The Hexaammine Copper(II) Fluoride Monohydrate [Cu(NH$_3$)$_6$][F(H$_2$O)F]: Synthesis and Crystal Structure

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We report the synthesis and crystal structure of the monohydrate of hexaammine copper(II) difluoride, [Cu(NH$_3$)$_6$]F$_2$ · H$_2$O, which was synthesized from CuF$_2$ · 2 H$_2$O in liquid ammonia. The compound crystallizes in the chiral space group $P3_2 21$ (no. 154) as traffic-blue, plate-shaped crystals with $a = 6.738(1)$, $c = 18.210(6)$ Å, $V = 715.9(3)$ Å^3 at 150 K with $Z = 3$. It contains the rare [F(H$_2$O)F]$^{2-}$ anion bound by strong O–H···F hydrogen bonding.

Key words: Copper(II) Fluoride, Liquid Ammonia, Ammine Complexes, Hydrates, Crystal Structure, Hydrogen Bonds

Introduction

W. Biltz and coworkers reported the reaction of CuF$_2$ · 2 H$_2$O with liquid ammonia. In their study, CuF$_2$ · 2 H$_2$O was extracted with ammonia to remove the water at temperatures between 30 and 65 °C to produce copper ammoniates [1]. With tensieudiometric measurements the authors established the existence of a dark-blue pentaammoniate of copper fluoride, CuF$_2$ · 5 NH$_3$, at −78 °C and putatively of CuF$_2$ · 3.33 NH$_3$ at 18 °C [1, 2]. To our knowledge, these are the only pure Cu(II) fluoride ammoniates reported, but their structures have not been determined yet. Biltz and coworkers have chosen the dihydrate of CuF$_2$ as starting material, since hydrates generally react much better with liquid NH$_3$ than the anhydrous salts. This is due to their lower lattice energy and the very good solubility of water in ammonia [1]. Here we show that CuF$_2$ · 2 H$_2$O reacts with liquid ammonia at −78 °C forming a traffic-blue solution. After storage for two months at −40 °C, single crystals of [Cu(NH$_3$)$_6$][F(H$_2$O)F] (**1**) of the same color were obtained which were characterized by low-temperature single-crystal X-ray diffraction.

Results and Discussion

[Cu(NH$_3$)$_6$]F$_2$ · H$_2$O crystallizes as traffic-blue (RAL 5017) single crystals in space group type $P3_2 21$ (for further crystallographic data see Table 1). The color of the compound has been determined with the naked eye by comparison with RAL color cards. The asymmetric unit contains one copper atom residing on the Wyckoff position 3a (.2.), one oxygen atom on the Wyckoff position 3b (.2.) and three nitrogen atoms and one fluorine atom on the 6c (1) position (Table 2). The copper atom Cu(1) is surrounded by three symmetry-inequivalent NH$_3$ molecules with nitrogen atoms N(1), N(2) and N(3). By application of the symmetry operation (.2.), the coordination number of the copper atom becomes six, and a coordination polyhedron best described as a slightly distorted tetragonal bipyramid is obtained (Fig. 1).

The Cu(II)–N distances are 2.120(4) and 2.103(4) Å for the equatorial nitrogen atoms N(1)/N(1)#1 and N(2)/N(2)#1, respectively (Table 3). The distance from the Cu atom to the axial nitrogen atoms N(3) and N(3)#1 is 2.370(5) Å which is significantly longer than the equatorial Cu–N distances. Thus, the polyhedron reveals the expected Jahn–Teller distortion for a Cu(II) d^9 system [3]. These findings fit to the values of the Cu–N distances reported in the literature: The equatorial Cu–N distances in [Cu(NH$_3$)$_6$]Cl$_2$ and [Cu(NH$_3$)$_6$]Br$_2$ are 2.07(7) and 2.15(8) Å, respectively, and for the axial Cu–N distances 2.62(11) and 2.45(28) Å are reported [4]. In a more recent study, [Cu(NH$_3$)$_6$]Cl$_2$
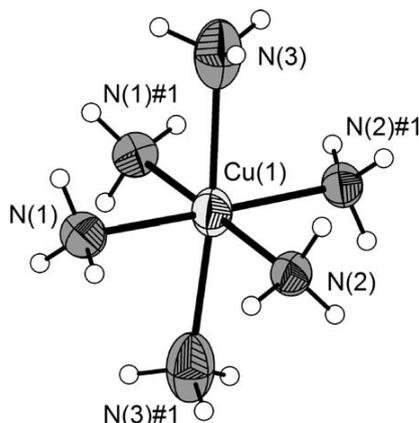
Fig. 1. A projection of the distorted tetragonal-bipyramidal coordination sphere of Cu(1). Displacement ellipsoids are shown at the 70% probability level at 150 K, H atoms as spheres with arbitrary radii. Symmetry transformation used to generate equivalent atoms: #1 x, y, $-z$.

Table 2. Wyckoff positions, atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) of **1**.

Atom	Position	x	y	z	U_{eq}
Cu(1)	3a	4680(1)	4680(1)	0	30(1)
N(1)	6c	5813(7)	7966(7)	460(2)	31(1)
H(1A)	6c	4584	8070	612	46
H(1B)	6c	6599	9058	115	46
H(1C)	6c	6745	8181	849	46
N(2)	6c	1350(8)	3503(7)	403(2)	27(1)
H(2A)	6c	1093	2570	795	41
H(2B)	6c	314	2707	43	41
H(2C)	6c	1201	4718	542	41
N(3)	6c	6043(9)	3651(8)	1050(3)	46(1)
H(3A)	6c	5076	3378	1433	69
H(3B)	6c	7461	4814	1168	69
H(3C)	6c	6118	2368	953	69
F(1)	6c	1251(5)	7694(5)	775(1)	35(1)
O(1)	3b	92(9)	0	1/6	36(2)
H(4)	6c	550(110)	−700	1360(30)	50(20)

Table 1. Selected crystallographic data for compound **1**.

	[Cu(NH$_3$)$_4$(NH$_3$)$_2$][F(H$_2$O)F]
Empirical formula	H$_{20}$CuF$_2$N$_6$O
Color and habitus	traffic-blue plate
Molecular mass, g mol^{-1}	221.76
Crystal system	trigonal
Space group	$P3_221$ (no. 154)
a, Å	6.7377(12)
c, Å	18.210(6)
V, Å^3	715.9(3)
Z	3
$\rho_{calcd.}$, Mg m^{-3}	1.54
λ, Å	0.71073
T, K	150(2)
$F(000)$, e	351
μ(MoK_α), mm^{-1}	2.3
Crystal size, mm^3	$0.3 \times 0.15 \times 0.1$
θ-range, deg	3.34 – 32.40
Refl. measured/independent/ observed [$I > 2\,\sigma(I)$]	5432/509/471
$R_{int}/R\sigma$	0.0703/0.0295
h, k, l range	−6 to 6, −6 to 6, −18 to 18
$R(F)$ ($I > 2\,\sigma(I)$/all data)	0.0301/0.0336
$wR(F^2)$ ($I > 2\,\sigma(I)$/all data)	0.0746/0.0765
S (all data)	1.088
Data/parameter/restraints	509/47/0
$(\Delta/\sigma)_{max}$	0.000
Flack parameter	0.05(6)
$\Delta\rho_{max/min}$, e Å^{-3}	0.39/ − 0.28

and [Cu(NH$_3$)$_6$]Br$_2$ were reinvestigated, and single-crystal X-ray diffraction on the chloride has shown Cu–N distances of 2.068(7) (equatorial) and 2.24(2) Å (axial). EXAFS studies revealed the following values for the chloride/bromide: 2.060(7) / 2.064(7) Å (equatorial) and 2.32(2)/2.34(2) Å (axial) [5]. A theoretical study on [Cu(NH$_3$)$_6$]$^{2+}$ in the gas phase showed three different Cu–N distances with 2.171 and 2.174 Å for the equatorial and 2.512 Å for the axial positions [6]. Therefore, the cationic unit of the chloride/bromide and of the title compound is best described as [Cu(NH$_3$)$_4$(NH$_3$)$_2$]$^{2+}$.

In the isotypic compound [Cd(NH$_3$)$_6$][F(H$_2$O)F] the Cd(II)–N distances of the axial and equatorial ligands are not different [7]. The Cd–N distances are 2.336(2) Å for Cd(1)–N(1) to 2.406(2) Å for Cd(1)–N(3), thus they are elongated compared to the ones in **1**. For [Cd(NH$_3$)$_6$]Cl$_2$ a similar Cd–N distance has been reported at 2.341(4) Å [5], and in [Cd(NH$_3$)$_6$]C$_{60}$ · 6 NH$_3$ the Cd–N distances are in the range from 2.321 to 2.407 Å [8].

The fluorine atom F(1) in **1** shows no direct contact to the copper atom. The Cu–F distance is 4.018(3) Å compared to 1.9062(9) and 1.90(7) Å in pure CuF$_2$ [9, 10]. In the isotypic Cd compound the Cd–F distance is very similar with 4.099(2) Å [7]. The fluoride anion is an acceptor of in total seven N–H⋯F hydrogen bonds from four [Cu(NH$_3$)$_6$]$^{2+}$ units and from the H$_2$O solvate molecule with oxygen atom O(1). The coordination sphere of F(1) is shown in Fig. 2, the coordination of the [Cu(NH$_3$)$_6$]$^{2+}$ cation by eight symmetry-equivalent F$^-$ anions in Fig. 3.

An accepted and simple model for the assessment of hydrogen bond strength is the shortening of the

Table 3. Selected distances (Å) and angles (deg) of **1**. Symmetry transformations for the generation of equivalent atoms: #1 $x, y, -z$; #2 $x-y, -y, -z+1/3$; #3 $x, y-1, z$; #4 $x-y+1, -y+1, -z+1/3$.

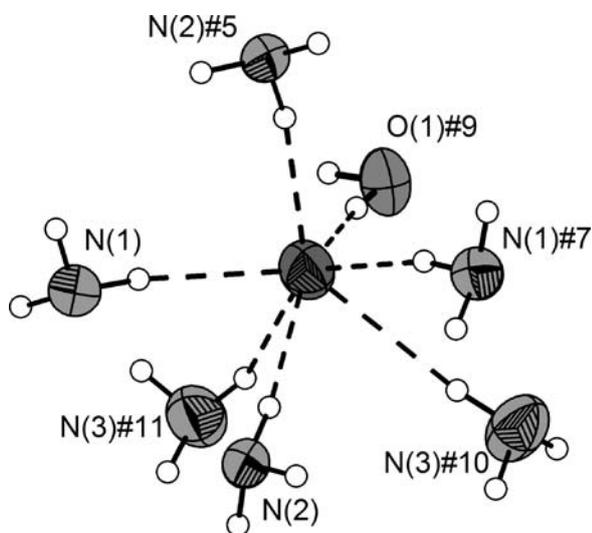| Atoms		Atoms	
Cu(1)–N(1)	2.120(4)	N(1)–H(1A)	0.91
Cu(1)–N(2)	2.103(4)	N(1)–H(1B)	0.91
Cu(1)–N(3)	2.370(5)	N(1)–H(1C)	0.91
Cu(1)–F(1)	4.018(3)	N(2)–H(2A)	0.91
Cu(1)–O(1)	4.355(2)	N(2)–H(2B)	0.91
N(1)–Cu(1)–N(1)#1	90.8(2)	N(2)–H(2C)	0.91
N(1)–Cu(1)–N(3)	89.8(2)	N(3)–H(3A)	0.91
N(2)–Cu(1)–N(3)	96.0(2)	N(3)–H(3B)	0.91
N(2)–Cu(1)–N(1)#1	177.1(2)	N(3)–H(3C)	0.91
N(3)#1–Cu(1)–N(3)	174.6(3)	O(1)–H(4)	0.88(6)
H(4)–O(1)–H(4)#2	104(5)	F(1)#3–O(1)–F(1)#4	107.09(9)

Fig. 2. A projection of the coordination sphere of the fluoride ion F(1). N–H···F and O–H···F hydrogen bonds are dashed in black. Displacement ellipsoids are shown at the 70% probability level at 150 K, H atoms as spheres with arbitrary radii. Symmetry transformations used to generate equivalent atoms: #5 $x+1, y, -z$; #7 $x, y-1, -z$; #9 $x, y+1, z$; #10 $x-1, y, z$; #11 $x-y, -y+1, -z+1/3$.

hydrogen···acceptor distance (H···A), compared to the sum of the van der Waals radii, and the deviation of the $D-H···A$ angles (D = donor) from 180°. When the shortening of the hydrogen bond is plotted as a function of the deviation of the angle, the strongest hydrogen bonds are found in the upper left, and the weakest ones in the lower right region of the plot [11]. Among all hydrogen bonds, the O–H···O, N–H···O, O–H···N, O–H···F and F–H···O contacts are the best explored in organic and inorganic compounds [12, 13].
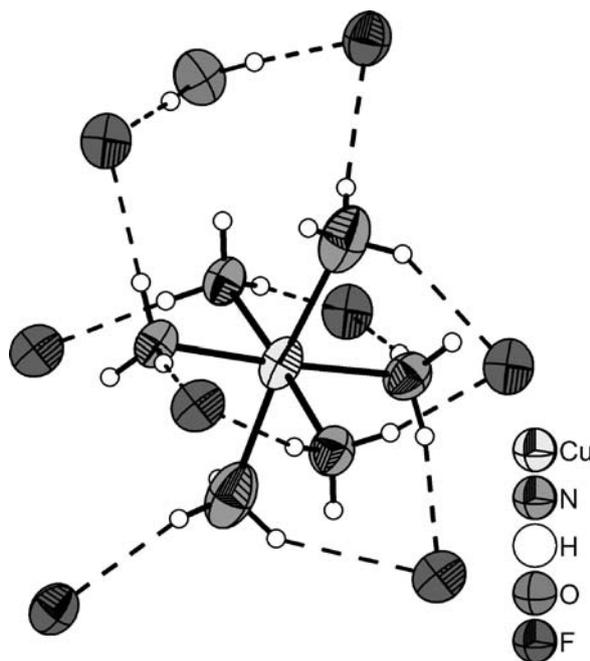

Fig. 3. Projection of the $[Cu(NH_3)_6]^{2+}$ cation and its coordination to symmetry-equivalent F$^-$ anions *via* N–H···F hydrogen bonding (dashed in black). The bridging of two fluoride ions by an H$_2$O molecule *via* O–H···F hydrogen bonds is also indicated. Displacement ellipsoids are shown at 70% probability level at 150 K, H atoms as spheres with arbitrary radii. Atomic numbering and symmetry transformations are omitted for clarity.

F–H···F [14 – 18] and N–H···N [19 – 22] hydrogen bonding has been investigated much less, and N–H···F hydrogen bonding – outside the area of modified proteins – is very little explored [7, 23 – 33]. The N–H···F hydrogen bonds in **1** show donor···acceptor ($D···A$) distances between 2.938(5) and 3.229(6) Å, and the $D···A$ distances for the N–H···O hydrogen bonds are 3.096(4) and 3.327(6) Å (Table 4). The deviation of the $D–H···A$ angles from 180° is in the range of 7.6 to 31.1° for N–H···F and 7.2 to 19.9° for the N–H···O hydrogen bonds. These data are summarized in Table 5, and a graphical presentation is given in Fig. 4. The isotypic Cd compound shows similar distances for the hydrogen bonds, with $D···A$ (N–H···F) distances between 2.900(2) and 3.135(3) Å, and $D···A$ (N–H···O) distances between 3.056(2) and 3.262(3) Å. The deviation of the $D–H···A$ angles from 180° is in the range from 5.0 to 28.8° for N–H···F, and from 14.0 to 19.0° for the N–H···O hydrogen bonds [7].

Table 4. Selected D–H, H···*A*, *D*···*A* hydrogen bond lengths (Å) and <*DHA* angles (deg) of **1** (*D* = donor, *A* = acceptor). Symmetry transformations for the generation of equivalent atoms: #4 $x-y+1$, $-y+1$, $-z+1/3$; #5 $x+1$, y, $-z$; #6 $x+1$, $y+1$, z; #7 $y-1$, x, $-z$; #8 $x+1$, y, z.

Atoms	*D*–H	H···*A*	*D*···*A*	<*DHA*
N(1)–H(1A)···F(1)	0.91	2.15	3.041(6)	166.2
N(1)–H(1B)···F(1)#5	0.91	2.07	2.959(5)	167.5
N(1)–H(1C)···O(1)	0.91	2.46	3.327(6)	160.1
N(2)–H(2A)··· O(1)#7	0.91	2.19	3.096(4)	172.8
N(2)–H(2B)···F(1)	0.91	2.14	3.038(5)	170.3
N(2)–H(2C)··· F(1)#6	0.91	2.03	2.938(5)	172.4
N(3)–H(3A)···F(1)#4	0.91	2.24	3.107(5)	158.5
N(3)–H(3B)···F(1)#8	0.91	2.42	3.229(6)	148.9
O(1)–H(4)···F(1)#8	0.88(6)	1.74(6)	2.621(5)	175(6)

Table 5. Shortening of H···*A* distances (%) as compared to the sum of their van der Waals radii [47] and deviation of *D*–H···*A* angles from 180° (*D* = donor, *A* = acceptor). Symmetry transformations for the generation of equivalent atoms: #4 $x-y+1$, $-y+1$, $-z+1/3$; #5 $x+1$, y, $-z$; #6 $x+1$, $y+1$, z; #7 x, $y-1$, $-z$; #8 $x+1$, y, z.

Hydrogen bond	Shortening (%)	Deviation from 180° (deg)
N(1)–H(1A)···F(1)	19.48	13.80
N(1)–H(1B)···F(1)#5	22.47	12.50
N(1)–H(1C)···O(1)	9.56	19.90
N(2)–H(2A)···O(1)#7	19.49	7.20
N(2)–H(2B)···F(1)	19.85	9.70
N(2)–H(2C)···F(1)#6	23.97	7.60
N(3)–H(3A)···F(1)#4	16.10	21.50
N(3)–H(3B)···F(1)#8	9.36	31.10
O(1)–H(4)···F(1)#8	34.83	5.00

The strongest N–H···F hydrogen bond with 24 % shortening and only 7.6° deviation from 180° is N(2)–H(2C)···F(1)#6 with a *D*···*A* distance of only 2.938(5) Å, while the weakest one is N(3)–H(3B)···F(1)#8 with only 9.4 % shortening and a deviation of 31.1° from linearity. The two N–H···O hydrogen bonds show 19.5 and 9.6 % shortening and 7.2 and 19.9° angle deviation. Since fluorine and oxygen are more electronegative than nitrogen, they should form stronger hydrogen bonds. In our case, the O(1)–H(4)···F(1)#8 hydrogen bond is the strongest one with 34.8 % shortening, only 5° angle deviation and with a *D*···*A* distance of only 2.621(4) Å. The educt, CuF$_2$ · 2 H$_2$O, also features O–H···F hydrogen bonding, with O···F distances of 2.717(1) [10], and 2.715(6) Å [9]. Compounds like FeSiF$_6$ · 6 H$_2$O, ZnF$_2$ · 4 H$_2$O, SrTiF$_6$ · 2 H$_2$O, and Te(OH)$_6$ · NaF have O···F distances ranging from 2.50 to 2.77 Å, and the
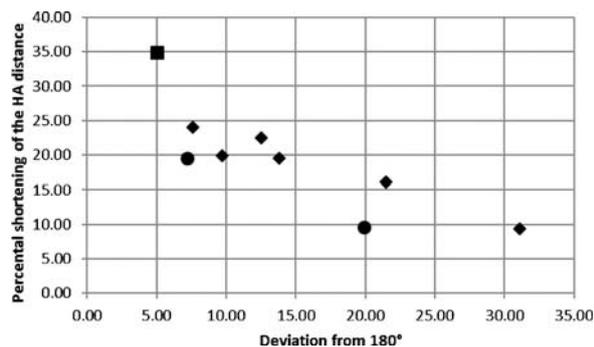

Fig. 4. A diagram showing the strengths of hydrogen bonds in **1**. The percental shortening of the H···*A* distance compared to the sum of the van der Waals radii is plotted as a function of the deviation of the *D*–H···*A* angle from 180° (*D* = donor, *A* = acceptor). The black square indicates O–H···F, black diamonds N–H···F and black balls N–H···O hydrogen bonding. The margins of error are typically within 0.7 % and 3 deg.

O···F distance of **1** is in good agreement with these values [34, 35].

Due to the short *D*···*A* distance of only 2.621(4) Å for O···F$^-$ in compound **1** and in view of the well known N$_2$H$_7$$^+$ ([H$_3$N–H···NH$_3$]$^+$) cation [36], the moiety can also be described as a bent, C_{2v}-symmetric [F···H–O–H···F]$^{2-}$ anion. This anion has been reported previously by Bowman-James and coworkers in the compound [H$_6$*L*(F)$_2$(H$_2$O)][SiF$_6$]$_2$ · 12 H$_2$O (*L* = PEAcrypt) [37]. They reported a comparable *D*···*A* distance in the range of 2.709(1) to 2.717(1) Å, which is approximately 0.2 Å longer compared to the [F(H$_2$O)F]$^{2-}$ anion of compound **1**. Molecular species of hydrated fluoride anions are known in the literature, for example [F(H$_2$O)]$^-$ [38], [F(H$_2$O)$_4$]$^-$ [39], [F(H$_2$O)$_4$]$_4^-$ [40], and [F$_4$(H$_2$O)$_{10}$]$^{4-}$ [41] were reported stabilized in various cryptand-like molecules. For the anion [F$_2$(H$_2$O)$_6$]$^{2-}$ comparable *D*···*A* distances ranging from 2.655 to 2.912 Å were reported [42]. To the best of your knowledge, compound **1** and the isotypic [Cd(NH$_3$)$_6$][F(H$_2$O)F] [7] are the first examples of the [F(H$_2$O)F]$^{2-}$ anion outside the stabilizing environment of a cryptand.

No clear discrimination of N–H···O and N–H···F hydrogen bond strength is possible from Fig. 4. However, only N–H···F and O–H···F hydrogen bonds, but no O–H···N hydrogen bonds are present in **1**. This may be due to the fact that first, fluorine is the better acceptor for hydrogen bonds forming the strongest hydrogen bonds, and second that NH$_3$ has a higher tendency to bind to Cu(II) than H$_2$O, and therefore the lone pair of

Table 6. Anisotropic displacement parameters (Å$^2 \times 10^3$) for **1**. U is defined as $\exp(-2\pi2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2b^*c^*klU_{23} + 2a^*c^*hlU_{13} + 2a^*b^*hkU_{12}))$.

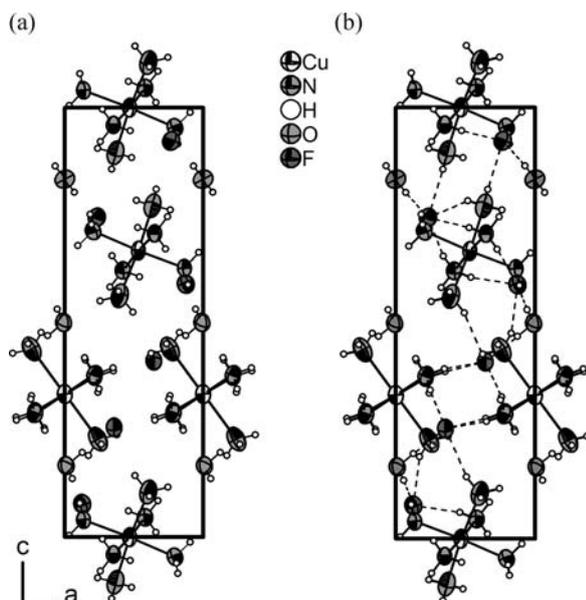| Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	23(1)	23(1)	42(1)	−1	1(1)	10(1)
N(1)	28(3)	28(3)	37(3)	4(2)	0(2)	14(2)
N(2)	22(3)	23(3)	35(3)	0(2)	−1	11(2)
N(3)	34(3)	33(4)	67(4)	−10	8(3)	12(3)
F(1)	34(2)	34(2)	42(2)	−3	−2	20(2)
O(1)	30(3)	45(4)	39(4)	−5	−2	22(2)

Fig. 5. Projection of the unit cell of **1** onto the *ac* plane (a) and hydrogen bonding network (dashed in black) of **1** (b). Displacement ellipsoids are shown at 70 % probability level at 150 K, H atoms as spheres with arbitrary radii. Atomic numbering and symmetry transformations are omitted for clarity.

a nitrogen atom is not available to act as an acceptor atom for hydrogen bonding.

A projection of the unit cell of **1** on the *ac* plane is shown in Fig. 5a, and the connectivity of the moieties by hydrogen bonding leading to a three-dimensional network is displayed in Fig. 5b.

In summary we have shown that CuF$_2$ · 2 H$_2$O reacts with dry liquid ammonia forming traffic-blue crystals of the composition [Cu(NH$_3$)$_4$(NH$_3$)$_2$][F(H$_2$O)F] (**1**) the structure of which has been presented. **1** is the ammoniate of CuF$_2$ with the highest ammonia content known so far. The hexaammine copper(II) ion shows the expected Jahn–Teller distortion with equatorial Cu–N distances of 2.103(4) and 2.120(4) Å and

axial Cu–N distances of 2.370(5) Å. An analysis of the hydrogen bonding in **1** revealed the expected strong N–H···O, O–H···F and N–H···F hydrogen bonds, which lead to the formation of a three-dimensional network of interconnected [Cu(NH$_3$)$_6$]$^{2+}$, H$_2$O and F$^-$ moieties, with F$^-$ as a linker between [Cu(NH$_3$)$_6$]$^{2+}$ and H$_2$O units *via* hydrogen bonding. To the best of your knowledge, the compound presents the first example of the [F(H$_2$O)F]$^{2-}$ anion outside the stabilizing environment of a cryptand.

Experimental Section

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 crystallographic details of [Cu(NH$_3$)$_6$]F$_2$ · H$_2$O (**1**)*

CuF$_2$ · 2 H$_2$O was synthesized from commercially available CuCl$_2$ (VWR) by repeated reaction with aqueous HF (40 %, VWR) and slow crystallization form the solution. CuF$_2$ · 2 H$_2$O (100 mg, 7.4 mmol) was then reacted with 15 mL of liquid ammonia at −78 °C. The color of the solution and of the solid remaining at the bottom of the reaction vessel changed to light-green, green and finally traffic-blue within half an hour. After 2 months of storage at −38 °C tiny traffic-blue crystals were observed. Due to the instability of the crystals above −20 °C, no elemental or spectroscopic analyses were carried out. One of the crystals was selected at low temperature (< −40 °C) and mounted onto the goniometer using the Mitegen system. The extinction conditions pointed to the chiral space groups $P3_1$, $P3_2$, $P3_121$ and $P3_221$ with similar R_{int} values. The mean $|E^2 - 1|$ result was 0.736, indicating a non-centrosymmetric space group. The structure was solved by Direct Methods using SHELXS-97 [43] and refined against F^2 using SHELXL-97 [44] in space group $P3_221$, giving the results reported in Table 1. Refinements and twin refinements in the other space groups led to similar R values. However, there were Flack values close to 1 and obvious correlations between the atoms. Searches for higher symmetry in these space groups using PLATON [45] or KPLOT [46] always showed a two-fold axis and clearly indicated the space group $P3_221$ to be correct. All atoms were localized by Fourier cycling methods and refined anisotropically, hydrogen atoms were refined isotropically by the usage of a riding model or freely where applicable. All fluorine,

oxygen and nitrogen atoms could be clearly discriminated by their isotropic and anisotropic displacement parameters (Table 6). Because the presence of Cu(II) was indicated by the crystal color, the F atom must reside on a Wyckoff position with multiplicity six as the Cu atom resides on the 3*a* position.

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-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-419094.

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