Beryllium Diammine Difluoride $[BeF_2(NH_3)_2]$

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Beryllium difluoride BeF_2 reacts with liquid ammonia forming discrete diammine difluoro beryllium(II) $[BeF_2(NH_3)_2]$ molecules. The colorless compound crystallizes in the monoclinic space group $P2_1/c$ with a = 4.8815(2), b = 6.8528(3), c = 10.3690(5) Å, β = 92.01(1)°, V = 346.65(3) $Å^3$ at 123 K with Z = 4. $[BeF_2(NH_3)_2]$ is the first structurally characterized example of a beryllium-ammonia complex. The compound has been investigated further by Raman, IR, and DTA-TG measurements and by quantum chemical ELF, AIM and NBO calculations.

Key words: Beryllium, Fluoride, Liquid Ammonia, Crystal Structure, ELF

Introduction

The first experiments in the BeF_2/NH_3 system were carried out by Biltz and coworkers [1]. These authors observed that BeF_2 obtained by cooling from the melt does not react with liquid ammonia. However, when a frozen aqueous solution of BeF_2 was treated with liquid ammonia, and the water was extracted completely, the monoammoniate $BeF_2 \cdot NH_3$ appeared to remain according to vapor pressure measurements. In 1967 the reaction of BeF_2 with NH_3 was reinvestigated by Grigor'ev and coworkers who established the diammoniate $BeF_2 \cdot 2\,NH_3$ to be the final product [2]. Based on infrared absorption spectroscopy data this phase was proposed to exist as $[Be(NH_3)_4][BeF_4]$ and not as $[BeF_2(NH_3)_2]$. In our own studies we were now able to show by single crystal structure determination that the beryllium fluoride diammoniate is in fact composed of discrete $BeF_2(NH_3)_2$ molecules interconnected *via* N–H···F hydrogen bonding in the crystal lattice.

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

Formula	$H_6N_2BeF_2$
M_r	81.08
Cryst. size, mm^3	$0.2 \times 0.15 \times 0.1$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	4.8815(2)
b, Å	6.8528(3)
c, Å	10.3690(5)
β, deg	92.01(1)
V, $Å^3$	346.65(3)
Z	4
T, K	123(2)
D_{calcd}, g cm^{-3}	1.554
$\mu(MoK_\alpha)$, cm^{-1}	0.173
$F(000)$, e	168
hkl range	± 7, $-7+10$, ± 15
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	1.380
Refl. measured	12498
Refl. unique	1232
R_{int}	0.0253
Param. refined	48
$R1(F)/wR2(F^2)$[a] (all refl.)	0.0456/0.1031
GoF (F^2)[a]	1.068
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	0.31/−0.23

[a] $R1(F) = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.067P)^2]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$, $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Results and Discussion

Preparation and single crystal structure analysis

Anhydrous beryllium fluoride BeF_2 reacts only slowly with an excess of liquid ammonia at −78 °C. After four weeks of storage of the mixture at −40 °C colorless crystals of $[BeF_2(NH_3)_2]$ (**1**) can be obtained. The single crystal structure determination (Table 1) has shown that one beryllium atom Be(1), two fluorine atoms F(1) and F(2) and two nitrogen atoms N(1) and N(2) of ammonia molecules are present in the asymmetric unit. All atoms occupy the common 4*e* positions of space group $P2_1/c$. The beryllium ion is surrounded by the two fluoride anions and the two ammonia molecules in a tetrahedral shape forming the novel $[BeF_2(NH_3)_2]$ molecule the

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Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Be(1)–F(1)	1.5308(11)	Be(1)–F(2)	1.5202(11)
Be(1)–N(1)	1.7586(12)	Be(1)–N(2)	1.7491(13)
N–H	0.91		
F(1)–Be(1)–F(2)	110.95(7)	F(1)–Be(1)–N(1)	108.28(7)
F(1)–Be(1)–N(2)	109.10(7)	F(2)–Be(1)–N(1)	110.41(7)
F(2)–Be(1)–N(2)	108.96(7)	N(1)–Be(1)–N(2)	109.11(7)

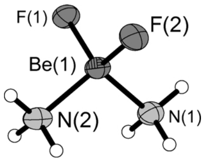

Fig. 1. A projection of the structure of the $[BeF_2(NH_3)_2]$ molecule which is close to C_{2v} symmetry. Thermal ellipsoids are shown at the 70 % probability level at 123 K.

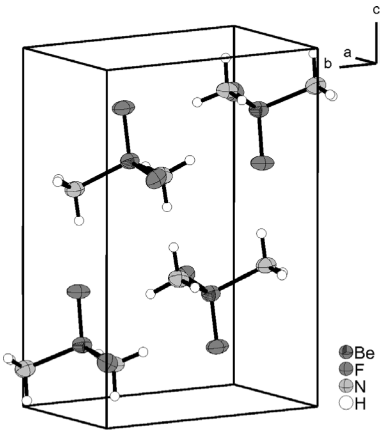

Fig. 2. A projection of the unit cell of **1** at 123 K. Thermal ellipsoids are shown at the 70 % probability level.

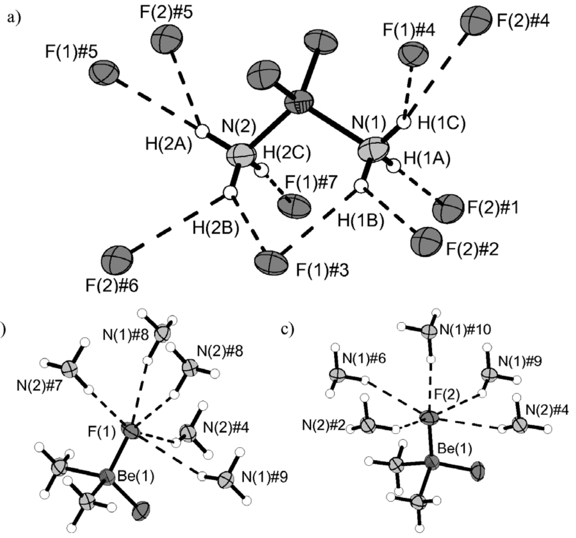

Fig. 3. The $[BeF_2(NH_3)_2]$ molecule and its hydrogen bonding to fluorine atoms of adjacent molecules. (Thermal displacement parameters are shown at the 70 % probability level at 123 K. Hydrogen bonds are shown as dashed lines). D–H, H···A, D···A hydrogen bond lengths (Å) and DHA angles (deg) (D = Donor, A = Acceptor):

N(1)–H(1A)···F(2)$^{\#1}$	0.91,	2.02,	2.9197(8),	171.7;
N(1)–H(1B)···F(2)$^{\#2}$	0.91,	2.64,	3.3070(9),	130.4;
N(1)–H(1B)···F(1)$^{\#3}$	0.91,	2.31,	3.0632(9),	140.1;
N(1)–H(1C)···F(2)$^{\#4}$	0.91,	2.40,	3.2089(10),	148.2;
N(1)–H(1C)···F(1)$^{\#4}$	0.91,	2.47,	3.2238(10),	140.5;
N(2)–H(2A)···F(1)$^{\#5}$	0.91,	2.31,	3.1303(9),	150.6;
N(2)–H(2A)···F(2)$^{\#5}$	0.91,	2.38,	3.1244(9),	138.6;
N(2)–H(2B)···F(1)$^{\#3}$	0.91,	2.25,	3.0261(9),	143.3;
N(2)–H(2B)···F(2)$^{\#6}$	0.91,	2.55,	3.1849(9),	127.5;
N(2)–H(2C)···F(1)$^{\#7}$	0.91,	2.03,	2.9335(8),	172.8.

Symmetry transformations for the generation of equivalent atoms: $^{\#1}\ x,\ -y+1/2,\ z+1/2$; $^{\#2}\ -x,\ y+1/2,\ -z+3/2$; $^{\#3}\ x-1,\ y,\ z$; $^{\#4}\ -x+1,\ y+1/2,\ -z+3/2$; $^{\#5}\ -x+1,\ y-1/2,\ -z+3/2$; $^{\#6}\ -x,\ y-1/2,\ -z+3/2$; $^{\#7}\ -x+1,\ -y,\ -z+2$.

structure of which is close to C_{2v} symmetry (Fig. 1). The Be–F bond lengths, 1.5308(11) Å for Be(1)–F(1) and 1.5202(11) Å for Be(1)–F(2), are significantly shorter compared to the Be–N distances, which are 1.7586(12) Å for Be(1)–N(1) and 1.7491(13) Å for Be(1)–N(2). This finding is as expected due to the strong Coulomb attraction of beryllium cations and fluoride anions and is in good agreement with Be–F distances found at 1.506(63) Å in tetrafluoroberyllates [3]. Be–N distances are 1.8 Å in nitrides, 1.6 Å in amidoberyllates, and 1.7 Å in complexes with organic nitrogen donor molecules [3 – 5]. The distances are also in agreement with quantum chemically calculated Be–F and Be–N bond lengths of 1.47 and 1.77 Å [6] and 1.84 Å, respectively (see below). We have not found an established example of a Be–NH_3 bond in the literature, and to the best of our knowledge even the fundamental species $[Be(NH_3)_4]^{2+}$ presented in textbooks has not been characterized by single crystal structure determinations.

The bond angles of **1** are all very close to tetrahedral which is somewhat surprising since strong fluorine-fluorine repulsions might be expected. The quite small F–Be–F bond angle of 110.95(7)° is probably due to the effect of the hydrogen bonding network present in the crystal lattice.

Bond lengths and angles are summarized in Table 2, and a projection of the unit cell of **1** is shown in Fig. 2. The discrete molecules of **1** are interconnected by N–H···F hydrogen bonds (Fig. 3a). Each ammonia molecule acts as a donor for two bifur-

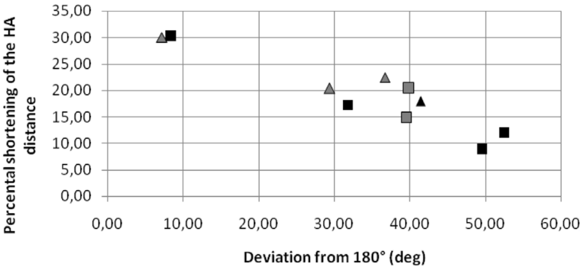

Fig. 4. A plot of hydrogen bond strenghts in compound **1**. Squares and triangles denote N(1) and N(2) as donor atoms, grey and black denote F(1) and F(2) as acceptor atoms, respectively. The stronger non-bifurcated hydrogen bonds in the upper left of the plot are clearly separated from the bifurcated ones in the right part of the plot. The margins of error are typically within 0.7 % and 3°, respectively.

cated and one regular N–H···F hydrogen bonds. Fluoride ion F(1) shows a coordination sphere similar to a trigonal prism as it is coordinated by five hydrogen atoms and one beryllium atom (Fig. 3b), while F(2) is surrounded by five hydrogen atoms and one beryllium atom in a shape similar to an octahedron (Fig. 3c). This hydrogen bonding leads in total to a $^3_\infty[BeF_2(NH_3)_2]$ network where one molecule is connected to nine others *via* hydrogen bonds. The strongest hydrogen bonds are formed in the linkages N(1)–H(1A)···F(2)$^{\#1}$ and N(2)–H(2C)···F(1)$^{\#7}$ with 30 % shortening compared to the sum of the van-der-Waals radii and only 8 and 7° deviation from 180° (Fig. 4). These hydrogen bonds are the only non-bifurcated ones. Bifurcated hydrogen bonding is generally considered to be weaker which is nicely confirmed in this work (Fig. 4). Compared to other N–H···F hydrogen bonds, for example in $[Ag(NH_3)_3(\mu\text{-}NH_3)Ag(NH_3)_4]MF_6 \cdot 8\,NH_3$ [7], $MF_4(NH_3)_4 \cdot NH_3$ (M = Zr, Hf) [8] and $[Ag(NH_3)_2]F \cdot 2\,NH_3$ [8], compound **1** appears to have shorter and hence stronger N–H···F hydrogen bonds. This phenomenon can be ascribed to the extreme "hardness" of the beryllium(II) cation which leads to a strong polarization of the N–H bond.

X-Ray powder diffractometry

Attempts to remove the liquid ammonia from the reaction mixture at r. t. under argon afforded a white powder. The X-ray powder diffraction pattern shows reflections which compare well with the powder pattern calculated for $BeF_2(NH_3)_2$ which is proof that **1** is stable at ambient temperature and pressure.

Table 3. IR bands and Raman lines (cm^{-1}) of $BeF_2(NH_3)_2$.

IR		Raman		Assignment
	Int.		Int.	
3367	vs, br	—	—	$\nu_{as}NH_3$
3210	vs	3206	vs, br	$\nu_s NH_3$
2346	w, br	2500	vw	δ(N–H···F)
1644	s, br	1691, 1625	m	$\delta_{as}(NH_3)$
1401	s	1324	vw	$\delta_s(NH_3)$
801	vs, vbr	580	mw	ν_{as}(BeF)
736	vs, vbr	496	w	ν_s(BeF)
–	–	326	m	ν_{as}(BeN)
–	–	310	w	ν_s(BeN)

MAS-NMR spectroscopy

^9Be NMR spectroscopy is a rarely employed analytical tool for the study of beryllium compounds in solutions and even less so in the solid state. ^9Be is a 100 % natural abundance isotope with spin 3/2 and a quadrupole moment of $5.2 \cdot 10^6$ cm^2. The ^9Be solid state resonance of $BeF_2(NH_3)_2$ is found at 1.77 ppm as a broad singlet. A chemical shift of 1.7 ppm has been given for the $[Be(NH_3)_4]^{2+}$ complex in solution. However, this $[Be(NH_3)_4]^{2+}$ complex has not been structurally characterized yet and therefore the assignment remains ambigous [9, 10]. In the ^1H NMR spectrum of solid **1** we found a very broad singlet at 2.97 ppm. For technical reasons no solid state ^{19}F NMR spectrum could be recorded. Solution ^9Be shift data for $[BeF_n(H_2O)_{4-n}]^{(n-2)-}$ are available, and the signal for $BeF_2(H_2O)_2$ is found in the range of 0.17 – 0.33 ppm [11]. The ^9Be solid state NMR spectrum confirms our finding by single crystal structure analysis as only one ^9Be resonance is observed which is expected for the $BeF_2(NH_3)_2$ species. If the diammoniate of BeF_2 would exist as $[Be(NH_3)_4][BeF_4]$, two ^9Be resonances are required.

Raman and infrared spectroscopy

The N–H stretching vibrations are found at 3206 cm^{-1} in the Raman spectrum and at 3367 and 3210 cm^{-1} in the FT-IR spectrum. Compared to the NH_3 valence vibrations of pure liquid ammonia at 3380, 3304 (Raman) and 3375, 3285 cm^{-1} (IR) these bands are red-shifted indicating the influence of the coordination to the Be atom and of the N–H···F hydrogen bonds [12]. By comparing spectra of beryllium fluorides and several ammine complexes known from the literature with our own data [5, 12 – 14], the Raman bands at 580 and 496 cm^{-1} can be assigned to the Be–F stretching modes and the Raman bands at 326 and 310 cm^{-1} to the Be–N vibrations. This distinction of Be–N and Be–F vibrations is not trivial but is in agreement with the reference data. It also agrees with relative band positions obtained from quantum chemical computations. It is reasonable to assume that Be–N bonds are weaker than Be–F bonds, which clearly determines the relative positions of IR and Raman bands. The IR band at 2346 cm^{-1} is assigned to the N–H···F hydrogen bond. Overall, the IR band positions are in agreement with the ones measured by Grigor'ev and coworkers, but these authors claim to have additionally observed bands of BeF_2 or of BeF_4^{2-} [2]. It is interesting to note that the IR spectrum of $BeF_2(NH_3)_2$ shows pronounced similarities to the IR spectrum of boron trifluoride ammonia (1/1), $BF_3 \cdot NH_3$ [15].

Thermal decomposition

The thermal decomposition of the beryllium diammine difluoride was studied previously by Grigro'ev and coworkers [2]. This diammoniate was found to be stable at r. t. The thermogravimetric analysis indicated that the first molecule of ammonia is lost between 80 and 130 °C, and the second one between 130 and 350 °C. X-Ray powder diffractometry showed the final decomposition product to be amorphous BeF_2. We were able to reproduce these findings. The first ammonia molecule is given off at 120.8 °C, the second one between 150 and 350 °C, leaving amorphous BeF_2 as a residue.

Quantum chemical calculations

The atomic parameters of the $BeF_2(NH_3)_2$ molecule were structurally optimized using GAUSSIAN03 at different levels of theory (HF, B3LYP, MP2, QCISD) using 6-311++G(3df,3pd) as basis sets [16]. The calculations converged for a structure with C_{2v} symmetry which was shown to be a stable ground state by frequency calculations and by a relaxed scan of the NH_3 rotation around the Be–N axis. While in the crystal structure the F–Be–F angle was determined to be 110.95(7)°, in the calculations mentioned above we find the F–Be–F angle in the range of 127.7–128.2° and the N–Be–N angle in the range of 108.9–109.8° for the gas phase. As already mentioned, the smaller F–Be–F angle in the crystal structure is probably caused by the hydrogen bond interactions. In the calculations we find the Be–N distances in the range of 1.83–1.85 Å and the Be–F distances in the range of 1.45–1.48 Å. These calculated bond lengths are in good agreement with the experimental data (Table 2).

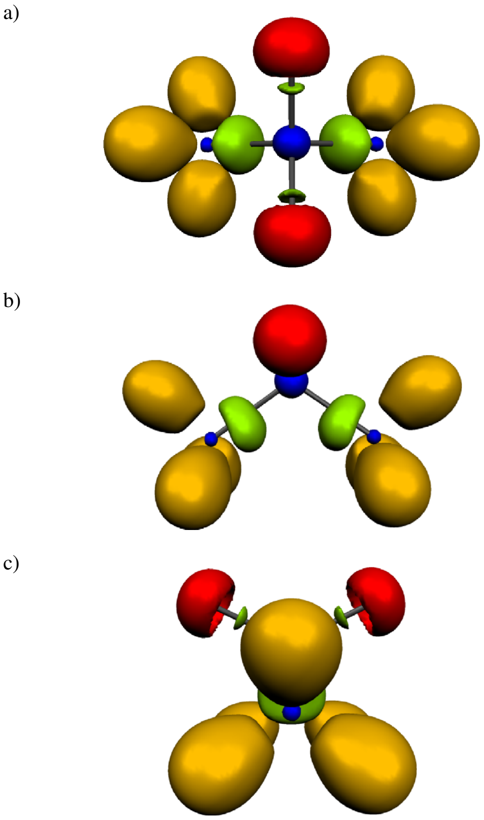

Fig. 5. (color online) The 3D-ELF of $BeF_2(NH_3)_2$ at $\eta(r) = 0.845$. Core basins are color-coded blue, monosynaptic valence basins red, protonated monosynaptic valence basins yellow, disynaptic valence basins green; a) shows the view along the C_2 axis with the fluorine atoms pointing towards the viewer, b) the view along a σ_v mirror plane, and c) the view along the other σ_v mirror plane.

With the application of the Electron Localization Function ELF on the wavefunctions derived at the HF and B3LYP level of theory, we tried to get a deeper insight into the chemical bonding of the $BeF_2(NH_3)_2$ molecule using the TOPMOD suite of programs [17–23]. The results of the population analyses on HF and B3LYP level are almost identical, so only the HF results are presented. Fig. 5 depicts the 3D-ELF of the $BeF_2(NH_3)_2$ molecule where the monosynaptic valence basins (lone pairs) on the fluorine atoms and the disynaptic valence basins (bonds) between Be–N and Be–F are clearly found. The Be–F bond is of course not expected to be completely ionic due to the strongly polarizing Be^{2+} cation. This is confirmed by the ELF analyses where a disynaptic valence basin between Be and F is found. A population analysis shows the Be, F and N core basins to be fully occupied with 2.05, 2.15

and 2.10 electrons, respectively. The protonated basins, that is, the N–H bonds, show the expected population of 1.95 electrons. The Be–N disynaptic basin is populated with 2.00 electrons, and hence a regular covalent bond may be assumed. The monosynapitc valence basins on the fluorine atoms, that is, the lone pairs of electrons, are populated with 6.38 electrons. The population of the Be–F disynaptic valence basin is found to be 1.45 electrons. This deficit of 0.55 electrons is assigned to the strongly polarized Be–F bond with its partly ionic character.

The application of the Atoms In Molecules AIM concept [24 – 27] to **1** shows basins with 9.93 electrons for the fluorine atoms and hence neon configuration. For beryllium we find a population of 2.20 electrons which is a little more than the helium configuration due to the strongly polarizing power of Be(II). The nitrogen atoms have a population of 8.21 electrons, and with the three hydrogen atoms attached (each 0.58 electrons) they also almost reach the neon configuration with 9.94 electrons. In total, 41.94 of the 42 electrons of the $BeF_2(NH_3)_2$ molecule are accounted for in the calculations. The results of the application of the AIM theory compare well with those obtained from the Natural Bond Orbital NBO analysis: The Be atom has a natural charge of $+1.7$ and the fluorine atoms of -0.9 each, while the nitrogen atoms have a natural charge of -1.1 due to the hydrogen atoms which have a mean natural charge of $+0.38$.

Conclusion

Beryllium difluoride dissolves in liquid ammonia to form the colorless molecular compound $BeF_2(NH_3)_2$ for which previously an ionic structure $[Be(NH_3)_4][BeF_4]$ had been proposed. The intermolecular N–H···F hydrogen bonding present in the crystal of the new compound has a pronounced influence on the F–Be–F bond angle which is predicted to be 18° larger in quantum chemical calculations for the molecule in the gas phase. The results of ELF, AIM and NBO calculations confirm the expectation that beryllium–fluorine bonding is partly covalent.

Experimental Section

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

Beryllium and its compounds are generally considered to be highly toxic. Therefore all necessary precautions should be taken against any contamination of the environment.

Synthesis of beryllium diammine difluoride

BeF_2 was obtained by literature procedures [28]. The crude product was treated with elemental fluorine at 125 °C to remove traces of water and oxygen. The obtained BeF_2 was amorphous. 100 mg (1.23 mmol) of BeF_2 was placed into a Schlenk tube, and about 10 mL of dry liquid ammonia was distilled into the reaction vessel at −78 °C. No dissolution process could be observed visually. After four weeks of storage at −40 °C colorless crystals had formed on the walls of the vessel of which one specimen was subjected to single crystal structure determination. Chemical analysis using standard titration methods to determine the ammonia content: NH_3: found 41.9 %, calcd. 42.0 %.

X-Ray powder patterns were recorded on a Stoe Stadi-P powder diffractometer using germanium-monochromated $CuK_{\alpha1}$ radiation and a linear position-sensitive detector. DTA-TG curves were obtained on a Netzsch STA 409 PC Luxx instrument and evaluated using the PROTEUS software [29]. Raman spectra were recorded on an ISA T64000 instrument using an Ar^+ laser tube (514.5 nm) in flame-sealed glass ampules. IR spectra were recorded on a JASCO FT-IR-460 plus spectrometer.

MAS-NMR spectra were recorded on a Bruker AV300 instrument at r. t. with resonance frequencies of 42.17 MHz for ^9Be and 300.13 MHz for ^1H. Spinning speeds were 12 kHz each with 20 and 2 s pulse repetitions, respectively.

*X-Ray structure determination of **1***

A colorless crystal of $0.2 \times 0.15 \times 0.1$ mm^3 size was mounted in hydrofluoroether oil (Galden PFPE, Solvay Solexis) and shock-cooled to 123 K. The diffraction intensities were collected on an Oxford Xcalibur3 diffractometer (MoK_α, λ = 0.71073 Å). Cell determination routines gave a primitive monoclinic unit cell. The data were reduced with the CRYSALISRED software, and an empirical absorption correction using spherical harmonics with SCALE3 ABSPACK was applied [30]. The structure was solved by Direct Methods (SHELXS-97) and refinded against F^2 with SHELXL-97 in space group $P2_1/c$ [31, 32]. All atoms where located *via* Difference Fourier Syntheses and refined anisotropically, hydrogen atoms isotropically using a riding model. With chemical reasoning, and based on their displacement parameters and occupational factors, the N and F atoms could be clearly distinguished.

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.fizinformationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420049.

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