The First Ammoniates of Alkali Metal Fluorides: Cesium Fluoride Ammonia (3/4) [$Cs_3F_3(NH_3)_4$] and Ammonium Cesium Difluoride [NH_4CsF_2]

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Two new compounds containing cesium fluoride have been obtained as side-products from the reactions of Cs_2CuF_6 and Cs_2KDyF_6 with liquid ammonia. Cs_2CuF_6 reacts with the solvent forming a still unknown blue substance and the colorless ammoniate $Cs_3F_3(NH_3)_4$ which crystallizes in the cubic space group $I\bar{4}3d$ (no. 220) with a = 10.273(1) Å and V = 1084.3(2) Å^3 at 123 K with Z = 4. Its crystal structure is isopointal to $Y_3Au_3Sb_4$ and shows an infinite three-dimensional network made up through N–H···F hydrogen bonds. Ammonium cesium difluoride NH_4CsF_2 crystallizes in the orthorhombic space group *Pnma* (no. 62) with a = 7.1791(1), b = 4.1244(1), c = 13.6417(2) Å and V = 403.92(1) Å^3 at 123 K with Z = 4. The crystal structure displays two-dimensional infinite layers of the composition $^2_\infty[(NH_4F_2)^-]$ with embedded Cs^+ ions. Analogous to the structure of the compound $Cs_3F_3(NH_3)_4$, the structural motif is formed through strong N–H···F hydrogen bonds, which seem to be the guiding force. To the best of our knowledge, the title compounds are the first reported ammoniates of alkali metal fluorides.

Key words: Cesium, Fluoride, Liquid Ammonia, Crystal Structure, Hydrogen Bond

Introduction

In the system of alkali metal halides and ammonia, there are only a small number of known compounds for which the crystal structures have been determined. Using a tensieudiometer, Biltz and coworkers investigated the reactions of alkali metal halides with liquid ammonia and found a number of various ammoniates [1 – 3]. According to their work, neither potassium chloride, rubidium chloride nor any cesium halide reacted with liquid ammonia [3]. Alkali metal fluorides did not show any results in tensieudiometric analyses, so they were thought to be unreactive towards liquid ammonia due to their high lattice energy and hence low solubility [4 – 6]. The conclusion of a general inertness towards ammonia may have slowed down research in the area of fluorine chemisty in liquid ammonia. To the best of our knowledge, there have been no further studies on this subject to date aside from ours.

The higher ammoniates discovered by Biltz and coworkers were found to be stable only at lower temperatures or under higher ammonia pressures. Therefore, the number of known ammoniate crystal structures is much smaller compared to the number of compounds they found. This might be due to the fact that the crystals cannot be selected fast enough before the decrepitation occurring when temperature or partial pressure of ammonia are not appropriate. The composition of some ammoniates found by Biltz and coworkers could be verified by X-ray structure determination, whereas the composition of other ammoniates was found to differ slightly from the tensieudiometric data. Table 1 gives an overview of the structures determined by single-crystal diffractometry and the compounds found through tensieudiometric measurements (italicized). Biltz and coworkers found ammoniates of NaBr and NaCl with the compositions $NaBr(NH_3)_{5.25}$ and $NaCl(NH_3)_5$. Later, Olovsson was able to determine the structure of these compounds *via* X-ray diffraction and found them to be isostructural, with a composition of $Na_7X_7(NH_3)_{36}$ (X = Br, Cl) [7]. So, the tensieudiometric measurements were only off by 0.11 and 0.14 molecules of ammonia per formula unit, respectively.

Apart from the problem of selecting temperature- and pressure-sensitive crystals, it is not easy to synthe-

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Table 1. Known compounds in the system $M_zX_yN_wH_v$ (with M = alkali metal and X = halide). Formulae in italics are the compositions of alkali metal halide ammoniates determined by tensieudiometric measurements, other formulae in plain type stand for compounds with known crystal structures.

	F	**Cl**	**Br**	**I**
Li	–	*$LiCl(NH_3)_x$* (x = 1, 2, 3, 4, 5, 6.5)	$LiBr(NH_3)$ [21] $LiBr(NH_3)_4$ [22] $Li_2Br(NH_2)$ [23] *$LiBr(NH_3)_x$* (x = 1, 2, 3, 4, 5, 6.5)	$LiI(NH_3)$ [21] $LiI(NH_3)_4$ [22] *$LiI(NH_3)_x$* (x = 1, 2, 3, 4, 5, 5.5, 7)
Na	–	$Na_7Cl_7(NH_3)_{36}$ [7] *$NaCl(NH_3)_5$*[a]	$Na_7Br_7(NH_3)_{36}$ [7] $Na_4Br(NH_2)_3$ [24] *$NaBr(NH_3)_x$* (x = 5.25[a], 5.75)	*$NaI(NH_3)_x$* (x = 4.5, 6)
K	–	$(NH_4)_{0.4}K_{0.6}Cl$ [25] $(NH_4)_{0.9}K_{0.1}Cl$ [25]	–	$(NH_4)_{0.73}K_{0.27}I$ [26] $(NH_4)_{0.55}K_{0.45}I$ [27] $(NH_4)_{0.5}K_{0.5}I$ [28] *$KI(NH_3)_x$* (x = 4, 6)
Rb	–	–	*$RbBr(NH_3)_3$*	*$RbI(NH_3)_6$*
Cs	(**1**); (**2**)	–	–	–

[a] The compound $NaBr(NH_3)_{5.25}$ was later found by Olovsson to have the composition $Na_7Br_7(NH_3)_{36}$ [7]. Likewise, the composition of $NaCl(NH_3)_5$ is actually $Na_7Cl_7(NH_3)_{36}$.

size crystalline ammoniates from salts with a very low solubility in liquid ammonia. As already mentioned, the alkali metal fluorides were considered generally insoluble by Biltz and coworkers, and in fact it was only with very slow crystallization over several months that we were able to obtain the ammoniate of cesium fluoride $Cs_3F_3(NH_3)_4$ (**1**) and ammonium cesium difluoride $(NH_4)CsF_2$ (**2**).

To the best of our knowledge the crystal structures of **1** and **2** are the first containing cesium fluoride together with ammonia or ammonium ions. Until now, no compounds of any cesium halide or any alkali metal fluoride containing either ammonia or ammonium ions were reported.

Results and Discussion

Preparation and single-crystal structure analysis of $Cs_3F_3(NH_3)_4$ (1)

In a reaction of Cs_2CuF_6 with liquid ammonia at −78 °C and subsequent storage of the mixture at −40 °C for eight weeks, the ammoniate of cesium fluoride crystallized in the form of colorless blocks with the composition $Cs_3F_3(NH_3)_4$. Table 2 shows the data of the single-crystal structure determination. The asymmetric unit contains only four atoms: one cesium atom Cs(1), one fluorine atom F(1), one nitrogen atom N(1), and one hydrogen atom H(1). The atoms occupy the Wyckoff positions 12*a*, 12*b*, 16*c*, and 48*e* of the space group $I\bar{4}3d$, respectively. The compound is isopointal to the structure of $Y_3Au_3Sb_4$, with Y on 12*a*, Au on 12*b* and Sb on 16*c* [8]. $Y_3Au_3Sb_4$ is a filled variant of the Th_3P_4 structure type, where the Wyckoff position 12*b* is not occupied.

Table 2. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$Cs_3F_3(NH_3)_4$	CsF_2NH_4
M_r	523.85	188.94
Crystal size, mm^3	$0.3 \times 0.3 \times 0.6$	$0.2 \times 0.05 \times 0.03$
Crystal system	cubic	orthorhombic
Space group	$I\bar{4}3d$	$Pnma$
a, Å	10.273(1)	7.1791(1)
b, Å	a	4.1244(1)
c, Å	a	13.6417(2)
V, Å^3	1084.3(2)	403.92(1)
Z	4	4
D_{calcd}, g cm^{-3}	3.21	3.11
μ (MoK_α), cm^{-1}	10.0	9.0
$F(000)$, e	928	336
hkl range	$\pm17, \pm17, -18 \rightarrow +8$	$\pm12, \pm7, -18 \rightarrow +24$
$((\sin\theta)/\lambda)_{\max}$, Å^{-1}	0.889	0.990
Refl. measured / unique / R_{int}	20423 / 529 / 0.0308	15422 / 1287 / 0.0297
Param. refined	13	36
$R(F)/wR(F^2)$[a] (all refl.)	0.0164 / 0.0337	0.0187 / 0.0366
A / B (weighting scheme)[a]	0.0092 / 3.2731	0.0220 / 0.0183
GoF (F^2)[b]	1.416	1.093
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.58 / −0.59	0.97 / −0.94

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

The ammonia molecule in compound **1** is surrounded by three symmetry-equivalent fluoride anions in the form of a trigonal pyramid (Fig. 1). Each fluoride anion is connected to a hydrogen atom of

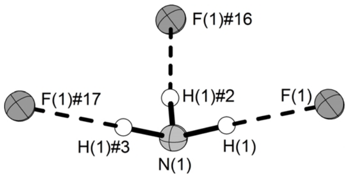

Fig. 1. A projection of the ammonia molecule N(1) and its hydrogen bonding to adjacent fluorine atoms of compound **1**. The displacement parameters are shown at 70 % at 123 K; hydrogen bonds are drawn as dashed lines. D–H, H···A and D···A hydrogen bond lengths (Å) and DHA angles (deg), with D = Donor and A = Acceptor: N(1)-H(1)···F(1) 0.99(5), 1.96(5), 2.9525(11), 177(6). Symmetry transformations to generate the equivalent atoms: #2) $y-1$, $1+z$, x; #3) z, $x+1$, $y-1$; #16) $-x+1/4$, $-z+3/4$, $y-5/4$; #17) $-z-1/4$, $y-9/4$, $x+1/4$.

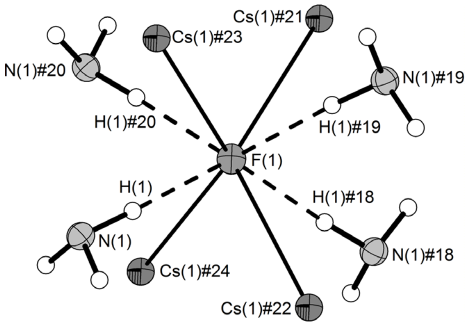

Fig. 2. A projection of the coordination sphere of the fluorine atom F(1) and its hydrogen bonding to adjacent ammonia molecules of compound **1**. The displacement parameters are shown at 70 % at 123 K; hydrogen bonds are drawn as dashed lines, distances to adjacent cesium atoms as full lines. Symmetry transformations to generate the equivalent atoms: #18) $y-5/4$, $-x+5/4$, $-z-1/4$; #19) $-y+5/4$, $x+5/4$, $-z-1/4$; #20) $-x$, $-y+5/2$, z; #21) $z-1/4$, $-y+9/4$, $-x-1/4$; #22) $-z+1/4$, $-y+7/4$, $x-1/4$; #23) $-x+1/4$, $z+5/4$, $-y+3/4$; #24) $-x-1/4$, $-z+5/4$, $y-3/4$.

the ammonia molecule *via* a N–H···F hydrogen bond (Fig. 2).

The fluoride anion is eightfold coordinated by four ammonia molecules and four cesium ions, as seen in Fig. 2. The ammonia molecules, as well as the cesium ions, surround the fluoride ion in the form of a bisphenoid. The distance Cs–F is with 3.1456(3) Å slightly longer than the distance of 3.01 Å in solid cesium fluoride, but is in the range of typical Cs–F distances [9, 10].

The cesium cation is surrounded by a cage made up of four fluoride ions which are connected *via* N–H···F hydrogen bonds to ammonia molecules. The fluoride ions coordinate the cesium ion in the shape of a bisphenoid. Fig. 3 shows a cesium cation surrounded by the nearest fluoride ions and ammonia molecules. Four edges of the bisphenoid are bridged by an ammonia molecule which forms hydrogen bonds to two fluoride ions. The remaining two edges are connected to other bisphenoids consisting of fluoride ions *via* N–H···F bonds to ammonia molecules.

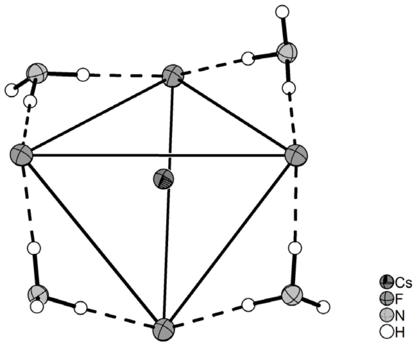

Fig. 3. Projection of the surrounding of the cesium cation Cs(1) of compound **1**. The displacement parameters are shown at 70 % at 123 K; hydrogen bonds are drawn as dashed lines, edges of the bisphenoid made up of fluoride anions as full lines.

The lone pair of the ammonia molecule is not, as often found in ammoniates, directed towards the cation, but towards the base of the trigonal pyramid made up by nitrogen and hydrogen atoms of another ammonia molecule. It appears that the N–H···F interaction is stronger than the Cs–F interaction. Between these ammonia molecules no N–H···N hydrogen bonds are formed as the distance H···N of 4.2 Å is more than the sum of the van der Waals radii of hydrogen and nitrogen of 3.0 Å [11]. The hydrogen atoms are ori-

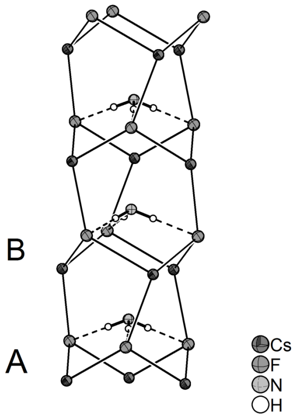

Fig. 4 Projection of the stacking of the six-membered Cs_3F_3 rings in **1**. Displacement parameters are shown at 70 % probability level; hydrogen bonds are drawn as dashed lines, full lines represent connections to adjacent cesium ions.

ented towards three fluoride ions, which form six-membered rings with three cesium ions (Fig. 4). The six-membered Cs–F ring shows a chair conformation with F–Cs–F angles of 99.6°. This ring is connected to similar six-membered rings forming $^1_\infty[Cs_3F_3(NH_3)]$ strands. Both the chair conformation and the stacking of the six-membered rings is analogous to the structure made up by the carbon atoms in the diamond structure. The stacking of the Cs–F rings is AB, similar to hexagonal diamond [11]. One difference to the diamond structure is the F–Cs–F angle, which is with 99.6° noticeably smaller than the tetrahedral angle in the diamond structure. Another difference is the stacking of the rings A and B. The rings do not only differ in their lateral position, as it is the case with the layers of carbon atoms in the structure of hexagonal diamond, but are also contorted around the axis made up by the nitrogen atoms of the intercalated ammonia molecules. The torsion angle H–N–N–H between the rings A and B is 42.8°, as can be seen in a projection along [111] (Fig. 5). Each $^1_\infty[Cs_3F_3(NH_3)]$ strand represents a channel with ammonia molecules sitting in the middle of a stack of six-membered rings consisting of fluoride and cesium ions (Fig. 6). Identical channels can be observed along the cell diagonals [111], $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$. The three-dimensional network of six-membered rings comprises those closely interconnected channels. Fig. 7 shows the linear arrangement of the ammonia molecules as polyhedra in the middle of the channels. The strong hydrogen bonding seems to be crucial for the formation of the six-membered ring and thus for the main structural motif of compound **1**.

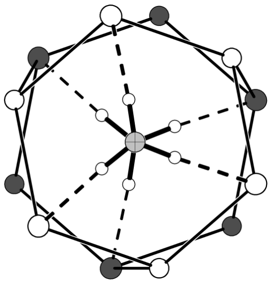

Fig. 5. Projection of two six-membered rings Cs_3F_3 of the compound **1** along [111]. White spheres represent cesium and fluoride ions of layer A, dark gray spheres represent atoms of layer B. One ammonia molecule is located in the center of each ring, coordinated *via* three N–H$\cdots$F hydrogen bonds. The torsion angle H–N–N–H between ammonia molecules of layers A and B is 42.8°.

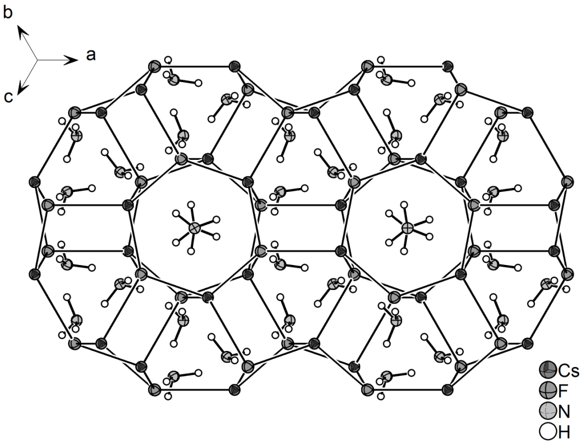

Fig. 6. Projection of compound **1** along [111]. Displacement parameters are shown at 70 % probability level. Thin lines represent connections between fluoride and cesium ions.

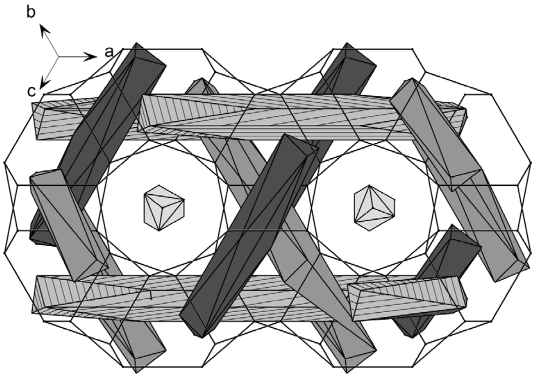

Fig. 7. Projection of compound **1** along [111]. Ammonia molecules belonging to one channel are drawn as polyhedra. The colors of the polyhedra refer to the direction of the channel. Light-gray polyhedra are oriented along [111], hatched light-gray polyhedra along$[\bar{1}11]$, medium-gray polyhedra are oriented along $[1\bar{1}1]$, and dark gray polyhedra along $[11\bar{1}]$. The network made up by cesium and fluoride is drawn as thin lines.

The H$\cdots$F hydrogen bond length is 1.96(5) Å. Compared to the sum of the van der Waals radii of hydrogen and fluorine of 2.9 Å this is a shortening of 32 %. This is a very high value of shortening, compared to hydrogen bonds found in other metal fluoride ammoniates. In our earlier work we discovered the ammoniate of silver(I) fluoride $Ag(NH_3)_2F\cdot 2(NH_3)$ [12]. The hydrogen bonds existing in this compound show a range of N–H$\cdots$F distances from 2.00(4) to 2.40(4) Å, which means a shortening compared to the sum of the van der Waals radii of 17 to 31 %.

Furthermore, the angle N–H$\cdots$F in compound **1** is 177(6)° and thus close to linearity, which stands for

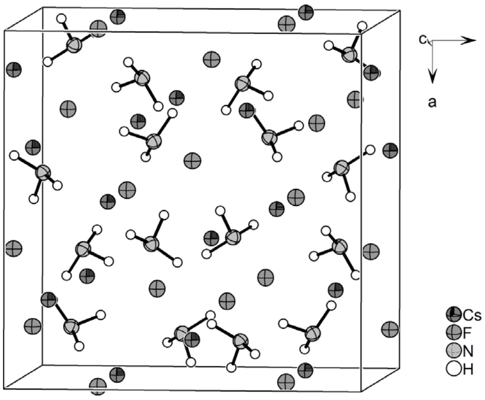

Fig. 8. Projection of the unit cell of compound **1** at 123 K. Displacement parameters are shown at 70 % probability level.

an almost ideal overlap of the orbitals. Both the short N–H···F distance and the virtually linear arrangement indicate a very strong hydrogen bond. Fig. 8 shows a projection of the unit cell of **1**.

Clearly N–H···F hydrogen bonding and Coulomb interactions between fluoride and cesium ions are the main factors in the formation of this three-dimensional framework.

*Preparation and single-crystal structure analysis of NH_4CsF_2 (**2**)*

Cs_2KDyF_6 was reacted with liquid ammonia at −78 °C. A change of color was observed for the precipitate from a bright-blue to yellow, but the solution remained colorless. The reaction vessel was stored for six months at −40 °C until the appearance of colorless needle-shaped crystals could be observed. The data from the single-crystal structure analysis can be seen in Table 2. The composition of the crystals was found to be NH_4CsF_2. The compound crystallizes in the space group *Pnma*. The asymmetric unit contains the atoms Cs(1), F(1), F(2), N(1), H(1A), H(1B), and H(1C). All atoms occupy the Wyckoff position 4*c* except for the hydrogen atom H(1B), which occupies position 8*d*.

The fluoride ion F(1) is octahedrally coordinated by two hydrogen atoms of ammonium ions N(1) and four cesium cations (Fig. 9). The distances between the cesium cations and the fluoride ion are 3.0573(8) and 3.1185(9) Å, a little elongated compared to the distance in solid cesium fluoride at 3.01 Å, but a typical distance for compounds containing cesium and fluoride [9, 10]. These values are similar to the Cs–F distance of 3.1456(3) Å observed in compound **1**. For a detailed discussion of the N–H···F hydrogen bonds see below.

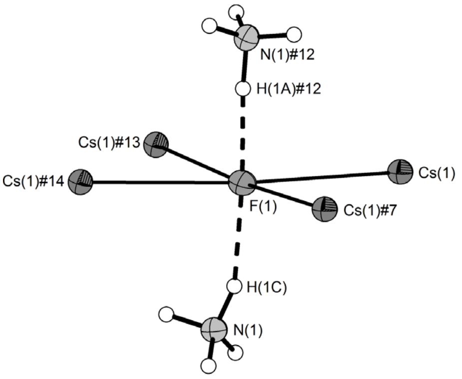

Fig. 9. The fluorine atom F(1) and its coordination to adjacent hydrogen and cesium atoms of compound **2**. The displacement parameters are shown at 70 % at 123 K, hydrogen bonds are drawn as dashed lines. Symmetry transformations to generate the equivalent atoms: #7) $x, y+1, z$; #12) $x-1/2, -y+3/2, -z+3/2$; #13) $x+1/2, -y+1/2, -z+3/2$; #14) $x+1/2, -y+3/2, -z+3/2$.

F(2) is coordinated square pyramidally by three cesium cations, with Cs–F distances of 3.0206(8) and 3.173(1) Å, and two ammonium cations, as can be seen in Fig. 10. The anisotropic displacement parameters of F(2) show a distinct elongation of the ellipsoid compared to F(1). This may be explained by the fact that F(2) is only five-coordinate, whereas F(1) is six-coordinate. The direction of the elongation suggests that the arrangement of the hydrogen bonds is structurally significant. Whereas F(1) sits in the middle of two almost collinearly arranged hydrogen bonds, the two hydrogen bonds at F(2) include an angle H(1B)-

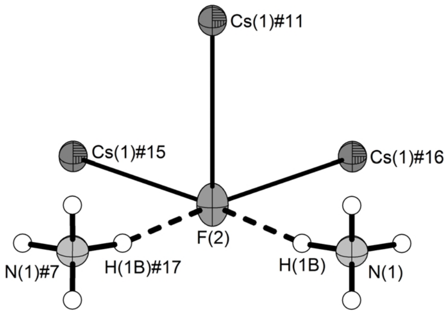

Fig. 10. The fluorine atom F(2) and its bonding to adjacent hydrogen atoms in **2**. The thermal displacement parameters are shown at 70 % at 123 K. Distances to adjacent cesium atoms are drawn as full lines, hydrogen bonds as dashed lines. Symmetry transformations to generate the equivalent atoms: #7) $x, y+1, z$; #11) $x+1, y+1, z$; #15) $-x+1, y+3/2, -z+1$; #16) $-x+1, y+1/2, -z+1$; #17) $x, -y+5/2, z$.

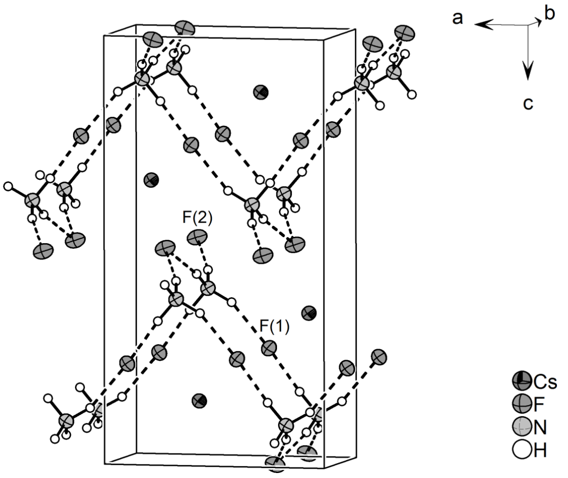

Fig. 11. Projection of the unit cell of compound **2** at 123 K. Displacement parameters are shown at 70 % probability level, hydrogen bonds are drawn as dashed lines.

F(2)-H(1C) of 97.9°, and the elongation of the ellipsoid is perpendicular to the plane made up by those three atoms.

The main feature of the crystal structure of compound **2** is the presence of infinite two-dimensional layers, as seen in Fig. 11. The layers with the stacking sequence AB are aligned parallel to (110) and consist of a network of ammonium ions which are connected *via* N–H···F hydrogen bonds to fluoride ions. Due to the tetrahedral angle between the hydrogen atoms of the ammonium ion, the layers have a corrugated appearance. Each layer consists of infinitely zigzagged strands of ammonium cations connected almost linearly by fluoride anions F(1) *via* hydrogen bonds. Each zigzagged strand is connected by bridging fluoride ions F(2) to two other parallel strands *via* the two remaining hydrogen bonds. The strands proceed along *a* and are bridged along *b*, forming two-dimensional infinite sheets. The sheets run parallel to (110) at a height of $c = 1/4$ (layer A) and $3/4$ (layer B). The cesium cation embedded into the ripples of the layers is surrounded by a trigonal prism made up of fluoride ions, four of which belong to one layer, while the other two belong to an adjacent layer.

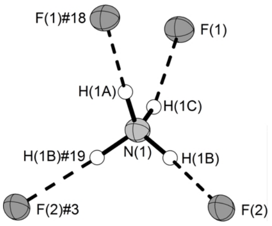

Fig. 12. The ammonium ion and its hydrogen bonding to adjacent fluoride anions in **2**. The displacement parameters are shown at 70 % at 123 K, hydrogen bonds are drawn as dashed lines. D–H, H···A, D···A hydrogen bond lengths (Å) and DHA angle (deg), with D = Donor and A = Acceptor: N(1)-H(1C)···F(1) 0.89(4), 1.88(4), 2.7308(19), 159(3); N(1)-H(1B)···(F2), 0.92(3), 1.76(2), 2.6615(13), 168(2); N(1)-H(1A)···F(1)#13, 0.92(4), 1.70(4), 2.621(2), 176(4). Symmetry transformations to generate the equivalent atoms: #3) $x, y-1, z$; #18) $x+1/2, -y+3/2, -z+3/2$; #19) $x, -y+3/2, z$.

The ammonium ion is tetrahedraly surrounded by fluoride ions with H···F distances of 1.70(2) to 1.88(4) Å (Fig. 12). The angles N–H···F lie between 159(3) and 176(4)°, the shortening of the hydrogen bonds compared to the sum of the van der Waals radii is 37 to 43 % and hence indicates very strong hydrogen bonds. Hydrogen bonds to ammonium ions are stronger compared to hydrogen bonds to ammonia molecules due to the additional coulomb interaction between cation and anion. The N–H···F distance is therefore a clear indicator that the observed unit is indeed an ammonium ion. Even strong hydrogen bonds of ammonia molecules, like the one observed in compound **1**, rarely have H···F distances shorter than 2.0 Å. In previous studies we synthesized the compound $[(NH_4)_3(UF_7NH_3)]\cdot NH_3$, which shows N–H···F hydrogen bonds towards ammonia molecules as well as towards ammonium ions, the latter ones in the cation $N_2H_7^+$ [13], which is also found in the compound N_2H_7F, the ammoniate of NH_4F [12].

In $[(NH_4)_3(UF_7NH_3)]\cdot NH_3$, the N–H···F hydrogen bond lengths towards the ammonia molecules range from 2.27 to 2.59 Å (22 to 11 % shortening compared to the sum of the van der Waals radii), whereas those to the ammonium ions are found to be in the range of 1.81(5) to 2.20(7) Å (38 to 24 % shortening). Solid NH_4F exhibits a H···F distance of 1.7 Å at 118 K [14, 15].

We have never observed N–H···F hydrogen bonds involving ammonia molecules with a H···F distance below 1.9 Å. Short H···F distances therefore allow to distinguish between ammonium ions and ammonia molecules beyond chemical reasoning, especially if not all hydrogen atoms can be located from the difference Fourier syntheses.

Conclusion

Cs_2CuF_6 reacts with liquid ammonia and yields $Cs_3F_3(NH_3)_4$ as a by-product. A crystal of the colorless compound was subjected to X-ray diffraction for structure elucidation. The compound shows a three-dimensional structure with strong N–H···F hydrogen bonds, the ammonia molecules sitting in the middle of channels made up of stacked Cs_3F_3 rings. This is to the best of the authors' knowledge the first characterized ammoniate of any cesium halide or alkali metal fluoride, as both groups of compounds were previously thought to be unreactive towards liquid ammonia.

$(NH_4)CsF_2$ (**2**) was obtained as a by-product in the reaction of Cs_2KDyF_6 with the solvent liquid ammonia. A determination of the crystal structure showed a complex layer structure, formed through strong hydrogen bonds. $(NH_4)CsF_2$ is the first compound – with a known crystal structure – containing ammonium alongside with cesium and fluoride ions. It appears that it is very difficult to obtain in crystalline form from aqueous solutions of NH_4F and CsF, mainly due to the extreme hygroscopicity of the compounds involved.

Both compounds show structures displaying very strong hydrogen bonds, which in both cases are responsible for the formation of the main structural motifs. In the case of $Cs_3F_3(NH_3)_4$, the threefold axis of the ammonia molecule and the three fluorine atoms attached *via* strong hydrogen bonds may be responsible for the cubic symmetry.

Finally, the consideration of the length of N–H···F hydrogen bonds can help to distinguish between ammonium ions and ammonia molecules beyond chemical reasoning in this class of compounds.

Experimental Section

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (Westfalen AG) using high-vacuum glass lines or a glove box (MBraun). Liquid ammonia (Air Liquide) was dried and stored over sodium (VWR) in a special high-vacuum glass line.

Synthesis of cesium fluoride ammoniate $Cs_3F_3(NH_3)_4$ (1)

72 mg (0.16 mmol) of Cs_2CuF_6 was placed into a flame-dried Schlenk tube [16]. The Schlenk tube was cooled to −78 °C and about 10 mL of dried ammonia was distilled into the vessel. The colorless Cs_2CuF_6 turned blue upon contact with liquid ammonia, which indicated the reduction of Cu^{IV} to Cu^{II}. The liquid phase remained colorless. The Schlenk tube was transferred to a deep freezer and stored at −40 °C, with occasional shaking every few days. After twelve weeks colorless crystals had formed in the solids among a blue amorphous powder. One crystal was selected for structure determination by X-ray diffraction.

Table 3. Atomic coordinates and isotropic displacement parameters ($Å^2 \times 10^3$) of compound **1**.

	x	y	z	U_{eq}
H(1)	0.068(5)	0.148 (6)	0.021 (6)	5(2)
Cs(1)	0	3/4	1/8	12(1)
F(1)	0	1/4	7/8	15(1)
N(1)	0.985(2)	1.0985(2)	0.0985(2)	13(1)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for compound **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13} + 2a^*b^*hkU_{12})$. $U_{11} = U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23}$.

	U_{11}	U_{12}
Cs(1)	12(1)	0
F(1)	15(1)	0
N(1)	13(1)	−1(1)

Table 5. Atomic coordinates and isotropic displacement parameters ($Å^2 \times 10^3$) for compound **2**.

	x	y	z	U_{eq}
H(1A)	0.720(6)	3/4	0.657(3)	4(1)
H(1B)	0.663(3)	0.929(6)	0.568(2)	33(6)
H(1C)	0.528 (7)	3/4	0.637(2)	3(1)
Cs(1)	0.1051(1)	1/4	0.6450(1)	13(1)
F(1)	0.3595(2)	3/4	0.7423(1)	17(1)
F(2)	0.7594(2)	1/4	0.5002(1)	19(1)
N(1)	0.6371(2)	3/4	0.6054(1)	14(1)

Table 6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for compound **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13} + 2a^*b^*hkU_{12})$. $U_{12} = U_{23} = 0$.

	U_{11}	U_{22}	U_{33}	U_{13}
Cs(1)	14(1)	12(1)	13(1)	0(1)
F(1)	15(1)	22(1)	16(1)	2(1)
F(2)	27(1)	15(1)	16(1)	4(1)
N(1)	14(1)	15(1)	14(1)	1(1)

Synthesis of ammonium cesium difluoride NH_4CsF_2 (2)

253 mg (0.42 mmol) of Cs_2KDyF_7 was put into a dried Schlenk tube [17]. After cooling to −78 °C, dried ammonia was distilled onto the blue powder. During condensation the powder changed its color from blue to brown and finally yellow in about twenty minutes. The liquid ammonia remained colorless. The vessel was then stored at −40 °C and shaken and checked for crystals several times per week. After twelve weeks a sample of the precipitate was investigated under a microscope at low temperatures. A colorless needle-shaped crystal was selected and examined by single-crystal X-ray diffraction.

X-Ray structure determination of compound 1

A colorless crystal of the dimensions $0.3 \times 0.3 \times 0.6\ mm^3$ was selected under cooled hydrofluoroether oil (Galden

PFPE, Solvay Solexis) and shock-cooled to 123 K. The measurement was carried out on an Oxford Xcalibur3 diffractometer (MoK_α, λ = 0.71073 Å). Cell determination routines gave a cubic unit cell. The data were reduced with the CRYSALISRED software [18]. The structure was solved by Direct Methods (SHELXS-97) and refined against F^2 with SHELXL-97 in space group $I\bar{4}3d$ [19, 20]. All atoms were located *via* difference Fourier syntheses. Refinement was carried out anisotropically. Hydrogen atoms were refined isotropically. N and F atoms could be clearly distinguished based on their displacement parameters and chemical reasoning (Tables 3, 4).

X-Ray structure determination of compound **2**

A colorless needle-shaped crystal of the dimensions 0.2 × 0.05 × 0.03 mm^3 was selected under cooled hydrofluoroether oil (Galden PFPE, Solvay Solexis) and shock-cooled to 123 K. The measurement was carried out on a Oxford Xcalibur3 diffractometer (MoK_α, λ = 0.71073 Å). Cell determination routines gave an orthorhombic cell. The data were reduced with the CRYSALISRED software [18]. The structure was solved by Direct Methods (SHELXS-97) and refined against F^2 with SHELXL-97 in space group *Pnma* [19, 20]. All atoms were located *via* difference Fourier syntheses. Refinement was carried out anisotropically. Hydrogen atoms were refined isotropically. N and F atoms could be clearly distinguished based on their displacement parameters and chemical reasoning (Tables 5, 6).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-421716 (**1**) and 421717 (**2**).

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