Tetraammine Tetrafluorido Cerium(IV) Ammonia (1/1), $[CeF_4(NH_3)_4] \cdot NH_3$

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The synthesis and crystal structure of the first ammine complex of a cerium fluoride, tetraammine tetrafluorido cerium(IV) ammonia (1/1), $[CeF_4(NH_3)_4] \cdot NH_3$, are presented. The compound crystallizes in the form of colorless, block-shaped single crystals in the tetragonal space group $P4/ncc$ with a = 9.03215(9), c = 10.96404(17) Å, V = 894.443(19) Å^3, and Z = 4. The compound contains discrete $[CeF_4(NH_3)_4]$ molecules interconnected by N–H···F hydrogen bonds.

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

Introduction

Metal fluorides dissolve only sparingly in liquid ammonia and their chemistry is therefore little explored [1]. Biltz and coworkers used hydrates of fluorides to lower the lattice energy and hence to improve their solubility in liquid ammonia [2]. The ammoniates obtained in this way were analyzed using volume-pressure measurements [3]. In our own investigations on the reactions of fluorides with anhydrous ammonia, we discovered that fluorides of the β-ZrF_4 structure type, which is also known for the tetrafluorides of the elements Hf, Ce, Th, U, Np, Pu, and Cm [4 – 7] show appreciable solubility and form the isotypic compounds $[MF_4(NH_3)_4] \cdot NH_3$ (M = Zr, Hf, U) [8, 9]. To our knowledge, the reaction of CeF_4 with liquid ammonia has not been investigated and we present here the first structural evidence for the existence of ammine complexes of cerium fluorides.

Results and Discussion

Cerium(IV) fluoride dissolves sparingly in liquid ammonia and forms the crystalline compound $[CeF_4(NH_3)_4] \cdot NH_3$ (see Table 4 for crystallographic details). As the title compound is isotypic to $[MF_4(NH_3)_4] \cdot NH_3$ (M = Zr, Hf, U) [8, 9], a detailed structural description will not be given. The crystals contain discrete $[CeF_4(NH_3)_4]$ molecules (Fig. 1) with four Ce–F distances of 2.1586(14) and four U–N distances of 2.586(2) Å. Selected bond lengths and angles are listed in Table 1. The molecules are interconnected *via* N–H···F hydrogen bonds. These hydrogen bonds have H···F distances of 2.24(3) and 2.35(3) Å with N–H···F angles of 177(3) and 160(4)°. Hydrogen bonds from the ammine ligands to the nitrogen atom of the crystal ammonia can also be inferred with an H···N distance of 2.60(3) Å and an N–H···N hydrogen bond angle of 144(2)°. Details of the hydrogen bonds are listed in Table 2. The coordination sphere of the cerium atom can be described as distorted square antiprismatic or bisphenoidal. The distance of the ammonia molecule of solvation to the next nearest fluorine atom

Table 1. Selected bond lengths and angles of the $[CeF_4(NH_3)_4]$ molecule[a].

Atoms	Distance (Å)	Atoms	Angle (deg)
Ce(1)–F(1)	2.1586(14)	F(1)$^{\#1}$-Ce(1)–F(1)$^{\#2}$	146.05(8)
Ce(1)–N(1)	2.586(2)	F(1)$^{\#1}$-Ce(1)–F(1)$^{\#3}$	104.98(8)
N(1)–H(1A)	0.66(3)	F(1)$^{\#1}$-Ce(1)–F(1)	84.95(8)
N(1)–H(1B)	0.84(3)	F(1)$^{\#1}$-Ce(1)–N(1)$^{\#1}$	72.62(7)
N(1)–H(1C)	0.84(3)	F(1)$^{\#2}$-Ce(1)–N(1)$^{\#1}$	140.62(7)

[a] Symmetry operations as in Fig. 1.

Table 2. Hydrogen bond parameters of the title compound (Å, deg).

	D–H	H···A	D···A	∠DHA
N(1)–H(1A)···F(1)$^{\#4}$	0.66(3)	2.35(3)	2.975(3)	160(4)
N(1)–H(1B)···F(1)$^{\#5}$	0.84(3)	2.24(3)	3.075(3)	177(3)
N(1)–H(1C)···N(2)$^{\#6}$	0.84(3)	2.60(3)	3.315(4)	144(2)

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

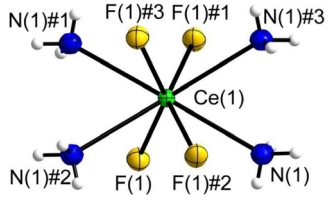

Fig. 1. The $[CeF_4(NH_3)_4]$ molecule at 123 K. Displacement ellipsoids are shown at the 70 % probability level, hydrogen atoms with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: $^{\#1}$ $-x+1$, $-y+1$, $-z+1/2$; $^{\#2}$ $-x+3/2$, $-y+1/2$, z; $^{\#3}$ $x-1/2$, $y+1/2$, $-z+1/2$.

	Zr	Hf	Ce	U
M-F	2.036(2)	2.040(5)	2.1586(14)	2.188(4)
M-N	2.397(3)	2.381(7)	2.586(2)	2.618(5)
F(1)-*M*-F(1)$^{\#1}$	85.08(11)	85.0(3)	84.95(8)	85.0(2)
F(1)-*M*-F(1)$^{\#2}$	104.96(11)	105.1(3)	104.98(8)	104.4(2)
F(1)-*M*-F(1)$^{\#3}$	145.86(11)	145.8(3)	146.05(8)	147.1(2)
N(1)-*M*-N(1)$^{\#1}$	140.70(13)	141.2(4)	141.59(11)	141.4(3)
N(1)-*M*-N(1)$^{\#2}$	121.31(14)	121.0(3)	122.44(12)	122.1(2)
N(1)-*M*-N(1)$^{\#3}$	72.93(14)	72.9(4)	71.34(11)	71.7(2)

Table 3. Comparison of bond lengths (Å) and bond angles (deg) of the isotypic compounds $[MF_4(NH_3)_4]\cdot NH_3$ (M = Zr, Hf, Ce, U)[a].

[a] Symmetry operations as in Fig. 1.

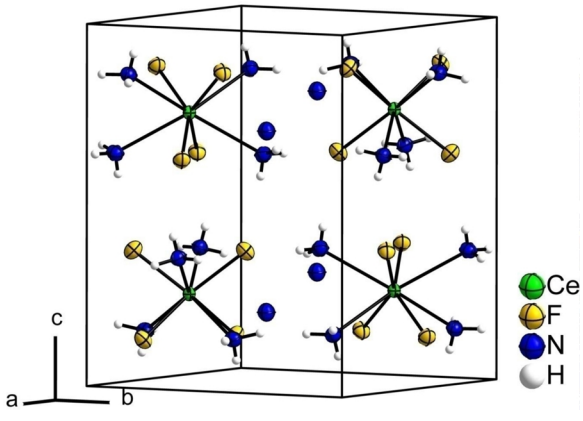

Fig. 2. The unit cell of the title compound at 123 K. Displacement ellipsoids are shown at the 70 % probability level, hydrogen atoms with arbitrary radii.

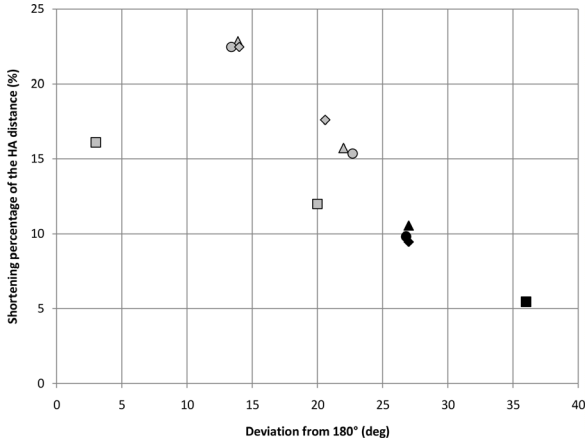

Fig. 3. Plot of the shortening percentage of the H···F and H···N distances as compared to the van der Waals radii of H, F and N, plotted *versus* the deviation of the N–H···X (X = F, N) angle from 180°. N–H hydrogen bonds to F atoms are shown in grey and in black to N atoms. Triangles stand for the Zr, circles for the Hf, boxes for the Ce, and diamonds for the U compound.

is 3.061(2) Å, and therefore further connectivities *via* N–H···F hydrogen bonds must be assumed. Fig. 2 shows a projection of the unit cell of the title compound. The extensive hydrogen bonding lends some stability to the crystals at low temperature, but upon warming ammonia is lost rapidly. From the chemical analyses and thermogravimetric studies on the analogous compound $[UF_4(NH_3)_4]\cdot NH_3$ it can be assumed that only the ammonia of crystallization is lost upon warming to r. t., and that the $[CeF_4(NH_3)_4]$ molecule should be stable to temperatures above 100 °C [9].

Table 3 shows a comparison of the bond lengths and angles of the isotypic compounds $[MF_4(NH_3)_4]\cdot NH_3$ (M = Zr, Hf, Ce, U) [8, 9]. While the bond angles are essentially similar, the bond lengths differ slightly. This can be attributed to the ionic radii of the tetravalent metal atoms with coordination number eight (Zr^{4+} 0.98, Hf^{4+} 0.97, Ce^{4+} 1.11, U^{4+} 1.14 Å) [10].

Comparing the hydrogen bonds of the four isotypic compounds is problematic, as for M = Zr, Hf, U the hydrogen atoms were refined using a riding model. In the Ce compound the hydrogen atoms of the ammine ligands could be located from the difference Fourier synthesis. To discuss the strength of the hydrogen bonds encountered 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 deviation from 180° generally appear in the upper left, weak hydrogen bonds in the lower right corner of the plot. As can be seen from Fig. 3, the hydrogen bond parameters are rather similar for the compounds with Zr, Hf, and U, but different for Ce, as is expected due to the different hydrogen atom treatment. However, the plot clearly shows the differences of hydrogen bond strength for N–H···F and N–H···N hydrogen bonds.

In summary, $[CeF_4(NH_3)_4]\cdot NH_3$ has been synthesized from CeF_4 in liquid ammonia. In crystals of this compound, the discrete $[CeF_4(NH_3)_4]$ molecules are interconnected by an extensive N–H···F hydrogen bond system.

Table 4. Crystal structure data for the title compound $[CeF_4(NH_3)_4]\cdot NH_3$.

Formula	$CeF_4H_{15}N_5$
M_r	301.29
Crystal system	tetragonal
Size, mm^3	$0.03 \times 0.03 \times 0.03$
Space group	$P4/ncc$
a, Å	9.03215(9)
c, Å	10.96404(17)
V, Å^3	894.443(19)
Z	4
ρ_{calc}, g/cm^3	2.24
λ (Å)	0.71073
T, K	123
μ(MoK$_\alpha$), mm^{-1}	5.1
R_{int} / R_σ	0.0340 / 0.0085
Data / parameters / restraints	721 / 37 / 0
$R(F)$[a] $[I \geq 2\sigma(I)]$ / all data	0.0155 / 0.0256
$wR(F^2)$[a] $[I \geq 2\sigma(I)]$ / all data	0.0425 / 0.0443
GoF (F^2, all data)[b]	1.162
$\Delta\rho_{max/min}$, e Å^{-3}	0.63 / −0.34

[a] $R1(F) = \|\|F_o| - |F_c\|/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, for the compound: $w = [\sigma^2(F_o^2) + (0.0182P)^2 + 1.4973P]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; [b] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

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 423232 for the compound, the name of the authors, and citation of the paper.

Experimental Section

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. CeF_4 was prepared from CeF_3 and a gas mixture of 10 % F_2 in Ar at 400 °C [4]. A reaction vessel was charged with 94 mg (0.43 mmol) of CeF_4 and, after evacuation, with approximately 10 mL of liquid ammonia at −40 °C. Colorless, block-shaped crystals suitable for the X-ray diffraction experiment were obtained after storage at −40 °C for three months. The crystals are temperature-sensitive and decrepitate at temperatures above −20 °C loosing 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.

Acknowledgements

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