Note

mer-Triammine Trifluorido Iron(III), *mer*-[FeF₃(NH₃)₃]

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Metal fluorides are scarcely soluble in liquid ammonia, and their ammine complexes are rare. The synthesis and crystal structure of the first ammine complex of an iron fluoride, the *mer*-triammine trifluorido iron(III), *mer*-[FeF₃(NH₃)₃], is presented. The compound crystallizes in the form of colorless, needle-shaped single crystals in the monoclinic space group $P2_1/n$ with Z = 4. The molecules are interconnected by strong N–H···F hydrogen bonds.

Key words: Iron, Fluoride, Ammine, Crystal Structure, Liquid Ammonia

Introduction

The chemistry of inorganic fluorides in liquid ammonia is scarcely explored due to their low solubility [1]. Biltz and coworkers found a way to avoid the solubility problem by using hydrates of fluorides and extracting them with liquid ammonia to obtain ammoniates [2]. The compositions of these ammoniates were analyzed using tensieudiometric, that is, volumepressure measurements [3]. To our knowledge, the reaction of FeF₃ with liquid ammonia has not been investigated and we present here the first structural evidence for the existence of ammine complexes of iron fluorides.

Results and Discussion

If moisture is completely excluded from the reaction of FeF₃ with liquid ammonia no reaction is observed. However, if the reaction vessel is not dried properly, FeF₃ reacts with liquid ammonia forming the title compound in quantitative yield. *mer*-[FeF₃(NH₃)₃] crystallizes in the monoclinic space group $P2_1/n$ with crystallographic details as shown in Table 3. All atoms reside

Table 1. Selected bond lengths and angles of the *mer*-[FeF₃- $(NH_3)_3$] molecule.

Atoms	Distance (Å)	Atoms	Angle (deg)
Fe(1)- $F(1)$	1.8981(15)	F(1)- $Fe(1)$ - $F(3)$	179.33(8)
Fe(1)-F(2)	1.9088(16)	F(1)- $Fe(1)$ - $F(2)$	89.87(7)
Fe(1)-F(3)	1.8988(15)	F(3)-Fe(1)-F(2)	89.46(7)
Fe(1)-N(1)	2.139(3)	N(3)-Fe(1)-N(1)	174.95(11)
Fe(1)-N(2)	2.122(2)	N(2)-Fe(1)-N(1)	88.70(11)
Fe(1)-N(3)	2.118(3)	N(3)-Fe(1)-N(2)	87.01(10)
	N	2)	



Fig. 1. The structure of the *mer*-[FeF₃(NH₃)₃] molecule at 150 K. Displacement ellipsoids are shown at the 70% probability level, hydrogen atoms with arbitrary radii.

on the common 4e Wyckoff position. The iron atom is coordinated by three symmetry-inequivalent fluoride ions and three inequivalent nitrogen atoms of ammonia molecules. The ligands are arranged in an octahedronlike manner to give the meridional isomer shown in Fig. 1. Explainable by VSEPR theory, the *mer*-isomer is more stable than the *fac*-isomer. The Fe-F distances are approximately 1.9 Å, the Fe-N distances are found around 2.1 Å. These bond lengths agree well with standard literature data [4]. The bond angles differ only little from the ideal 90 and 180°, with the largest deviation at 5° for the N(1)-Fe-N(3) angle. The N–H distances are found in a range from 0.78(3) to 0.89(3) Å, with H–N-H bond angles from 101(2) to 118(3)°. For individual bond lengths and angles see Table 1.

All hydrogen atoms are involved in N–H···F hydrogen bonds (Fig. 2) to nine symmetryequivalent [FeF₃-(NH₃)₃] molecules, where each fluorine atom is an acceptor of three hydrogen bonds. For details of the hydrogen bonding see Table 2. To discuss the strength of the encountered hydrogen bonds, a plot is used where the shortening percentage of the distance of the hydrogen atoms to the fluorine atoms as compared to the sum of their van der Waals radii is plotted *versus* the deviation of the N–H···F angle from 180°. Strong hydrogen bonds with a large shortening percentage and a small

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	D–H	$H{\cdots}A$	$D{\cdots}A$	∠DHA
N(1)- $H(1A)$ ···· $F(3c)$	0.78(3)	2.34(3)	3.122(3)	175(3)
N(1)- $H(1B)$ ···· $F(1f)$	0.86(4)	2.08(4)	2.929(3)	170(3)
N(1)- $H(1C)$ ···F(1h)	0.86(4)	2.28(4)	3.119(3)	163(3)
$N(2)-H(2A)\cdots F(2d)$	0.89(3)	2.11(3)	2.984(3)	169(3)
N(2)- $H(2B)$ ···· $F(2h)$	0.88(3)	2.01(3)	2.892(3)	175(3)
N(2)- $H(2C)$ ···F(3g)	0.87(3)	2.00(3)	2.836(3)	161(3)
$N(3)-H(3A)\cdots F(3d)$	0.84(3)	2.09(3)	2.906(3)	165(3)
$N(3)-H(3B)\cdots F(1b)$	0.86(3)	2.13(3)	2.976(3)	168(3)
$N(3)-H(3C)\cdots F(2e)$	0.84(4)	2.07(4)	2.893(3)	168(3)

Table 2. Hydrogen bond details of the title compound (Å, $deg)^a$.

^a Symmetry operations as in Fig. 2.



Fig. 2. The N–H···F hydrogen bonds (dashed) of the ammine ligands to adjacent, symmetry-equivalent fluoride ions of nine other [FeF₃(NH₃)₃] molecules are projected. Displacement ellipsoids are shown at the 70 % probability level, hydrogen atoms with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: a = 1/2 - x, 1/2 + y, 1/2 - z; b = -1/2 + x, 3/2 - y, 1/2 + z; c = 1/2 + x, 3/2 - y, -1/2 + z; e = -x, 2 - y, 1 - z; f = 1/2 + x, 3/2 - y, -1/2 + z; g = -x, 1 - y, 1 - z; h = 1/2 - x, -1/2 + y, 1/2 - z.

deviation from 180° generally appear in the upper left, weak hydrogen bonds in the lower right corner of the plot (Fig. 3).

All hydrogen bonds of the compound show deviations from 180° of only 5 to 19° . This is a quite narrow range, and because in reference compounds shortening percentages between 19 to 33 % are found, rather strong hydrogen bonds must be assumed. In other ammine complexes of fluorides, like [BeF2- $[Ag(NH_3)_2]F \cdot 2NH_3, \quad [M(NH_3)_4F_4] \cdot NH_3$ $(NH_3)_2],$ $(M = Zr, Hf), (N_2H_7)F, (NH_4)_2(N_2H_7)[UF_7-$ (NH₃)], $[UF_4(NH_3)_4]$ ·NH₃, $[BF_3(NH_3)] \cdot 3NH_3$ [SiF₄(NH₃)₂]·2NH₃, [Cs₃F₃(NH₃)₄], and [NH₄CsF₂], a diagonal trend from the upper left to the lower right is observed [5-10], and deviations from 180° extend well beyond 40° . These data confirm that the N–H···F hydrogen bonds of the title compound are really rather strong. This is not unexpected, as Fe³⁺ must strongly

Table 3. Crystal data and structure determination details for *mer*-[Fe(NH₃)₃F₃].

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Formula	Fe(NH ₃) ₃ F ₃
M _r	163.95
Crystal system	monoclinic
Size, mm ³	0.2 imes 0.01 imes 0.01
Space group	$P2_1/n$
a, Å	7.3559(8)
b, Å	9.5447(9)
<i>c</i> , Å	7.7722(7)
β , deg	92.009(9)
$V, Å^3$	545.35(9)
Ζ	4
$\rho_{\rm calc}$, g/cm ³	2.00
λ, Å	0.71073
Т, К	150
μ (Mo K_{α}), mm ⁻¹	2.7
$R_{\rm int} / R_{\sigma}$	0.0596 / 0.0963
Data / parameters / restraints	1869 / 101 / 0
$R(F)^{\mathrm{a}}$ $[I \ge 2\sigma(I)]$ / all data	0.0355 / 0.0871
$wR(F^2)^a [I \ge 2\sigma(I)] / all data$	0.0606 / 0.0669
GoF (F^2 , all data) ^b	0.797
$\Delta \rho_{\text{max}/\text{min}}$, e Å ⁻³	0.64 / -0.58
Extinction	0.0036(9)

 $\begin{array}{c} 0.0036(9) \\ a \\ R1(F) \\ = \\ \left\|F_{o}\right\| - \\ \left|F_{c}\right\|/\Sigma|F_{o}|, \\ wR(F^{2}) \\ = \\ \Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}, \\ for the compound: \\ w \\ = \\ \left[\sigma^{2}(F_{o}^{2}) + \\ (0.0261P)^{2} + \\ 0.000P\right]^{-1}, \\ where \\ P \\ = \\ \left(Max(F_{o}^{2}, 0) + \\ 2F_{c}^{2}\right)/3; \\ b \\ GoF \\ = \\ \left[\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/(n_{obs} - n_{param})\right]^{1/2}. \\ \end{array}$



Fig. 3. Plot of the shortening percentage of the $H \cdots F$ distance as compared to the van der Waals radii of H and F, plotted *versus* the deviation of the N–H···F angle from 180°. The margins of error are typically within 0.7% and 3°, respectively.

acidify the protons of the ammine ligands making the nitrogen atoms better H-donors. The N-H···F hydrogen bonding in crystals of the title compound leads to a complex three-dimensional network of [FeF₃(NH₃)₃] molecules. A projection of the unit cell of *mer*-[FeF₃(NH₃)₃] is shown in Fig. 4.

The compound *mer*-[FeF₃(NH₃)₃] offers the first structural evidence of ammine complexes of iron fluorides. The strong and extensive N–H···F hydrogen bonding in the crystals lends this compound sufficient



Fig. 4. The unit cell of the title compound at 150 K. Displacement ellipsoids are shown at the 70 % probability level, hydrogen atoms with arbitrary radii.

stability at low temperature, but decomposition occurs on warming.

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), http://www.fiz-karlsruhe.de/icsd.html, on quoting the depository number CSD 423231 for the compound, the names of the authors, and the citation of the paper.

Experimental Part

All work was carried out under argon (4.8, Westfalen AG) using standard Schlenk techniques. Liquid ammonia (3.8, Westfalen AG) was dried and stored over sodium metal at -78 °C. FeF₃ was prepared from the reaction of FeCl₃·6H₂O with 100 % F₂ gas at 300 °C. A reaction vessel was charged with 130 mg (1.15 mmol) of FeF3 and, after evacuation, with approximately 10 mL of liquid ammonia at -40 °C. Colorless, needle-shaped crystals suitable for the X-ray diffraction experiment were obtained. The crystals are temperature-sensitive and decrepitate at temperatures above -20 °C losing ammonia. All crystals were handled in a perfluorinated ether under nitrogen atmosphere at temperatures below -50 °C, and mounted on the diffractometer using the MiTeGen MicroLoop system. The structure was solved using Direct Methods and refined on F^2 [11, 12]. All non-hydrogen atoms were localized by Fourier cycling methods and refined anisotropically. The hydrogen atoms were localized by Fourier cycling methods and refined isotropically.

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