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Crystal Structures of $Ag_2ZrF_6{\cdot}8NH_3$ and $Ag_2HfF_6{\cdot}8NH_3$ and Their Synthesis by the "Reactive Fluoride Route" in Liquid Ammonia

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Starting from the ternary transition-metal fluorides $Ag_3M_2F_{14}$ (M = Zr, Hf) and dry liquid ammonia, $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]ZrF_6$ (**1**) and $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]HfF_6$ (**2**) have been prepared as colorless single crystals crystallizing isotypically in the space group *Pnma*-D_{2h}^{16} (No. 62). The compounds feature weak Ag···Ag interactions known as argentophilicity, which is yet unknown in fluorides. It is also shown that ionic silver(II) fluorides are suitable starting materials for fluorine chemistry in liquid ammonia and are easily reduced to Ag^I by oxidizing ammonia. This driving force bypasses the generally high lattice energy of ionic fluorides, so that they can be dissolved easily. We would like to introduce the term "reactive fluoride route" for this method of dissolving reactive ionic fluorides in liquid ammonia.

Introduction

Nitride fluorides – a scarcely known group of compounds – have attracted solid state chemists because of their putative magnetic, optical, and structural features.[1,2] Their properties should be similar to the well-characterized oxides and oxide fluorides but also clearly distinct when it comes to details. The idea of replacing two O^{2-} ions by N^{3-} and F^- anions was first put forward by Andersson.[3,4] Biltz and co-workers started the chemistry with halides in liquid ammonia and characterized several ammoniates with tensieudiometric measurements 95 years ago.[5] Ionic fluorides were described to be quite unreactive towards ammonia because of their high lattice energies and hence lower solubility in ammonia.[6–8] Biltz and co-workers found that readily available hydrates of ionic fluorides with lower lattice energies could easily be extracted with ammonia, which resulted in fluoride ammoniates.[6] Several representatives have been characterized structurally by Meyer and co-workers who used NH_4F, NH_4HF_2, or $N_2H_6F_2$ to oxidize the respective metals and half-metals in sealed metal ampoules at higher temperatures to produce for example $Zr(NH_3)F_4$ and $Hf(NH_3)F_4$.[8,9] Others used supercritical ammonia at 400 °C for the preparation of $AlF_3(NH_3)_2$ and $InF_2(NH_2)(NH_3)$[10] or ammonolysis at higher temperatures with gaseous ammonia ($NH_4[Ge(NH_3)F_5]$,[11] $Sn(NH_2)_2F_2$[12]). Our method is based on the use of metal fluorides with the metal in an "unusual" oxidation state – here Ag^{II} – in order to bypass the high lattice energy and allow dissolution in liquid ammonia. We set out by using elemental fluorine and other fluorination agents for the preparation of known and new fluorides to obtain a large pool of starting materials, which shall be used subsequently as starting materials for the synthesis of nitride-, imide-, and amide fluorides or their ammoniates. Our interest in these compounds is the development of various strategies of synthesis and extensive characterization of the products. Here we report the synthesis of $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]ZrF_6$ (**1**) and $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]HfF_6$ (**2**) from the ionic compound $Ag_3M_2F_{14}$[13,14] (M = Zr, Hf) and liquid ammonia at –40 °C and show that fluoride ammoniates are accessible under these very mild conditions.

Results and Discussion

By reaction of blue-violet $Ag_3M_2F_{14}$[13,14] (M = Zr, Hf) with liquid ammonia at –40 °C, $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]ZrF_6$ (**1**) and $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]HfF_6$ (**2**) were obtained. They crystallize as colorless plates isotypically in the orthorhombic crystal system having the space group *Pnma* (Table 4). The zirconium and hafnium atoms occupy the 4*c* position and are each surrounded by four symmetrically nonequivalent fluorine atoms on the 4*c* and 8*d* Wyckoff positions yielding an octahedron-like coordination sphere of isolated ZrF_6^{2-} and HfF_6^{2-} anions (Figure 1). The M–F distances (Table 1) are close to 2.0 Å, and the Hf–F distance is about 0.01 Å shorter than the Zr–F distance. The largest deviation of the F–M–F angles from 90 and 180° is as small as 2.5(1)° in the zirconium compound and only 2.1(2)° in the hafnium compound, leading to an almost perfect MF_6^{2-} (M = Zr, Hf) octahedral arrangement. Their deviation from O_h symmetry will be discussed below.

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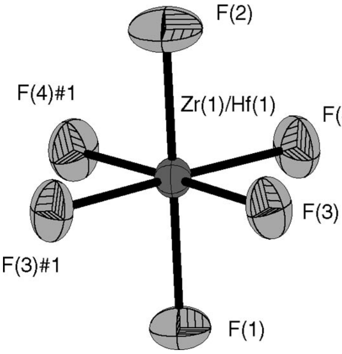

Figure 1. Projection of the ZrF_6^{2-}/HfF_6^{2-} anion in **1** and **2**. Thermal ellipsoids are shown at the 70% probability level. Symmetry operations for the generation of equivalent atoms: #1 *x*, –*y* + 1/2, *z*.

Table 1. Selected interatomic distances [Å] and angles [°] for the MF_6^{2-} anion (M = Zr, Hf) in **1** and **2**. Symmetry operations for the generation of equivalent atoms: #1 *x*, –*y* + 1/2, *z*.

	1	**2**
M(1)–F(1)	2.004(2)	1.987(4)
M(1)–F(2)	1.984(2)	1.971(4)
M(1)–F(3)	2.016(2)	1.999(3)
M(1)–F(4)	1.996(2)	1.988(3)
F(2)–M(1)–F(1)	179.10(12)	179.83(19)
F(4)#1–M(1)–F(3)	177.92(7)	178.01(12)
F(4)–M(1)–F(1)	90.08(7)	89.79(13)
F(2)–M(1)–F(4)	90.54(8)	90.33(13)

Two counterions, Ag(1) and Ag(2), are present, both occupy the 4*c* position. Ag(1) is coordinated by four NH_3 molecules in total. The ammonia molecules with nitrogen atoms N(1), N(3), and N(3)#1 show Ag–N-distances (see Table 2) between 2.207(2) and 2.422(3) Å; the remaining NH_3 molecule coordinates with nitrogen atom N(2) to Ag(1), over a long distance of 3.142(4) Å (Figure 2). The silver cation Ag(2) has a coordination sphere resembling a tetrahedron, with distances to the nitrogen atoms N(4), N(5), N(6), and N(6)#1 of 2.386(3), 2.302(3), 2.356(2) Å, and 2.356(2) Å, respectively (Figure 2, Table 2). In both compounds, the Ag–N distances and N–Ag–N angles are almost identical within 0.01 Å or 0.1°. As can be seen from Figure 2 and Table 2, the two silver cations, Ag(1) and Ag(2), are quite close to each other with a distance of only 3.1321(5) Å for **1** and 3.1414(9) Å for **2**, which is shorter than the sum of the van der Waals radii of 3.44 Å,[15,16] and the nitrogen atom N(4) acts as a μ-bridging ligand between Ag(1) and Ag(2) with distances of 3.031(4) Å in **1** and 3.017(6) Å in **2**. The other nitrogen atoms are more than 3.45 Å away.

The $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]^{2+}$ moieties are interconnected by symmetry-equivalent N(3)–H(3B)···N(2) hydrogen bonds to one-dimensional infinite $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]^{2+}$ strands running along the *b* axis (Figure 3). These strands are not isolated, however, since N–H···F hydrogen bonding to the MF_6^{2-}anions is also present. The MF_6^{2-} anions are completely surrounded by ammonia

Table 2. Selected atomic distances [Å] and angles [°] for the silver ammine cations in **1** and **2**.

	1	**2**
Ag(1)–Ag(2)	3.1321(5)	3.1414(9)
Ag(1)–N(1)	2.422(3)	2.413(5)
Ag(1)–N(2)	3.142(4)	3.134(8)
Ag(1)–N(3)	2.207(2)	2.208(4)
Ag(1)–N(4)	3.031(4)	3.017(6)
Ag(2)–N(4)	2.386(3)	2.376(6)
Ag(2)–N(5)	2.302(3)	2.289(6)
Ag(2)–N(6)	2.356(2)	2.353(4)
N(1)–Ag(1)–N(2)	126.30(11)	125.9(2)
N(1)–Ag(1)–N(3)	101.41(6)	101.50(11)
N(2)–Ag(1)–N(3)	85.14(7)	85.03(11)
N(4)–Ag(2)–N(5)	143.10(13)	142.5(2)
N(4)–Ag(2)–N(6)	94.13(8)	94.10(13)
N(5)–Ag(2)–N(6)	102.90(7)	103.11(13)

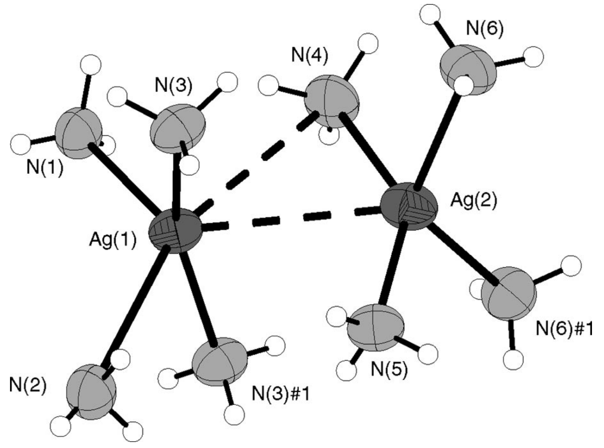

Figure 2. Projection of the coordination spheres of Ag(1) and Ag(2). The argentophilic interaction Ag(1)···Ag(2) and the long Ag(1)···N(4) interaction with the μ-bridging nitrogen atom are shown with dashed lines. Only one of the two possible arrangements of hydrogen atoms around N(4) is shown. Thermal ellipsoids are shown at the 70% probability level. Symmetry operations for the generation of equivalent atoms: #1 *x*, –*y* + 1/2, *z*.

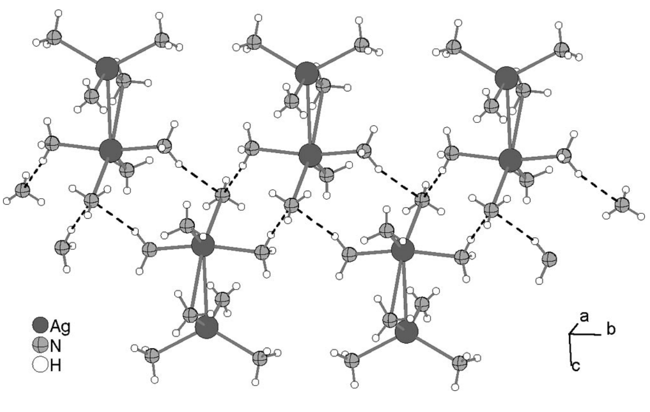

Figure 3. Projection of the interconnection of the $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]^{2+}$ ions by N–H···N–hydrogen bonding to formally one-dimensional infinite strands parallel to the *b* axis. Dashed black bonds indicate hydrogen bonding, gray bonds indicate the $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]^{2+}$ units.

molecules. The NH_3 molecules with nitrogen atoms N(1) (Figure 4a) and N(2) (Figure 4b) show three N–H···F hydrogen bonds, out of which one in both cases is bifurcated with a small DHA (D: donor, A: acceptor) angle of 145.7°/146.1° (**1**) and 144.6(13)°/146.4(17)° (**2**), respectively. Other N–H···F hydrogen bonds are listed in Table 3. N(6) (Figure 4e) binds by N–H···F hydrogen bridges to three symmetry-equivalent MF_6^{2-} anions. The NH_3 molecules with nitrogen atoms N(3) (Figure 4c) and N(5) (Figure 4d) are bound to two symmetry-equivalent MF_6^{2-} anions; N(3) features additional N–H···N hydrogen bonding to a symmetry-equivalent NH_3 molecule with nitrogen atom N(2). The hydrogen atoms around N(4) are disordered in two positions. Three hydrogen bonds – one being bifurcated – are displayed by N(4), and the two positions due to disorder are shown in Figure 5a and b. Hydrogen bond strengths will be discussed below. These manifold interactions lead to a rather complex three dimensional network of MF_6^{2-} octahedra which are interconnected by NH_3 molecules. The voids of the network are shown in the projection in Figure 6a. They are filled with the Ag^I cations (Figure 6b).

As a result of their highly ionic nature, fluorides in general have high lattice energies. This may lead to sparse solubility as compared to the other halides, the iodides being the easiest to dissolve in liquid ammonia.[17] It is known for about 80 years that fluorides like MF (M = Li, Na, K, Rb, Cs) or MF_2 (M = Zn, Mg, Ca, Fe, Ni) do not react with liquid ammonia at all but their hydrates do in an exchange reaction.[18] However, hydrates of fluorides are not generally available, especially for the more reactive fluorides with high oxidative potential. We have chosen the silver(II) compounds $Ag_3M_2F_{14}$ (M = Zr, Hf) as starting materials, since

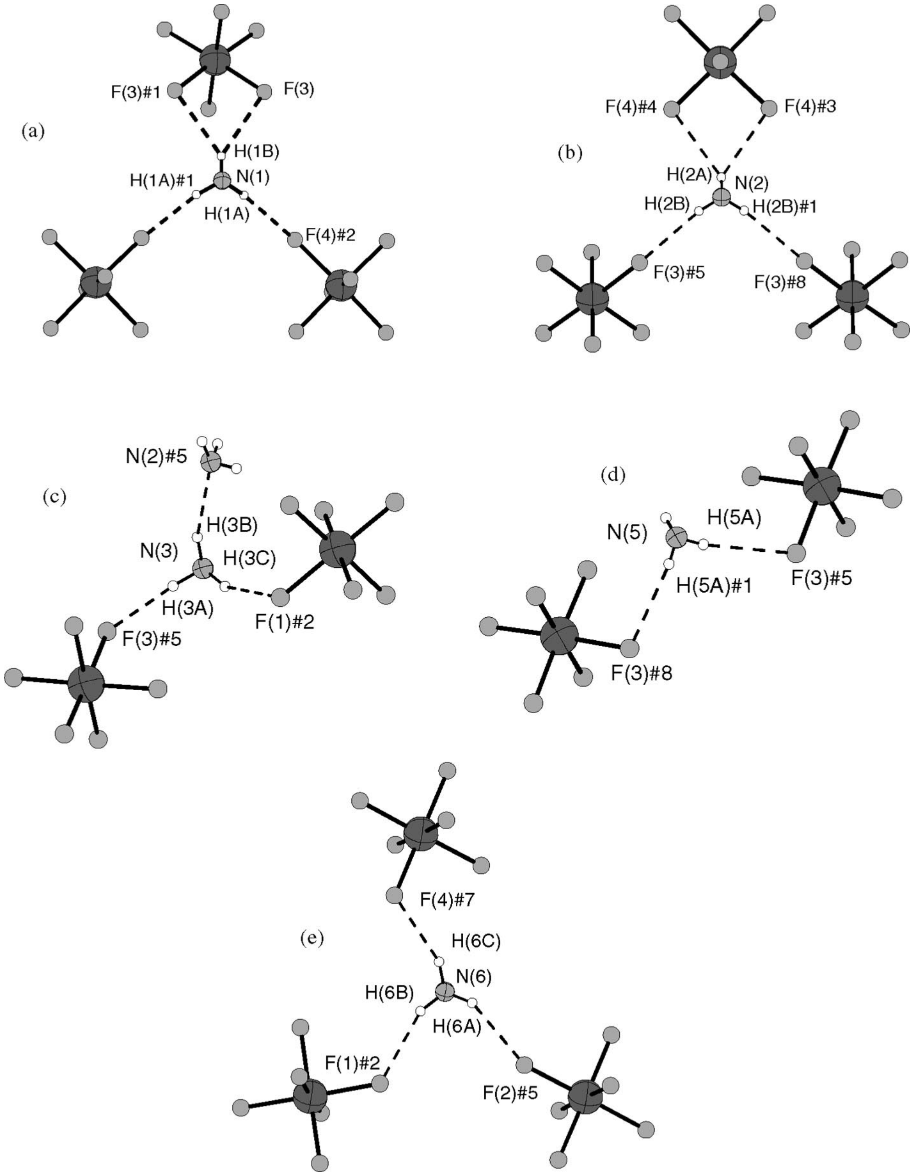

Figure 4. Projection of the N–H···F hydrogen bonding of the NH_3 molecules with nitrogen atoms (a) N(1), (b) N(2), (c) N(3), (d) N(5), and (e) N(6) to MF_6^{2-} anions. Symmetry operations for the generation of equivalent atoms: #1 *x*, –*y* + 1/2, *z*; #2 –*x* + 1/2, –*y*, *z* – 1/2; #3 *x* – 1/2, –*y* + 1/2, –*z* + 1/2; #4 *x* – 1/2, *y*, –*z* + 1/2; #5 –*x*, –*y*, –*z*; #6 –*x* + 1/2, *y* + 1/2, *z* – 1/2; #7 *x*, *y*, *z* – 1; #8 –x, *y* + 1/2, –*z*.

Table 3. Selected D–H, H···A, and D···A hydrogen bond lengths [Å] and DHA angles [°]. Symmetry operations for the generation of equivalent atoms: #2 –*x* + 1/2, –*y*, *z* – 1/2; #3 *x* – 1/2, –*y* + 1/2, –*z* + 1/2; #5 –*x*, –*y*, –*z*; #6 –*x* + 1/2, *y* + 1/2, *z* – 1/2; #7 *x*, *y*, *z* – 1.

	1	**2**
	D–H, H···A, D···A, DHA	D–H, H···A, D···A, DHA
N(1)–H(1A)···F(4)#2	0.94, 2.16, 3.075(3), 164.0	0.93, 2.17, 3.080(5), 164.1
N(1)–H(1B)···F(3)	0.78, 2.49, 3.173(3), 145.7	0.78, 2.49, 3.172(6), 146.1
N(2)–H(2A)···F(4)#3	0.73(4), 2.64(4), 3.261(4), 144.6(13)	0.70(7), 2.64(6), 3.252(8), 146.4(17)
N(2)–H(2B)···F(3)#5	0.83(4), 2.44(4), 3.262(3), 171(4)	0.80(6), 2.48(6), 3.277(6), 174(6)
N(3)–H(3A)···F(3)#5	0.91, 2.13, 3.034(3), 172.9	0.91, 2.12, 3.025(5), 172.5
N(3)–H(3B)···N(2)#5	0.91, 2.40, 3.265(4), 159.9	0.91, 2.39, 3.260(7), 160.8
N(3)–H(3C)···F(1)#2	0.91, 2.46, 3.293(3), 152.7	0.91, 2.46, 3.284(5), 151.5
N(4)–H(4A)···F(4)#2	0.91, 2.62, 3.361(3), 138.5	0.91, 2.58, 3.369(5), 145.6
N(4)–H(4B)···F(3)#6	0.91, 2.54, 3.276(3), 138.4	0.91, 2.56, 3.285(5), 136.6
N(4)–H(4B)···F(4)#6	0.91, 2.60, 3.361(3), 141.2	0.91, 2.60, 3.369(5), 142.3
N(4)–H(4C)···F(3)#2	0.91, 2.51, 3.276(3), 141.5	0.91, 2.59, 3.285(5), 133.4
N(5)–H(5A)···F(3)#5	0.72, 2.43, 3.143(3), 170.6	0.72, 2.44, 3.155(5), 170.5
N(6)–H(6A)···F(2)#5	0.91, 2.34, 3.171(3), 151.5	0.91, 2.34, 3.173(5), 152.8
N(6)–H(6B)···F(1)#2	0.91, 2.35, 3.206(3), 157.5	0.91, 2.37, 3.218(6), 155.8
N(6)–H(6C)···F(4)#7	0.91, 2.29, 3.142(3), 156.6	0.91, 2.30, 3.150(5), 155.3

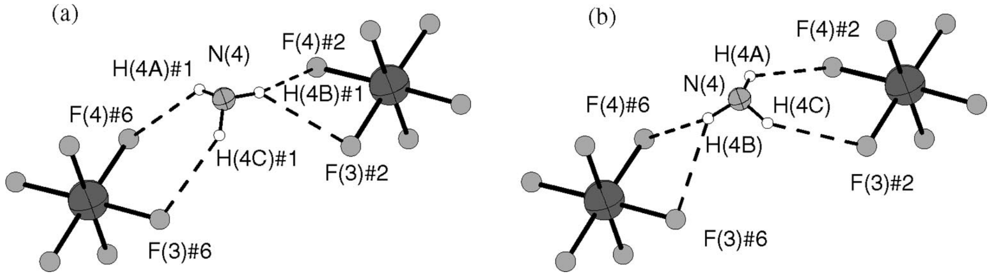

Figure 5. Projection of the N–H···F hydrogen bonding of the NH_3 molecule with nitrogen atom N(4). The two possible arrangements of hydrogen atoms towards the MF_6^{2-} anions are shown in (a) and (b). Symmetry operations for the generation of equivalent atoms: #1 *x*, –*y* + 1/2, *z*; #2 –*x* + 1/2, –*y*, *z* – 1/2; #6 –*x* + 1/2, *y* + 1/2, *z* – 1/2.

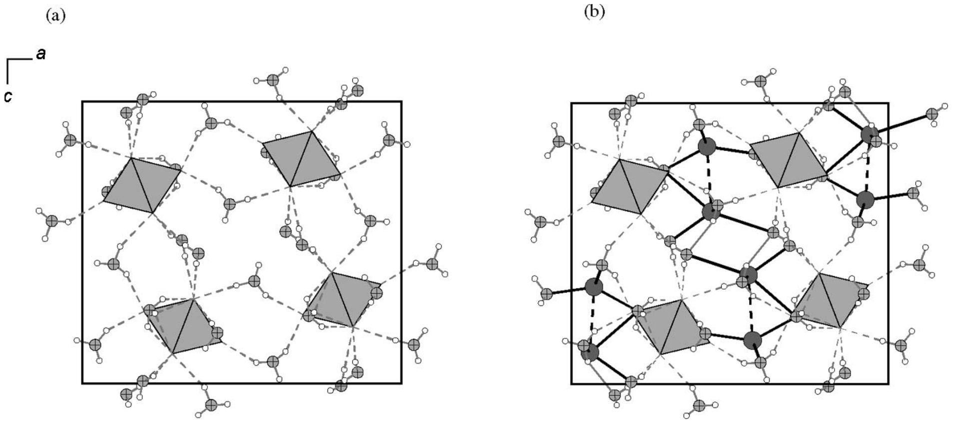

Figure 6. (a) Projection in the *ac* plane of the interconnection of MF_6^{2-} octahedra (polyhedral design) with ammonia molecules by N–H···F and N–H···N hydrogen bonding (gray dashed line). (b) The voids of (a) are filled with Ag^I cations, Ag–N bonds are drawn in black, the Ag···Ag interaction is shown as a black dashed line.

we expected them to oxidize ammonia. To the best of our knowledge, redox potentials for Ag^{2+}/Ag^+ have not been determined in liquid ammonia. With a grain of salt, the aqueous redox potentials of Ag^{2+}/Ag^+ (acidic 1.980 V, alkaline 0.604 V) may be used for a more quantitative impression, and the reactions should be exergonic in any case [$NH_3(l)/N_2$: acidic 0.04 V, alkaline –1.55 V, values for liquid ammonia].[17] As can be seen during the experiment, the compounds easily oxidize NH_3 and are reduced to Ag^I at –78 °C, since the color changes upon solution in ammonia from a deep blue-violet to colorless, and tiny bubbles are observed. A further driving force for this reaction may be the high solvation energy of Ag^I in liquid ammonia of 720.13 kJ mol^{-1} (at –34 °C), which is approximately 151 kJ mol^{-1} more than that in H_2O (at 25 °C),[17] which further enhances the reduction of Ag^{II} to Ag^I ammine complexes. We have also tried to synthesize **1** and **2** from AgF and MF_4 (M = Zr, Hf), but this leads to different products that will be reported elsewhere.

The crystal structures of the starting materials $Ag_3M_2F_{14}$ (M = Zr, Hf) feature three different types of fluorine coordination polyhedra, all connected by the corners of their equatorial planes: Ag-centered octahedra and hexagonal bipyramids and pentagonal bipyramids hosting M, which form together almost planar, two-dimensional infinite layers stacked along $[20\bar{1}]$.[13,14] The M–F distances in the pentagonal bipyramids are between 1.91 and 2.13 Å. Upon reaction with liquid NH_3, these pentagonal bipyramids rearrange to isolated MF_6^{2-} octahedra with M–F distances between 1.97 and 2.02 Å, which is in agreement with Zr–F and Hf–F distances of MF_6^{2-} anions reported in the literature.[19,20] The isolated MF_6^{2-} anions are expected to be perfect octahedra, since M^{IV} is a d^0 system, and a quantum chemical calculation for a ZrF_6^{2-} anion on the B3LYP level of theory by using GAUSSIAN03[21] with a pcm solvent model (acetonitrile) affirms O_h symmetry for the stable ground state, with Zr–F distances of 2.0403 Å [3-21G(d) for Zr and 6-311G(d) for F], which is consistent with reported values of 2.061 Å.[22] All occupied orbitals showed negative orbital energies, and no imaginary entries in the Hesse matrix, confirming a stable ground state, were present. However, because of the strong N–H···F hydrogen bonding environment in (**1**) and (**2**) – which in addition does not have octahedral symmetry – the MF_6^{2-} unit is slightly distorted. Such deviations from perfect symmetry can also be put on a quantitative scale with values ranging from 0 to 100, 0 being no deviation from the respective point group.[23,24] For the MF_6^{2-} octahedra of (**1**) and (**2**), symmetry values of 0.000116 and 0.000133, respectively, are obtained, indicating only a small deviation from the ideal O_h symmetry.

The silver-fluorine distances in the starting material, $Ag_3M_2F_{14}$, are between 1.997 and 2.789 Å. In (**1**) and (**2**), all Ag–F distances are larger than 4 Å, and thus direct Ag–F contacts are not present. This can be understood by Pearson's HSAB concept, since the softer Ag^+ cation has a higher tendency to bind to the softer NH_3 molecule, and the harder Zr^{4+}/Hf^{4+} ions combine with the harder F^- anions.[25] Relatively short Ag···Ag distances indicate the presence of argentophilic interactions in the title compounds, and thus the cations of (**1**) and (**2**) are best described as $[Ag(NH_3)_4(\mu\text{-}NH_3)Ag(NH_3)_3]^{2+}$ with a weak homoatomic interaction of 3.1321(5) Å (**1**) and 3.1414(9) Å (**2**), respectively. The Ag···Ag distances fit the values of argentophilic interactions reported in the literature (2.9–3.2 Å),[26–28] and the Ag···Ag distance of 3.14 Å in $Ag(NH_3)_2NO_3$ is only 0.2 Å larger than that in elemental silver.[29,30]

Despite the high quality of the single crystals, some of the hydrogen atoms could not be located unambiguously. The positions of these hydrogen atoms obtained from applying a riding model fitted perfectly to the expected hydrogen bonding network, however. For the discussion of hydrogen bond strengths, a simple model was employed: The percentage shortening of the hydrogen–acceptor distance compared to the sum of the van der Waals radii of the atoms is plotted against the deviation of the D–H···A angle from 180°,[15,31] assuming that short H···A distances and bond angles of 180° define the strongest hydrogen bonds. These are found in the upper left, the weakest in the lower right of the diagram. All bifurcated hydrogen bonds from N(1), N(2), and N(4) are found in the lower right region of the plot, and thus are weaker than the regular hydrogen bonds (Figure 7). The strongest hydrogen bonds are expected between N···F as compared to N···N,[31–34] although the diagram shows no clear distinction between these two arrangements.

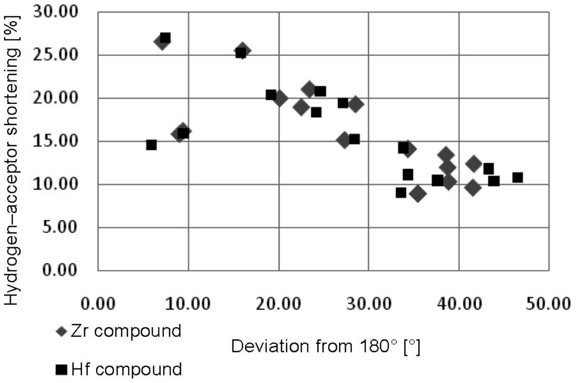

Figure 7. A diagram showing hydrogen bond strength in **1** and **2**. The percentage shortening of the H···A distance compared to the sum of the van der Waals radii of the atoms is plotted against the deviation of the D–H···A angle from 180°.

Conclusions

Two new ammoniates of fluorides $Ag_2ZrF_6{\cdot}8NH_3$ (**1**) and $Ag_2HfF_6{\cdot}8NH_3$ (**2**) were synthesized by the introduction of the reactive fluoride route – here by the reduction of Ag^{II} to Ag^{I} – in liquid ammonia, and their crystal structures were determined. The generally high lattice energy and sparse solubility of some solid-state fluorides can be bypassed in this way. Other fluoride compounds should be suitable starting materials for chemistry with liquid ammonia as well and should deliver starting materials for syntheses of amide-, imide-, or nitride fluorides. Argentophilic interactions are possible in fluorides if the Ag^{I} cations are separated from the fluorine environment by NH_3. Sometimes – especially when a large excess of ammonia was employed in the synthesis of the title compounds – we also observed the formation of a second type of crystals, which seem to be another ammoniate of silver hexafluorozirconate/hexafluorohafnate with a putative trigonal unit cell with a = 14.2871(4) Å and c = 12.8263(4) Å. However, low crystal quality hampered the solution and refinement of the crystal structure.

Experimental Section

All work was carried out by excluding moisture and air in an atmosphere of dried and purified argon or fluorine with high-vacuum

Table 4. Summary of crystallographic data.

	1	**2**
Empirical formula	$H_{24}Ag_2F_6N_8Zr$	$H_{24}Ag_2F_6HfN_8$
Color and appearance	Colorless plate	Colorless plate
Molecular mass [g mol^{-1}]	557.23	644.50
Crystal system	orthorhombic	orthorhombic
Space group	$Pnma\text{-}D_{2h}^{16}$	$Pnma\text{-}D_{2h}^{16}$
a [Å]	15.2249(4)	15.1808(8)
b [Å]	7.6960(2)	7.6860(4)
c [Å]	13.4433(5)	13.4562(9)
V [Å^3]	1575.16(8)	1570.06(16)
Z	4	4
ρ_{calc} [Mg m^{-3}]	2.350	2.727
λ [Å]	0.71073	0.71073
T [K]	150	150
μ(Mo-K_a) [mm^{-1}]	3.167	9.121
Crystal size [mm]	$0.15 \times 0.1 \times 0.03$	$0.15 \times 0.1 \times 0.03$
R_{int}, $R\sigma$	0.0291, 0.0137	0.0332, 0.0211
$R(F)$ [$I > 2\sigma(I)$, all data]	0.0265, 0.0325	0.0209, 0.0292
$wR(F^2)$ [$I > 2\sigma(I)$, all data]	0.0655, 0.0705	0.0480, 0.0522
S (all data)	1.085	1.059
Data, parameter, restraints	2558, 102, 0	1537, 102, 0
$\Delta\rho_{max}$ [e Å^{-3}]	1.166	0.858
$\Delta\rho_{min}$ [e Å^{-3}]	–1.625	–1.019
Extinction coefficient	0.0032(2)	0.00084(9)

glass lines, monel lines, or a glovebox (M. Braun, Garching), respectively. Liquid ammonia was dried and stored over sodium in a special high-vacuum glass line.

Caution: *Handling of elemental fluorine used in this work is potentially hazardous because of its extreme reactivity and toxicity. Fluorine must be used by experienced and fully trained personnel only.*

Synthesis and Crystallographic Information for $Ag_2ZrF_6{\cdot}8NH_3$ (1) and $Ag_2HfF_6{\cdot}8NH_3$ (2): Blue-violet $Ag_3M_2F_{14}$ (M = Zr, Hf) was prepared by using Ag_2O, $ZrOCl_2{\cdot}8H_2O$ or HfO_2 (VWR) and elemental fluorine (Solvay Fluor) according to the literature.[13,14] Dried and distilled liquid ammonia (Air Liquide) (15 mL) were condensed onto $Ag_3M_2F_{14}$ (100 mg) in Schlenk tubes at –78 °C, and a faint sky-blue slurry was obtained, whose color faded. The Schlenk tubes were stored at –38 °C and sporadically shaken. After three weeks, colorless plate-shaped crystals of $Ag_2ZrF_6{\cdot}8NH_3$ (**1**) and $Ag_2HfF_6{\cdot}8NH_3$ (**2**) had formed. These crystals were subjected to low-temperature X-ray analysis (Table 4) with an Oxford Xcalibur3 system.

The structures were solved by using Direct Methods,[35] and refinement was done on F^2.[36] All atoms were localized by Fourier cycling methods and refined anisotropically, hydrogen atoms isotropically in a riding model or freely where applicable. To justify the selection of the space group *Pnma*, searches for additional symmetry were performed by using PLATON[37] and KPlot,[38] which confirmed the correctness of the assignment. The crystals are not stable above –30 °C, because of their ammonia vapor pressure. This thermal instability also limited the application of different analytical methods; e.g., solid-state NMR or low-temperature ^{19}F NMR spectroscopy in liquid ammonia in flame sealed, thick-walled tubes failed because of the low solubility of the compounds. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), http://www.fiz-karlsruhe.de/icsd.html, on quoting the depository numbers CSD-418759 for (**1**), CSD-418758 for (**2**), the names of the authors, and the citation of the paper.

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