Scientific paper

Synthesis, Crystal Structure and Magnetic Properties of a new Hydroxylammonium Fluoroferrate

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Abstract

This paper reports on the synthesis of a new hydroxylammonium fluoroferrate, with the formula $(NH_3OH)_3FeF_6$, obtained after dissolving iron powder in hydrofluoric acid and adding solid NH_3OHF. This new compound has been characterized by chemical and thermal analysis, single-crystal X-ray diffraction, and magnetic measurements. The title compound crystallizes trigonal, R3c, with cell parameters a = 11.4154(2) Å, c = 11.5720(2) Å, Z = 6. The structure consists of NH_3OH^+ cations and isolated FeF_6^{3-} octahedra in which the central ion lies on a threefold axis. The oxygen and nitrogen atoms of the hydroxylammonium cations are donors of hydrogen bonds to fluoride anions, resulting in a network of hydrogen bonds between counterions. The effective magnetic moment μ_{eff} = 5.8 BM was calculated and perfectly matches the expected value of high-spin Fe(III) ions. The thermal decomposition of the compound was studied by TG, DSC, and X-ray powder diffraction.

Keywords: Hydroxylammonium, Fluoroferrate, Crystal structure, Hydrogen bonds

1. Introduction

Investigating hydroxylammonium fluorometallates is interesting for the study of hydrogen bonds since these compounds include all the three elements, capable of forming strong hydrogen bonds: O, N and F. However, this area is still relatively underexplored because of the difficulties when handling these materials. Free hydroxylamine is unstable above 0 °C, whilst its salts can be handled at room temperature. A number of new hydroxylammonium fluorometallates of transition and group III metals with the general formula $(NH_3OH)_xMF_y$ (M = Cr, Co, Cu, Zn, Al) have been synthesized within our laboratory over the last decade,[1–4] using solid NH_3OHF prepared by adding an ethanol solution of NH_2OH to an aqueous solution of HF. This method provides several advantages compared to earlier research that used aqueous or ethanolic hydroxylammonium solutions in the synthesis of fluorometallates.

Since hydroxylamine can be thought of as a derivative of ammonia, obtained by the replacement of one hydrogen atom by the –OH group, the coordination chemistry of hydroxylammonium is similar to that of ammonia in many cases. Stoichiometric ammonium fluoroferrates with the formula $(NH_4)_3FeF_6$ were reported some time ago.[5] This compound crystallizes in a face-centered cubic lattice at room temperature and undergoes a phase transition into a tetragonal lattice at 263 K.[6,7] A detailed thermal analysis of $(NH_4)_3FeF_6$ was reported by Bukovec et al.[8] Recently, crystallographic, magnetic, and dielectric studies of $(NH_4)_3FeF_6$ were reported,[9] using variable temperature X-ray powder diffraction, together with dielectric and magnetic measurements. Laptash's group studied the synthesis of stoichiometric and non-stoichiometric ammonium fluoroferrates $(NH_4)_xFeF_{2x}$ ($2 \leq x \leq 3$) and their thermal decomposition.[10,11] The decomposition product during the initial stage was reported to be NH_4FeF_4 and the decomposition was accompanied by a partial reduction of Fe(III) to Fe(II) due to the isolated ammonium. The end-product of the decomposition was a FeF_2 / FeF_3 mixture. The same group also the known structure of $(NH_4)_3FeF_6$ and studied the orientation disorder in the structure.[12] There are also some reports regarding hydrazinium fluoroferrates: Slivnik and Rahten prepared[13] $N_2H_6FeF_5$ while Milićev and Maček studied the vibrational spectra of the compound.[14] However, there seem to be no reports about hydroxylammonium fluoroferrates in the literature.

2. Experimental

2. 1. Materials and Synthesis

Solid hydroxylammonium fluoride, NH_3OHF, was prepared as described earlier[15]: first, NH_2OH was isolated in an ethanolic solution by the reaction of solid NH_3OHCl (Merck) with freshly prepared sodium ethylate. Then, the solution was dropwise added to 40% aqueous HF (Merck), cooled to 0 °C, in a molar ratio $NH_2OH : HF = 1 : 1$. After allowing the solution to stand overnight, the obtained crystals of NH_3OHF were filtered off, dried in a dessicator and used for further synthesis.

Iron powder (≥ 99%, Aldrich) was dissolved in excess amounts of boiling 40% HF. ***Caution!*** *Hydrofluoric acid is an extremely hazardous chemical and causes severe skin burns and eye damage. It penetrates through skin and damages the bones. The vapor causes extreme irritation of the eyes and respiratory tract. When handling it wear a face-shield, suitable gloves, and perform all operations in a hood!* The solution was allowed to stand overnight and solid NH_3OHF was added in different molar ratio. After 1–2 weeks the solvent evaporated at room temperature, crystals of hydroxylammonium fluoroferrate were obtained, and dried in a dessicator above silica gel. In a typical procedure, 0.1 g (= 1.79 mmol) of Fe, 0.285 g (= 5.38 mmol) of NH_3OHF and ≈ 5 mL of HF was used. The reaction yield, based on the molar amount of Fe, was 0.356g (= 73%).

2. 2. Methods

The amounts of hydroxylammonium and fluoride in the product were determined by standard methods: NH_3OH^+ by titration[16] with $KMnO_4$ and F^- with a combination fluoride electrode, using direct calibration and TISAB IV buffer. Iron was determined from the residue after thermal analysis. Thermogravimetric analysis (TG) was carried out on a METTLER TA 4000 system in the temperature range 30–700 °C (TG) in air and nitrogen flow (100 mL/min) with a heating rate of 10 K/min, using Al_2O_3 crucibles.

Magnetic measurements were performed with a Quantum Design MPMS XL-5 SQUID magnetometer. The dc magnetic susceptibility $\chi = M/H$ was determined in the temperature range 2–300 K in a magnetic field H of 1 kOe. The data were corrected for the sample holder contribution and temperature independent diamagnetic susceptibility of inner shell electrons as obtained from Pascal's tables.[17]

The X-ray powder diffraction data for the products were collected with an AXS Bruker/Siemens D5005 diffractometer using CuK_α radiation and a $Ni–K_\beta$ filter at ambient temperature. The samples were finely ground, placed on a silicone-crystal holder and measured in the range $10° < 2\Theta < 70°$ with a step of 0.0358° and a scanning speed of 1 s/step. The obtained data were analyzed using the EVA program and the PDF datafile.[18]

2. 3. X-ray Structure Determination

For X-ray structure determination, the used crystals were mounted on the tip of glass fibers. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation at 293(1) K. Data reduction and integration were performed with the DENZO-SMN program suite.[19] The coordinates of all of the nonhydrogen atoms were found via direct methods using the SIR97[20] structure solution program. Full-matrix least-squares refinement was employed on F^2 magnitudes with anisotropic displacement factors for all nonhydrogen atoms using SHELXL-97[21]. All hydrogen atoms were first located in the Fourier difference map. For the hydroxylic hydrogen, its coordinates were allowed to ride on the coordinates of the oxygen carrier atom, the distance O–H was free to refine whereas the direction of the O–H vector did not change. The coordinates of the ammonium hydrogens were not refined. The isotropic displacement parameters of all the hydrogen atoms were constrained to be 1.5-times larger than those of the carrier atoms. Details on crystal data, data collection and refinement are given in Table 1. Figures depicting the structures were prepared by ORTEP-3.[22] The final structural data (including coordinates, displacement and geometrical parameters) have also been deposited with the FIZ Karlsruhe Crystal Structure Deposition (CSD) Center as supplementary material with the deposition number 424249. Copies of the data can be obtained, free of charge, contacting crysdata@fiz-karlsruhe.de.

3. Results and Discussion

The chemical analysis of the product, prepared by using the molar ratio $NH_3OHF : Fe = 3 : 1$, was as follows: 37.3% NH_3OH^+ (calc. 37.5%), 20.1% Fe (calc. 20.5%), 41.5 % F^- (calc. 41.9%). From these results, the chemical formula can be written as $(NH_3OH)_3FeF_6$. The obtained

Table 1. Crystal data, data collection and refinement summary.

Crystal data	
M_r	271.98
Cell setting, space group	trigonal, *R* 3 *c* (161)
Temperature (K)	293(1)
a (Å)	11.4154(2)
c (Å)	11.5720(2)
V (Å^3)	1305.93(4)
Z	6
D_x (Mg m^{-3})	2.075
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.821
Crystal form, colour	Colorless prism
Crystal size (mm)	0.15 × 0.3 × 0.5
Data collection	
Diffractometer	Nonius Kappa CCD
Data collection method	ω and φ scans
Absorption correction	multi-scan
No. of measured, independent and observed reflections	1211, 653, 636
Criterion for observed reflections	$F^2 > 2.0\sigma(F^2)$
R_{int}	0.034
θ range (°)	3.57–27.44
Refinement	
Refinement on	F^2
R (on F_{obs}), *wR* (on F_{obs}), *S*	0.0327, 0.0946, 1.104
No. of contributing reflections	653
No. of parameters	42
No. of restraints	1
$(\Delta/\sigma)_{\max}$, $(\Delta/\sigma)_{\mathrm{ave}}$	0.000, 0.000
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (eÅ^3)	0.626, –0.731

crystals are colorless, like in the related ammonium and hydrazinium compounds.[9,13]

3. 1. Thermal Analysis

The results of thermal analysis are shown in Figure 1. The compound is stable up to 85 °C and decomposes over several partly overlapping steps. In order to obtain samples of intermediate products, the title compound was also heated to 170, 220, and 350 °C and the obtained products were determined by X-ray powder diffraction. The diffraction patterns of hydroxylammonium fluoroferrate and products obtained by heating are presented in Figure 2.

During the first decomposition step, between 85 and 220 °C, the mass is falling quickly and the measured mass loss at 220 °C is 44.4%, while the decomposition product at 220 °C corresponds to NH_4FeF_4. The results confirm the following overall reaction in this temperature range ($\Delta m_{\mathrm{calc}}/m = 44.9\%$):

$$(NH_3OH)_3FeF_6 \rightarrow NH_4FeF_4 + N_2 + 2HF + 3H_2 \quad (1)$$

It should be mentioned that at 170 °C some ammonium fluoroferrate, $(NH_4)_2FeF_5$, can be observed next to NH_4FeF_4, and an unidentified decomposition product (marked with X in Fig. 2). We propose that at least part of $(NH_3OH)_3FeF_6$ decomposes over two steps:

$$2(NH_3OH)_3FeF_6 \rightarrow (NH_4)_2FeF_5 + 2N_2 + FeF_3 + 4HF + 6H_2O \quad (2)$$

$$(NH_4)_2FeF_5 \rightarrow NH_4FeF_4 + NH_3 + HF \quad (3)$$

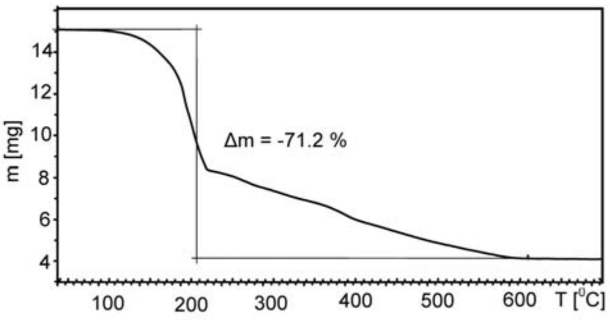

Figure 1: Thermogravimetric analysis of $(NH_3OH)_3FeF_6$ in nitrogen atmosphere (100 mL/min)

At 350 °C, the prevalent product is FeF_3. Thus, the proposed chemical reaction taking place during the final stage of the thermal decomposition can be written as:

$$NH_4FeF_4 \rightarrow FeF_3 + NH_3 + HF \quad (4)$$

The measured mass loss at 370 °C, after the decomposition of $(NH_3OH)_3FeF_6$ to FeF_3, ($\Delta m_{\mathrm{meas}}/m = 59.2\%$) is in very good agreement with the calculated value ($\Delta m_{\mathrm{calc}}/m = 58.5\%$). Above 700 °C, the mass does not change any more, and the powder diffraction patterns show the presence of pure hematite due to the reaction:

$$2FeF_3 + 3H_2O \rightarrow Fe_2O_3 + 6HF \quad (5)$$

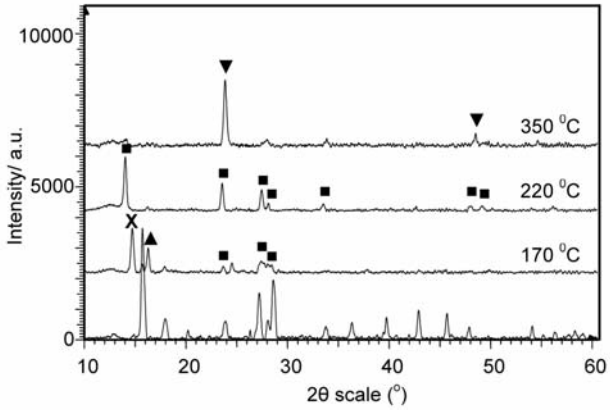

Figure 2: X-ray diffraction patterns of $(NH_3OH)_3FeF_6$ (lowest) and the products of thermal decomposition at different temperatures: ▲ = $(NH_4)_2FeF_5$ (PDF 00-041-1120), ■ = NH_4FeF_4 (PDF 00-020-0094), ▼ = FeF_3 (PDF 00-033-0647).

The measured mass loss for the overall decomposition of $(NH_3OH)_3FeF_6$ to Fe_2O_3 ($\Delta m_{meas}/m$ = 71.2%) is again in very good agreement with the calculated value ($\Delta m_{calc}/m$ = 70.6%). The thermal behavior of the title compound is in agreement with results, obtained for other hydroxylammonium fluorometallates of transition metals, that decompose to corresponding ammonium fluorometallates in the first step and metal fluorides and oxides during subsequent steps.[2,23,24]

3. 2. Magnetic Measurements

The measured susceptibility monotonically increases with decreasing temperature as shown in Figure 3. The inset shows the temperature dependence of effective magnetic moment calculated per formula unit $(NH_3OH)_3FeF_6$. At room temperature the effective magnetic moment μ_{eff} is 5.8 BM which is very close to the calculated value for high-spin (S=J=5/2) Fe(III) ions. The effective magnetic moment remains practically constant throughout the whole investigated temperature interval from 300 K down to 2 K, thus indicating a perfect paramagnetic behavior. The temperature dependent susceptibility above 100 K in Fig. 3. was theoretically described using a Curie-Weiss law: $\chi(T) = C/(T - \theta)$. The best agreement between the measured data and the Curie–Weiss law was obtained using C = 4.24 emu K/mol and θ = 0.2 K. A negligible value of Curie temperature θ confirms a perfect paramagnetic behavior of non-interacting localized magnetic moments of Fe (III) ions. The effective magnetic moment $\mu_{eff} \approx (8*C)^{1/2}$ = 5.8 BM was calculated from the Curie constant C and was in agreement with the measured room temperature value shown within the inset of Fig. 3, and perfectly matches the expected value for the high-spin Fe(III) ions.

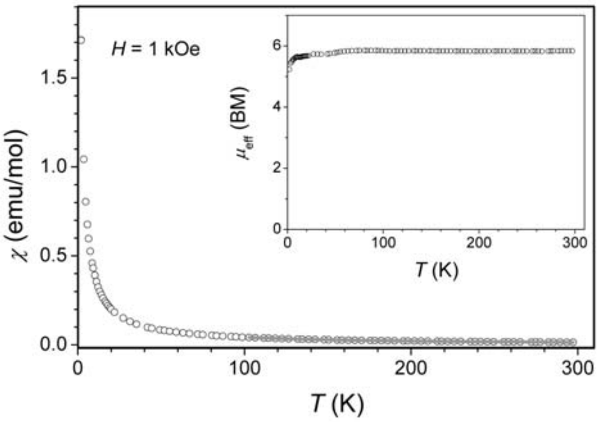

Figure 3: Temperature-dependent susceptibility and effective magnetic moment (inset) of $(NH_3OH)_3FeF_6$ in the magnetic field of 1 kOe. The full line in the inset is a fit with Curie-Weiss law with parameters described in the main text.

3. 3. Crystal Structure

Information on bond lengths and angles can be seen in Table 2. The ionic title compound crystallizes in trigonal symmetry and consists of NH_3OH^+ cations and isolated FeF_6^{3-} octahedra in which the central ion lies on three-fold axis. Both crystallographically independent Fe–F bonds, 1.917(3) and 1.952(4) Å, respectively, are of typical lengths for such Fe–F bonds in related inorganic compounds with octahedral arrangement of fluoride ions around the central iron(III) ion.[25,26] The N–O bond in hydroxylammonium cation is also of usual length as in related fluorometalates (1.403(3) Å).[1,23,27–29] ORTEP drawings of building units and the crystal packing are shown in Figures 4 and 5.

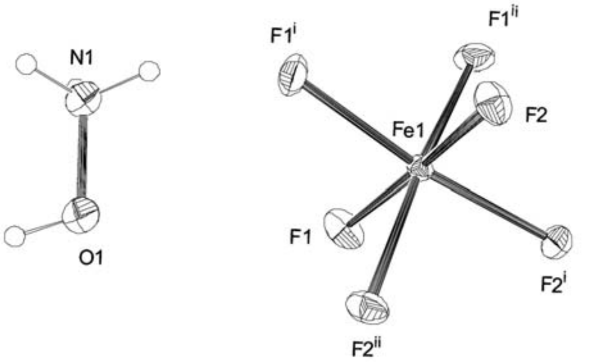

Figure 4: An ORTEP drawing of the building units. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-y$, $x-y$, z; (ii) $-x + y$, $-x$, z.]

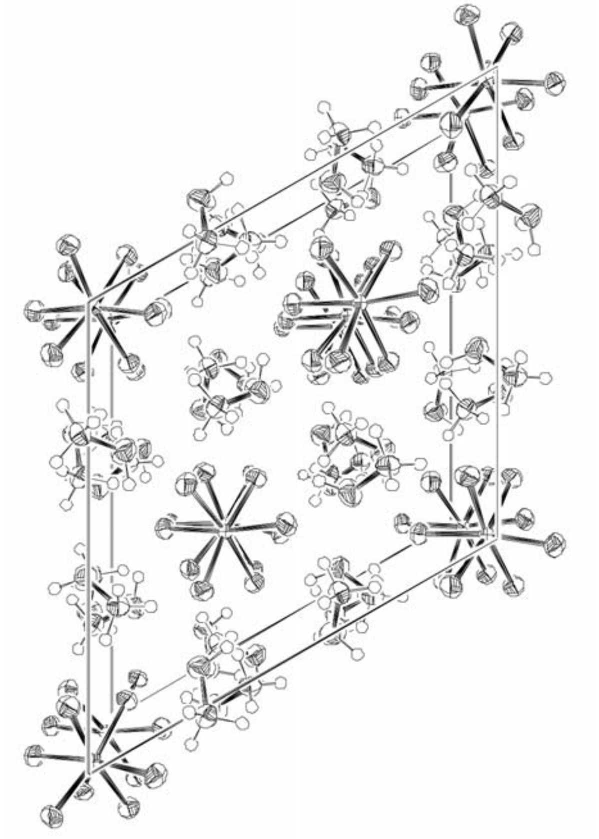

Figure 5: Crystal packing of $(NH_3OH)_3FeF_6$ – a view normal to [001] axis

The presence of hydroxylammonium cation with two possible donor atoms and coordinated strongly electronegative fluoride anions results in a network of hydrogen bonds of both O–H...F and N–H...F types between the counterions. These bonds can be considered as double charge-assisted hydrogen bonds ((±) CAHB). The bond O1–H1...F2 (2.491(3) Å) belongs to one of the strongest O–H...F hydrogen bonds and represents the strongest H-bond within the structure. As expected, the N–H...F bonds are slightly longer but still quite strong (Table 3) and comparable with other hydroxylammonium fluorometallates.[1,2,23,28–30] In addition to the formation of three regular N–H...F hydrogen bonds to three adjacent hexafluoroferrate(III) anions, all three hydrogens on N also take part in three short van der Waals contacts to O1 of the neighboring cation, forming the N–H...O angles of 79.5, 94.0 and 86.6°, respectively (the corresponding N–H bondlengths are 0.92, 1.01 and 0.90 Å with corresponding contact distances for H...O of 2.76, 2.48 and 2.65 Å). Thus, the inter-cationic distance N...O of 2.742(3) Å is significantly shorter than the sum of the corresponding van der Waals radii.

Similar inter-cationic N...O distances, shorter than 2.8 Å, can be found in crystal structures of hydroxylammonium fluorometallates with isolated MF_6^{x-} anions.[1,23,28] If water molecules are also present, the inter-cationic N...O distance becomes longer for ~0.1 Å.[23,29] In cases of chain or layered hydroxylammonium fluorometallates, inter-cationic N...O distances become longer by ~0.2 Å in comparison with those containing isolated MF_6^{x-} anions.[2,30]

Table 3 provides details on hydrogen bonds geometries that are analogous/similar to those in isostructural hydroxylammonium indate (III),[23] and the part of the crystal packing representing hydrogen bonds is shown in Figure 6.

Table 2. Bond lengths (Å) and angles (°) of the title compound.

Fe1 – F1	1.917(3)
Fe1 – F2	1.952 (4)
O1 – N1	1.401(3)
F1 – Fe1 – F2	172.23(9)
F1 – Fe1 – F2^{i}	94.52(9)
F2 – Fe1 – F2^{i}	90.62(15)
F1 – Fe1 – F2^{ii}	83.51(9)
F2 – Fe1 – F2^{ii}	90.62(15)

Symmetry codes: (*i*) –*y* + 1, *x*–*y*, *z*; (ii) –*x* + *y* + 1, –*x* + 1, *z*.

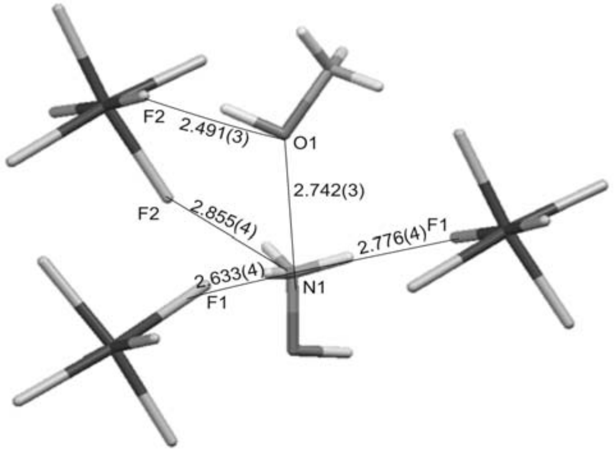

Figure 6: A part of the crystal packing representing the hydrogen bonding scheme. (For details see Table 3).

4. Acknowledgements

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Table 3. Hydrogen bond lengths (Å) and angles (°) in the title compound.

D–H...A	**Distance D–H**	**Distance H...A**	**Distance D...A**	**Angle D–H...A**	**Symmetry operations of A**
O1–H1...F2	1.17	1.37	2.491(3)	157.8	*x*–1/3, *y*+1/3, *z* + 1/3
N1–H1A...F2	0.92	1.95	2.855(4)	169.1	*x*, *x*–*y*, *z*+1/2
N1–H1B...F1	1.01	1.64	2.633(4)	167.9	–*y* + 1, *x*–*y*, *z*
N1–H1C...F1	0.90	1.89	2.776(4)	167.4	–*x*+*y* + 1/3, *y*–1/3, *z* + 1/6

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Povzetek

V prispevku poročamo o sintezi novega hidroksilamonijevega fluorometalata s formulo $(NH_3OH)_3FeF_6$. Spojino smo pripravili z reakcijo med trdnim NH_3OHF in vodno raztopino železa v HF. Spojino smo karakterizirali s kemijsko in termično analizo, rentgensko difrakcijo na monokristalu in magnetnimi meritvami. Hidroksilamonijev fluoroferat kristalizira trigonalno, R3c, s parametri osnovne celice a = 11.4154(2) Å, c = 11.5720(2) Å, Z = 6. Strukturo sestavljajo kationi NH_3OH^+ in izolirani oktaedri FeF_6^{3-}, v katerih centralni atom leži na trištevni osi. Kisikovi in dušikovi atomi v hidroksilamonijevih kationih so donorji vodikovih vezi do fluoridnih anionov, kar povzroči nastanek mreže vodikovih vezi. Izračunani efektivni magnetni moment μ_{eff} = 5.8 BM se odlično ujema s teoretično vrednostjo za visokospinske Fe(III) ione. Termični razkroj spojine smo preučevali s termogravimetrično metodo in rentgensko praškovno analizo.