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Synthesis and structure of hydroxylammonium fluoroaluminate

Matjaž Kristl · Amalija Golobič · Brina Dojer · Miha Drofenik

Abstract Hydroxylammonium fluoroaluminate with the formula $(NH_3OH)_2AlF_5$ was synthesized by the reaction of solid NH_3OHF and an aqueous solution of aluminum in HF, and its structure was determined by single-crystal X-ray diffraction. The structure consists of NH_3OH^+ cations and centrosymmetrical AlF_6 octahedra, which are formed by sharing two opposite corners connected in polymeric $(AlF_5)_n^{2-}$ anions. Oxygen and nitrogen atoms of hydroxylammonium cations are donors of hydrogen bonds to terminal fluorine atoms of fluoroaluminate chains. The compound crystallizes monoclinic $P2/c$, with cell parameters $a = 10.8675(3)$ Å, $b = 7.3098(2)$ Å, $c = 7.2071(2)$ Å, and $\beta = 91.080(2)°$. The thermal decomposition of the compound was studied by TG, DSC, and X-ray powder diffraction. By controlled heating of $(NH_3OH)_2 AlF_5$, a new compound with the formula $(NH_3OH)AlF_4$ was obtained, and the final product of the decomposition is γ-AlF_3.

Keywords Aluminate · Fluoride · Thermochemistry · X-ray structure determination · Hydrogen bonds

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Introduction

Hydroxylamine with the formula NH_2OH is a derivative of ammonia, in which one hydrogen atom is replaced with an –OH group. The investigation of hydroxylammonium fluorometallates with the general formula $(NH_3OH)_xMF_y$ is interesting for the study of hydrogen bonds since they include all three elements that are capable of forming strong hydrogen bonds (O, N, and F). However, the area of metal fluorides is still relatively underexplored because of the difficulty in handling these materials. Our laboratory developed a novel method that uses solid NH_3OHF, prepared by adding an ethanolic solution of NH_2OH to an aqueous solution of HF [1]. This method provides many advantages compared to earlier research that used aqueous or ethanolic hydroxylammonium solutions in the synthesis of fluorometallates. Over the last 15 years, we have been able to synthesize a number of new hydroxylammonium fluorometallates, including compounds of Zr, Ga, In, Si, Cr, Co, and Cu, and to report their crystal structure [2–7].

The synthesis and some properties of two new hydroxylammonium fluoroaluminates with the formulae $(NH_3OH)_2AlF_5$ and $(NH_3OH)AlF_4 \cdot H_2O$ were reported more than 20 years ago [8]; however, no single crystals suitable for structure determination could be obtained. The authors were only able to determine the unit cell parameters from powder data as orthorhombic with cell parameters $a = 6.475$ Å, $b = 7.295$ Å, and $c = 10.827$ Å for $(NH_3OH)_2 AlF_5$ and $a = 7.003$ Å, $b = 8.489$ Å, and $c = 10.745$ Å for $(NH_3OH)AlF_4 \cdot H_2O$. Since no subsequent reports about hydroxylammonium fluoroaluminates could be found in the literature, we decided to reinvestigate the synthesis in order also to establish the structural data.

It is a well-known fact that the chemistry, structure, and thermal behavior of hydroxylammonium fluorometallates is often closely related to the chemistry of ammonium and hydrazinium fluorometallates. Ammonium fluoroaluminates have long been known, whereas the first detailed report on the thermal analysis of $(NH_4)_3AlF_6$ using TGA and DTA methods was reported by Bukovec and Šiftar [9]. Later, Bentrup and Kolditz [10] reported the synthesis and thermal decomposition of the new compound with the formula $(NH_4)_2[AlF_5(H_2O)]$, while Menz and Bentrup [11] studied the thermal decomposition of $(NH_4)_3AlF_6$, $(NH_4)_2[AlF_5(H_2O)]$, and NH_4AlF_4 in a self-generated atmosphere. Hydrazinium(2+) pentafluoroaluminate, $N_2H_6AlF_5$, was first reported by Pugh and Hotz [12] and later studied by Šiftar and Bukovec [13, 14]. Milićev and Rahten [15] prepared and studied two new hydrazinium(1+) fluoroaluminates, $(N_2H_5)_2AlF_5 \cdot H_2O$ and $(N_2H_5)_2AlF_5$, the latter obtained by thermal decomposition of the newly prepared $(N_2H_5)_2AlF_5 \cdot H_2O$. The synthesis, characterization, and structure of $(N_2H_5)_3AlF_6$ were published by Rahten et al. [16].

The final product of the thermal decomposition, AlF_3, has found wide application as a catalyst, while the activity strongly depends on its structure and specific surface area. Fluorometallates with hydroxylammonium cations yield considerable volumes of gaseous products during thermal decomposition, allowing a large specific surface area of the formed product.

Results and discussion

The chemical analysis of a typical product obtained by the described method was: 34.3% NH_3OH^+ (calc. 35.8%), 14.4% Al (calc. 14.2%), and 51.1% F^- (calc. 50.0%). From the results, the molar ratio $NH_3OH^+:Al^{3+}:F^-$ was calculated as 2.04:1:5.05, and thus the chemical formula can be written as $(NH_3OH)_2AlF_5$. The results of the chemical analyses for the other as-prepared samples differ by less than ±1% points from these values.

The product obtained by thermal decomposition at 275 °C was identified by chemical analysis as $(NH_3OH)AlF_4$, giving the results 24.3% NH_3OH^+ (calc. 24.8%), 20.4% Al (calc. 19.7%), and 55.1% F^- (calc. 55.5%).

Thermal analysis and powder diffraction

The results of the thermal analysis for $(NH_3OH)_2AlF_5$ are shown in Fig. 1. Under experimental conditions, the compound is stable up to 157 °C and undergoes three decomposition steps by heating to 700 °C. In the first step, between 157 and 245 °C, the measured mass loss
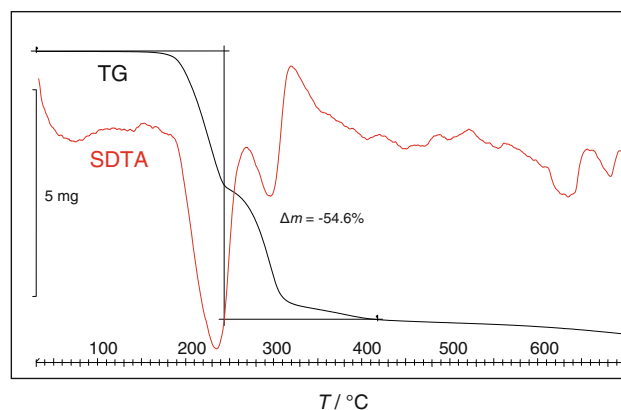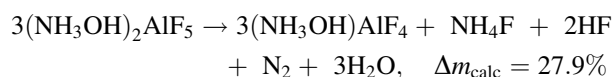

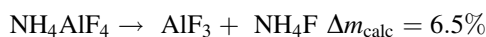**Fig. 1** TG—SDTA curves representing the decomposition of $(NH_3OH)_2AlF_5$ at a heating rate of 10 K/min in nitrogen

($\Delta m_{meas} = 28.6\%$) is in good agreement with the value calculated for the decomposition to $(NH_3OH)AlF_4$:

$$3(NH_3OH)_2AlF_5 \rightarrow 3(NH_3OH)AlF_4 + NH_4F + 2HF + N_2 + 3H_2O, \quad \Delta m_{calc} = 27.9\%$$

In the second step, between 245 and 310 °C, the sample loses 21.9% of its initial weight, again in very good agreement with the proposed reaction:

$$3(NH_3OH)AlF_4 \rightarrow NH_4AlF_4 + 2AlF_3 + 2HF + N_2 + 3H_2O, \quad \Delta m_{calc} = 21.4\%$$
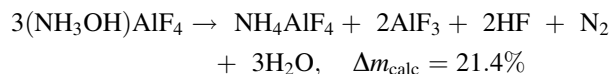
In the last step, NH_4AlF_4 decomposes to AlF_3:

$$NH_4AlF_4 \rightarrow AlF_3 + NH_4F \quad \Delta m_{calc} = 6.5\%$$

The measured mass loss for the overall decomposition of $(NH_3OH)_2AlF_5$ to AlF_3, observed at 435 °C ($\Delta m_{meas} = 54.6\%$), is also in good agreement with the calculated value ($\Delta m_{calc} = 55.8\%$). The simultaneous differential thermal analysis (SDTA) curve shows that the first and second step of the decomposition are endothermic with peak temperatures of 233 and 298 °C under experimental conditions.

The XRD powder diffraction patterns of intermediates and the final product of the thermal decomposition are shown in Fig. 2. The pattern of the new compound $(NH_3OH)AlF_4$ with some traces of NH_4AlF_4 can be observed after the first decomposition step, either by heating $(NH_3OH)_2AlF_5$ up to 275 °C with 10 K/min or by heating it to 240 °C with 2 K/min and 1 h isothermally. Ammonium fluoroaluminate, NH_4AlF_4, could not be prepared in pure form since the second step always yields a mixture of NH_4AlF_4 and AlF_3. The final product at 500 °C was identified as pure γ-AlF_3.

The comparison with known ammonium and hydrazinium fluoroaluminates shows that the second and third step of the decomposition of $(NH_3OH)_2AlF_5$ is similar to the

Fig. 2 X-ray diffraction patterns of (NH₃OH)₂AlF₅ (*lowest*) and the products of thermal decomposition at different temperatures: (*x*) (NH₃OH)AlF₄, (*downward triangles*) NH₄AlF₄ (PDF 00-020-0077), and (*squares*) γ-AlF₃ (PDF 00-020-0006)
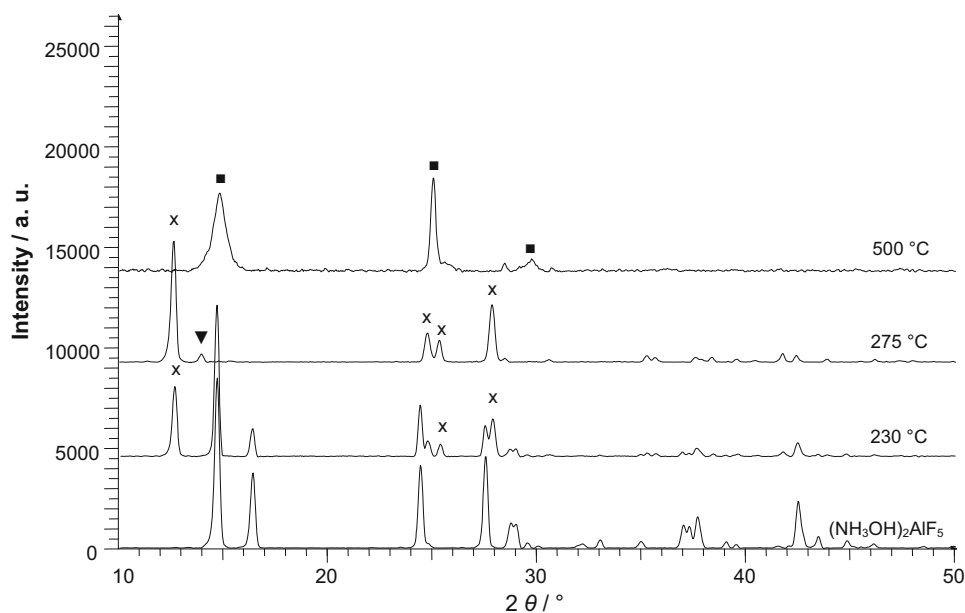
decomposition of $(NH_4)_3AlF_6$ [9], which yields NH_4AlF_4 as an intermediate product at 170–220 °C and γ-AlF₃ at $T > 400$ °C. The investigations of Bentrup and Kolditz [10] also showed that the thermal decomposition of $(NH_4)_2[AlF_5(H_2O)]$ yields NH_4AlF_4 in the first step between 175 and 310 °C and γ-AlF₃ above 463 °C, while no $(NH_4)_2AlF_5$ could be obtained. By the thermal decomposition of $(N_2H_5)_2AlF_5 \cdot H_2O$, the same products were obtained: NH_4AlF_4 at 255 °C and γ-AlF₃ at 450 °C. It should be pointed out that besides already known and well-characterized α- and β-phases of AlF₃, different new phases like η-AlF₃, κ-AlF₃, and θ-AlF₃ were prepared by the thermal decomposition of fluoroaluminates with different cations [17].

Crystal structure of (NH₃OH)₂AlF₅

The atomic coordinates and equivalent displacement parameters are given in Table 1. Bond lengths and angles are presented in Table 2.

The ORTEP-3 and ATOMS drawings of a structure with atom labeling scheme are shown in Figs. 3 and 4, respectively. Differently from in ammonium [17–20] or hydrazinium fluoroaluminates [16], where anions are isolated AlF₆ octahedra or fluoroaluminate layers, the structure of (NH₃OH)₂AlF₅ is built up from infinite chains of corner sharing, *trans*-connected centrosymmetric AlF₆ octahedra, and hydroxylammonium cations.

Two crystallographically non-equivalent aluminum atoms Al1 and Al2 are coordinated to six fluorine atoms. Aluminum to bridging fluorine distances Al1–F2 and Al2–F4 [1.8371(3) and 1.8196(2) Å] are slightly longer than

Table 1 Fractional coordinates and equivalent temperature factors (Å²)

	x/a	y/b	z/c	U_{eq}
Al1	1.00000	0.50000	0.50000	0.0117(3)
Al2	0.50000	0.00000	0.50000	0.0119(3)
F1	0.92760(8)	0.71756(11)	0.53460(12)	0.0257(4)
F2	1.00000	0.54901(18)	0.25000	0.0247(6)
F3	0.85098(7)	0.39923(11)	0.47769(11)	0.0238(4)
F4	0.50000	−0.03472(18)	0.25000	0.0312(7)
F5	0.65402(8)	−0.08064(13)	0.51466(12)	0.0287(4)
F6	0.55313(8)	0.23337(11)	0.47394(11)	0.0257(4)
O1	0.63858(10)	0.42035(15)	0.75553(14)	0.0280(6)
O2	0.87086(15)	−0.0538(2)	0.79400(17)	0.0516(8)
N1	0.67825(12)	0.58688(17)	0.67989(15)	0.0239(6)
N2	0.82574(15)	0.09978(18)	0.70615(18)	0.0326(7)
H1	0.60105	0.36887	0.66567	0.046(6)*
H2	0.88806	−0.15213	0.72489	0.066(8)*
H11	0.62439	0.63885	0.62539	0.056(7)*
H12	0.73930	0.56109	0.60090	0.041(5)*
H13	0.72730	0.63510	0.79081	0.106(11)*
H21	0.86482	0.14453	0.61281	0.105(11)*
H22	0.77049	0.07782	0.62878	0.036(5)*
H23	0.80568	0.14683	0.79724	0.077(9)*

U_{eq} is defined as one-third of the trace of the orthogonalized Uij tensor

* In case of H atoms there is U_{iso} instead of U_{eq}

aluminum to terminal fluorine atom distances [1.7758(9)–1.8119(8) Å]. This is very similar to another structure containing *trans* $(AlF_5)_n^{2-}$ infinite chains, i.e., *trans*-[H₄pentaerythrityl tetramine]·(AlF₅)₂, where bridging

Table 2 Bond lenghts (Å) and angles (°) with e.s.d.s in parentheses

Al1–F1	1.7938(8)	Al2–F5	1.7758(9)
Al1–F2	1.8371(3)	Al2–F6	1.8119(8)
Al1–F3	1.7836(8)	O1–N1	1.4049(16)
Al2–F4	1.8196(2)	O2–N2	1.375(2)
F1–Al1–F2	88.37(5)	F4–Al2–F6	91.30(5)
F1–Al1–F3	88.78(4)	F5–Al2–F6	90.97(4)
F2–Al1–F3	90.51(3)	Al1–F2–Al1[iii]	157.51(8)
F4–Al2–F5	89.72(3)	Al2–F4–Al2[iv]	163.96(8)

Symmetry codes: (*iii*) $-x + 2$, y, $-z + 1/2$; (*iv*) $-x + 1$, y, $-z + 1/2$

distances are 1.81(1) and 1.82(1) Å and terminal 1.786(5) and 1.786(6) Å [21]. In that structure both non-equivalent aluminum atoms alternate within the same chain with an Al–F–Al angle of 180°. In the title compound non-equivalent aluminum atoms are from different chains, both running parallel to the *c* edge with tilting of the neighboring octahedra (Al1–F2–Al1[(i)] and Al2–F4–Al2[(ii)] angles are 157.51(8) and 163.96(8)°, ($i = -x + 2$, y, $-z + ½$; $ii = -x + 1$, y, $-z + 1/2$). The projection along the chains shows that the neighboring AlF$_6$ octahedra are not eclipsed. Torsion angles F–Al–Al–F (considering the closest terminal fluorine atoms from the neighboring AlF$_6$ octahedra), which are in both symmetry non-equivalent chains of the title compound similarly [in the range 38.39(4)–39.22(4)°], show that the octahedra are staggered. From the upper part of Fig. 4 each chain of (AlF$_5$)$_n^{2-}$ anions

can be seen to be surrounded by a "cylinder" of hydroxylammonium cations. These are donors of O−H···F and N−H···F hydrogen bonds to all terminal fluorine atoms of anions. The bridging fluorine atoms are not involved in hydrogen bonding. Since the donors carry positive and acceptors negative charges, these hydrogen bonds are charge-assisted, and hence they are rather strong and short [22–26]. The geometry of hydrogen bonds is presented in Table 3.

As in other known structures of hydroxylammonium fluorometallates with mononuclear anions {i.e., (NH$_3$OH)$_3$ InF$_6$ [7], (NH$_3$OH)$_3$CrF$_6$ [4], and (NH$_3$OH)$_3$GaF$_6$ [2]}, one-dimensional {i.e., chains in (NH$_3$OH)$_2$ZrF$_6$ and (NH$_3$OH)$_3$ZrF$_7$ [6]}, or two-dimensional structure {i.e., layers in (NH$_3$OH)$_2$CuF$_4$ and (NH$_3$OH)$_2$CoF$_4$ [5]}, the strongest hydrogen bonds are donated by hydroxyl O atoms and accepted by F atoms. The H-bonds with contact distances 2.6035(13) and 2.5908(16) Å for O1···F6 and O2···F1, respectively, can be considered as medium to strong. The O···F contact distances in the above-mentioned hydroxylammonium fluorometallates are in the range between 2.50–2.61 Å.

The N atoms of cations are, as in all the above-mentioned hydroxylammonium fluorometallates, donors of charge-assisted hydrogen bonds to F atoms of anions through each of their H atoms. The H-bond with contact distance N2···F5 2.6513(17) Å can be considered as medium to strong. The others are weaker with N···F contacts in the range 2.7170(15)–3.0756(15) Å. There are

Fig. 3 ORTEP-3 view of the structure of (NH$_3$OH)$_2$AlF$_5$. Ellipsoids are at 50% probability level. Hydrogen atoms are drawn as *circles* of arbitrary radii. Labeled are non-hydrogen atoms from the asymmetric unit
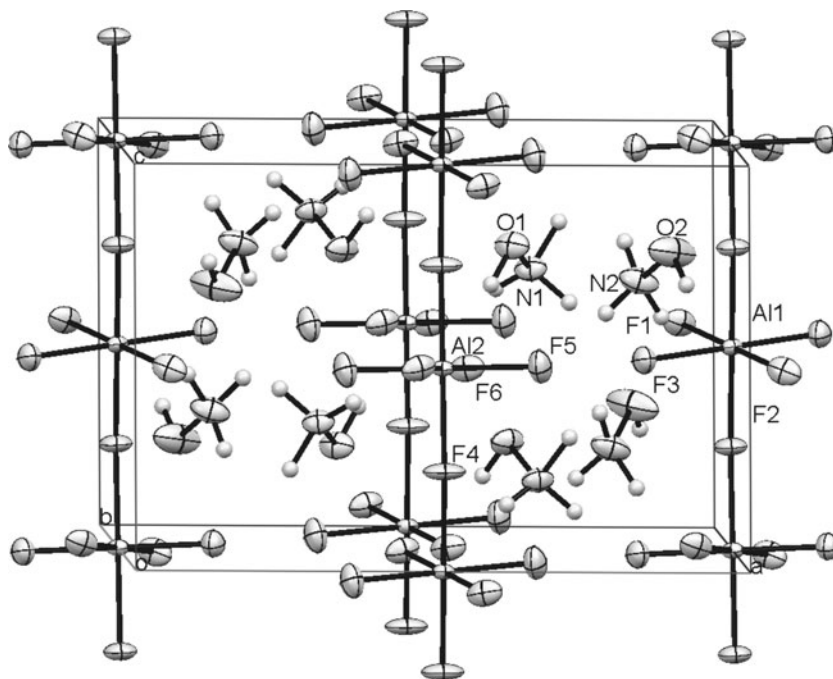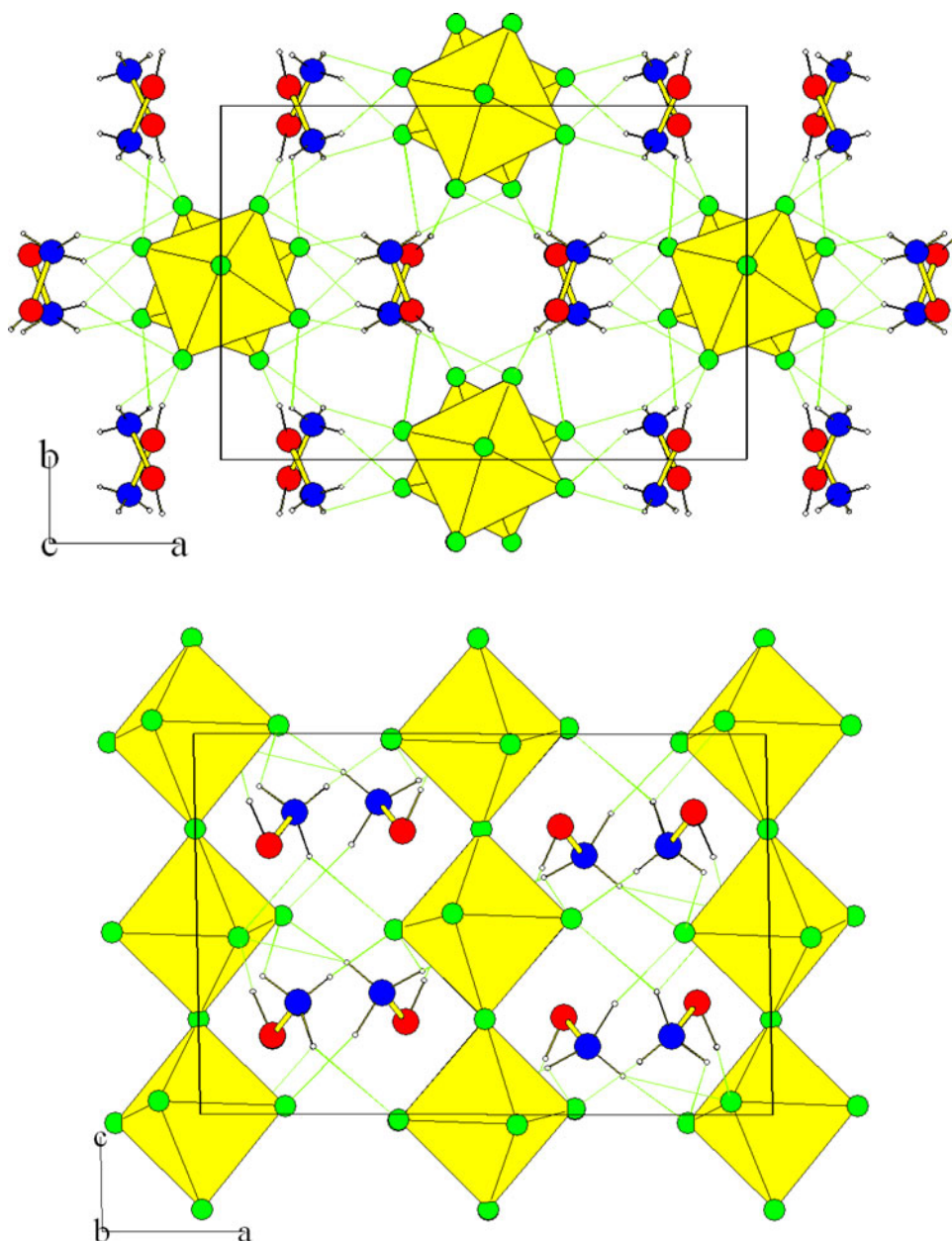
Fig. 4 ATOMS [34] drawings of structure of $(NH_3OH)_2AlF_5$ as viewed along *c* axis (*upper*) and along *b* axis (*bottom*). *Yellow polyhedra* represent AlF₆ octahedra, *green lines* hydrogen bonds, *green circles* F atoms, *blue circles* N atoms, and *red circles* O atoms

also weak hydrogen bonds with donor acceptor contact distances of approximately 3 Å among cations themselves.

Experimental

Synthesis

Solid hydroxylammonium fluoride, NH_3OHF, was prepared as described [1]: hydroxylamine was isolated in an ethanolic solution by the reaction of solid NH_3OHCl (Merck) with freshly prepared sodium ethylate. The ethanolic solution was slowly added to 40% aqueous HF (Sigma-Aldrich), cooled to 0 °C, in a molar ratio $NH_2OH:HF = 1:1$. The solution was allowed to stand overnight, then the obtained white crystals of NH_3OHF were filtered off, dried, and used for further synthesis.

Aluminum foil (0.3 mm thick, Merck) was dissolved in excess amounts of boiling 15% HF. After the solution cooled down to room temperature, solid NH_3OHF was added. By evaporation of the solvent at room temperature, colorless crystals of $(NH_3OH)_2AlF_5$ were obtained and dried in a desiccator over silica gel. In a typical procedure, we used 0.1 g (3.7 mmol) of Al, 0.39 g (7.4 mmol) of NH_3OHF, and 3–4 cm³ of 15% HF. *Caution!* Hydrofluoric acid is an extremely hazardous chemical and causes severe

Table 3 The geometric parameters of hydrogen bonds

D−H···A	D···A (Å)	D−H (Å)	H···A (Å)	D−H···A (°)
O1−H1···F6	2.6035 (13)	0.85	1.77	167
O2−H2···F1[v]	2.5908 (16)	0.90	1.73	160
N1−H11···F5[vi]	2.7170 (15)	0.80	2.23	120
N1−H11···F6[vii]	3.0288 (15)	0.80	2.25	167
N1−H12···F1	3.0756 (15)	0.90	2.40	132
N1−H12···F3	2.7626 (15)	0.90	1.92	154
N1−H13···F3[viii]	2.8264 (14)	1.02	1.90	150
N2−H21···F3	2.7559 (15)	0.87	2.11	131
N2−H21···O2[ix]	3.0384 (18)	0.87	2.39	132
N2−H22···F5	2.6513 (17)	0.83	1.89	152
N2−H23···F1[viii]	2.9177 (16)	0.78	2.36	129
N2−H23···F5[x]	2.9330 (17)	0.78	2.35	133

Symmetry codes: (v) $x, y − 1, z$; (vi) $x, y + 1, z$; (vii) $−x+1, −y+1, −z+1$; (viii) $x, −y+1, z + 1/2$; (ix) $x, −y, z − 1/2$; (x) $x, −y, z + 1/2$

skin burns and eye damage [27]. When handling it wear a face shield, suitable gloves, and perform all operations under a hood!

Methods

Hydroxylammonium was determined by titration with $KMnO_4$ [28] and fluorine with a combination fluoride electrode using direct calibration and TISAB IV buffer to provide constant ionic strength, decomplex fluoride, and adjusted solution pH. Aluminum was determined by gravimetric analysis using 8-hydroxyquinoline.

Thermal analysis (TG and SDTA) was carried out on a METTLER TGA/SDTA 851[e] system in the temperature range 30–700 °C in a nitrogen stream of 100 cm^3/min with different heating rates (10 K/min or less), using Al_2O_3 crucibles.

X-ray powder diffraction data for the products of the thermal decomposition were collected with an AXS-Bruker/Siemens/D5005 diffractometer using CuK_α radiation at 293(1) K. Finely ground samples were placed on a Si single crystal holder and measured in the range $10° < 2\theta < 50°$. The diffraction data have been analyzed using the EVA program and the PDF datafile [29].

X-ray structure determination

Single crystal diffraction data of $(NH_3OH)_2AlF_5$ have been collected on a Nonius Kappa CCD diffractometer at room temperature (293(2) K) with MoK_α radiation and a graphite monochromator. The data were processed using the DENZO program [30]. Structure was solved by direct methods using SIR97 [31]. A full-matrix least-squares refinement on F was employed with anisotropic temperature displacement parameters for all non-hydrogen atoms and isotropic for hydrogen atoms. The positions of hydrogen atoms were obtained from difference Fourier

Table 4 Crystal data, data collection, and refinement parameters for the title compound

$(NH_3OH)_2AlF_5$	$F(000) = 384$
$M_r = 190.05$	$D_x = 2.205$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.8675(3)$ Å	Cell parameters from 1,424 reflections
$b = 7.3098(2)$ Å	$\theta = 0.4–27.5°$
$c = 7.2071(2)$ Å	$\mu = 0.42$ mm^{-1}
$\beta = 91.080(2)°$	$T = 293$ K
$V = 572.43(3)$ Å^3	Needle, colorless crystal
$Z = 4$	$0.28 \times 0.05 \times 0.04$ mm
Nonius Kappa CCD diffractometer	1,320 independent reflections
φ and ω scans	1,093 reflections with $F^2 > 2.00$ sig(F^2)
Absorption correction: multi-scan (DENZO-SMN [23])	$R_{int} = 0.033$
11,715 measured reflections	$\theta_{max} = 27.5°$
Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.039$	H-atoms from difference Fourier maps
$wR = 0.021$	Only H-atom isotropic displacement parameters refined
$S = 1.24$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
1,225 reflections	$\Delta\rho_{min} = -0.56$ e Å^{-3}
103 parameters	

maps and were not refined. The XTAL3.6 program package [32] was used for structure refinement and interpretation. Drawings of the structure were produced using ORTEP-3 [33] and ATOMS [34]. Details of the crystal data, data collection, and refinement parameters are listed in Table 4. Structural and other crystallographic data may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-422375.
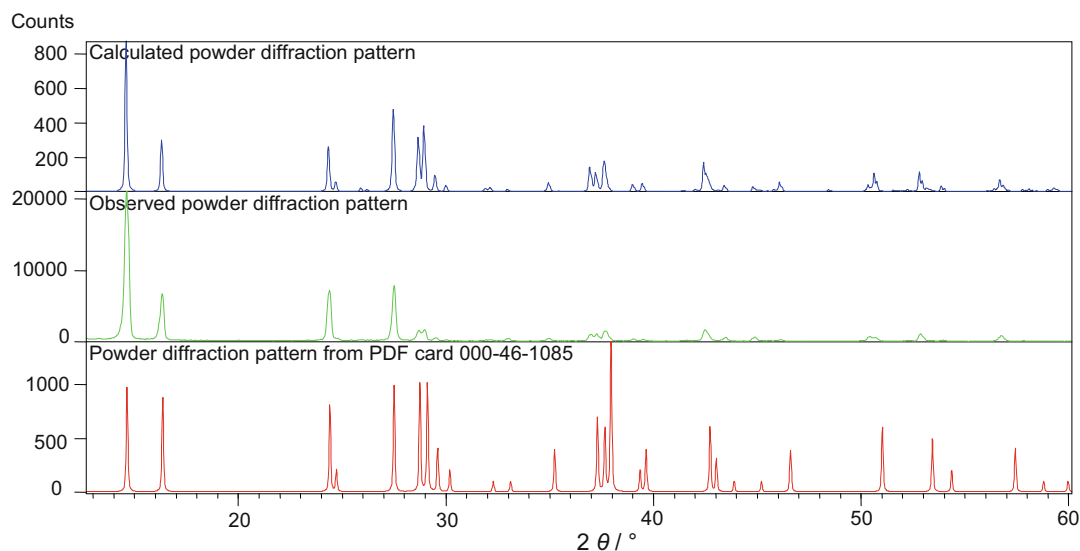
Fig. 5 Comparison of X-ray powder patterns reported for $(NH_3OH)_2AlF_5$ by the PDF database (*lowest*) observed and calculated from the structure

The comparison of X-ray powder pattern obtained by Pintarič et al. [8] with the observed and calculated (from the structure) powder patterns of $(NH_3OH)_2AlF_5$ from present study shows that they belong to the same phase, as can be seen from Fig. 5. Small discrepancies in positions of peaks are probably because of slightly different temperatures of data collection (the shift increases with the increase of diffraction angle).

Since the intensities in powder pattern obtained by Pintarič were obtained visually from Gunier films, there are also small differences in comparisons with the novel study. On the other hand, the results of single crystal diffraction show that indexing and unit cell parameters reported in the old study have to be corrected. The crystal system is not orthorhombic, but monoclinic with a β value of 91.080(2)°, and the length of the shortest edge is 7.2071(2) instead of 6.475 Å. With the old orthorhombic unit cell parameters three peaks (at 29.98, 39.05, and 46.14°) are not indexed, while with the monoclinic parameters all peaks are indexed.

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