr(NH_2)_6]$ and molecular structure of the hexamido zirconate(IV) anion. Displacement parameters at 70% at -150°C .

liquid ammonia, faintly blue solutions were generated (Jander et al., 1966).

So far, we studied the reaction of ZrF_4 with an excess of potassium in liquid ammonia. After several weeks, the bluish solution became colorless and contained colorless crystals which were subjected to a single-crystal X-ray analysis at low temperatures. The composition of the very moisture-sensitive compound was established to be $K_2[Zr(NH_2)_6]$ (Figure 12) (Kraus et al., 2011). Thus, zirconium(IV) is not reduced by solvated electrons but is converted into the hexamido zirconate(IV). The amide ions are generated by the reduction of ammonia protons to hydrogen under formation of KNH_2 , as illustrated by Eqs. (7) and (8).



This result is very promising in many respects: amides, imides or nitrides of strong fluoride ion acceptors like Be or even Zr act, on the one hand, as fluoride ion acceptors and on the other, they may transfer amide or imide or even nitride ions to another metal, and pure ternary amides have often only been obtained by high-pressure, high-temperature reactions with ammonia or using metal-organic educts. With the synthesis of $K_2[Zr(NH_2)_6]$, we have shown that such compounds are also accessible at low temperatures from the fluorides.

Summary

For a long time, preparative fluorine chemistry in liquid ammonia seemed to be a futile goal, but we have shown that fluorine chemistry in liquid ammonia is possible. By three methods, the usage of high oxidation states, of strong fluoride ion acceptors and of ammonia-soluble metals and amides, we have established novel accesses to nitrogen- and fluorine-containing compounds via activation of NH_3 in liquid ammonia.

The interest in nitrogen- and fluorine-containing species has initiated a rich chemistry in such different fields as beryllium and uranium chemistry. We were able to synthesize fundamental compounds like $BeF_2(NH_3)_2$, or the cation $[Be(NH_3)_4]^{2+}$, which can be considered as promising educts for many further exploratory syntheses. We synthesized $[UF_4(NH_3)_4] \cdot NH_3$ and compounds containing the $[UF_7(NH_3)_3]^{3-}$ anion as convenient starting materials for further syntheses in uranium chemistry.

We have prepared amines of so called “insoluble” fluorides like NH_4F or the alkali metal fluorides and studied their reactions in liquid ammonia. We elaborated preparative syntheses for fluorides, ammine fluorides and amides from these reactions, and it can be expected that other classes of compounds will follow.

Received April 16, 2012; accepted May 29, 2012

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