SYNTHESIS AND CHARACTERISATION OF HYDROXYLAMMONIUM FLUOROCHROMATE

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Abstract

Reactions in the system Cr – NH_3OHF – HF – H_2O were investigated. Green crystals of a new compound with the formula $(NH_3OH)_3CrF_6$ have been isolated from the water solution and characterized by chemical analysis. The compound crystallizes as triclinic, *P*-1, with cell parameters: a = 6.5461(2) Å, b = 6.9347(2) Å, c = 9.4072(3) Å, α = 86.772(1)°, β = 83.804(1)°, γ = 70.283(1)°. The effective magnetic moment, μ_{eff} = 3.82 BM, was calculated from magnetic susceptibility measurements in the temperature range 80-290 K. The thermal decomposition of the compound was studied by TG and DSC analysis. $(NH_3OH)_3CrF_6$ decomposes above 125 °C in three steps and the residue has been identified by X-ray powder diffraction as $\alpha - Cr_2O_3$.

Introduction

Fluorochromates of the ammonium cation are well known and there are several papers reporting their structure[1-4] and detailed thermal analysis.[5-8] Information is available also on hydrazinium fluorochromates,[9,10] their thermal analysis[11] and structure.[12] However, no reports about hydroxylammonium fluorochromates could be found in literature. As hydroxylamine, NH_2OH, may be thought of as derived from ammonia by replacement of a hydrogen atom by the –OH group, we expected that hydroxylammonium fluorochromates could be successfuly synthesized since the chemistry of hydroxylammonium is similar to that of ammonium and hydrazinium compounds.

This laboratory has reported the synthesis and properties of a number of new hydroxylammonium fluorometalates, including compounds of Al, Ga, In, Ti, Zr, Hf and Si in the past decade.[13-20] Free hydroxylamine is unstable above 0 °C, so the

hydroxylammonium salt of hydrofluoric acid was used for reactions in the system Cr–NH_3OHF–HF–H_2O. The main aim of the work was to fulfill the inorganic systematics. All hydroxylammonium fluorometalates are also interesting in the study of hydrogen bonds since they include all three elements, which form strong hydrogen bonds (O, N and F).

Results and discussion

A new green, microcrystalline compound with the formula $(NH_3OH)_3CrF_6$ was obtained independent of the different molar ratios of reactants used for the synthesis. From the results of the chemical analysis, the molar ratio NH_3OH^+:Cr^{3+}:F^- was calculated as 2.94:1:5.93. The results of the chemical analysis for the other as-prepared samples differ less than ±1% points from this values.

Figure 1 shows the thermal behaviour of the compound in a nitrogen atmosphere. The compound is stable up to 110 °C, a small weight loss (<1%) on the TG curve, accompanied by an endothermal change on the DSC curve, can be attributed to the loss of traces of adsorbed water. The decomposition becomes significant above 125 °C and three partly overlapping peaks can be observed with peak temperatures 162 °C (weight loss, Δm = 5.5%), 217 °C (Δm = 45.2%) and 335 °C (Δm = 6.9%). The DSC curve also shows three peaks in the same temperature range: a strong exothermic peak at 210 °C, an endothermic peak at 223 °C and a weak exothermic peak at 247 °C.

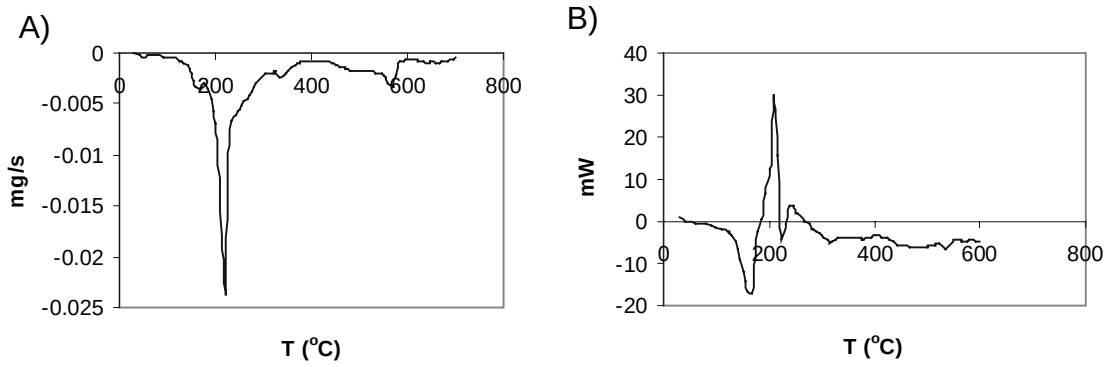

Figure 1. Thermal analysis of $(NH_3OH)_3CrF_6$: A) DTG (Derivative Thermogravimetry), B) DSC (Differential Scanning Calorimetry).

It is obvious from the TG and DSC curves that different reactions take place simultaneously. Attempts to isolate intermediates after individual decomposition steps by changing experimental conditions (heating rate, amount and particle size of the sample, isothermal heating) and to identify the intermediates by X-ray powder diffraction were unsuccessful. Similar behaviour has been reported in the literature[5,6,10] for ammonium and hydrazinium compounds of the type due to the simultaneous thermal decomposition, hydrolysis and the formation of amorphous chromium compounds.

The final residue of the thermal decomposition at 700 °C was identified as α-Cr_2O_3 by X-ray powder diffraction. This result indicates that hydrolysis of the products occurs during the heating. The overall measured mass loss ($\Delta m_{meas.}$ = 70.5%) is in good agreement with the calculated value ($\Delta m_{calc.}$ = 71.6%) for the reaction:

$$2(NH_3OH)_3CrF_6 \rightarrow Cr_2O_3 + 10HF + 2N_2 + 2NH_4F + 3H_2O \qquad \text{eq. 1}$$

Figure 2 shows the temperature dependence of the inverse magnetic susceptibility. In the temperature range 80–290 K, the magnetic behaviour of $(NH_3OH)_3CrF_6$ obeys the *Curie–Weiss* law: $\chi = C/(T-\theta)$ with θ = 14 K and a fitted Curie constant of 1.786 emu K mol^{-1} which gives an effective magnetic moment, $\mu_{eff.}$ = 3.78 BM. The obtained result was corrected for the contribution of the diamagnetic part of the compound[21] to give the result, $\mu_{eff.}$ = 3.82 BM. This experimental value is in agreement with the value, calculated for the isolated Cr^{3+} ion ($\mu_{eff.}$ = 3.87 BM). The results confirm the 3+ oxidation state of chromium and are in agreement with data, found for similar compounds of Cr^{3+} in literature (3.68 BM < $\mu_{eff.}$ < 3.86 BM).

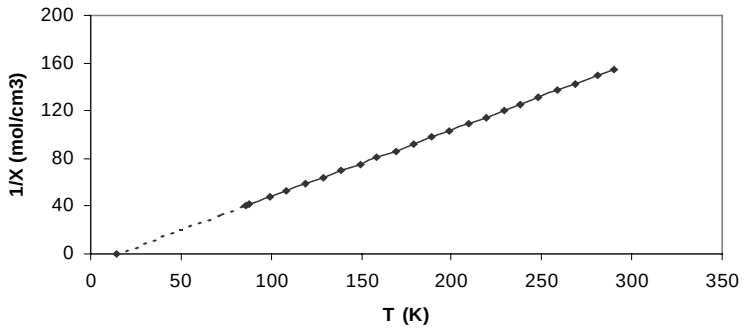

Figure 2. Magnetic susceptibility measurement of $(NH_3OH)_3CrF_6$.

By recrystallization of the microcrystalline phase from 40% HF, single crystals of $(NH_3OH)_3CrF_6$ were isolated. The compound crystallizes as triclinic, *P*-1, with two formula units in the unit cell. The stereoscopic picture is shown in Figure 3.

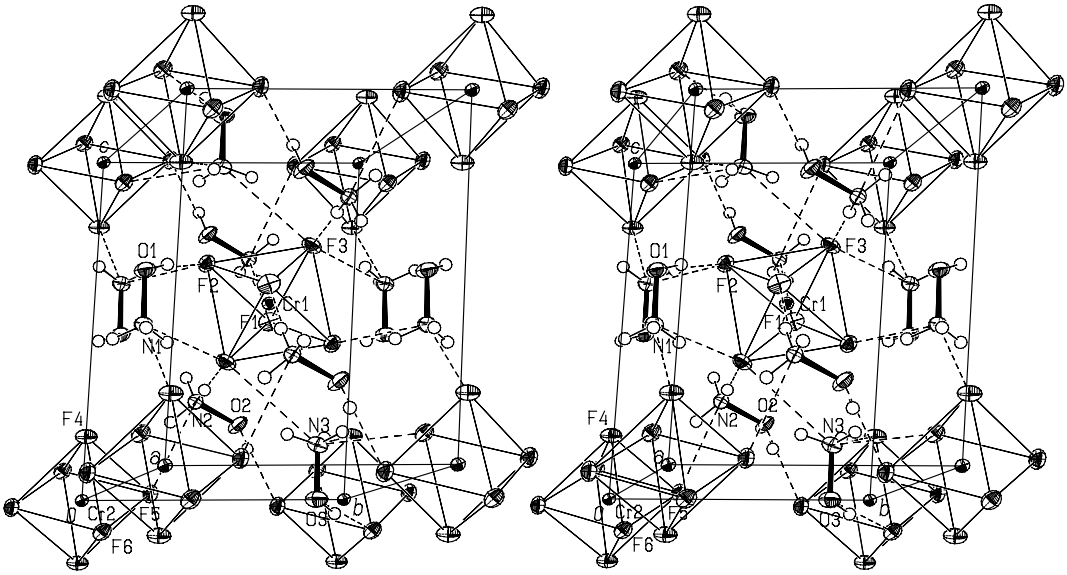

Figure 3. Stereoscopic picture of the $(NH_3OH)_3CrF_6$ unit cell.

The structure consists of eight CrF_6^{3-} octahedra on the corners and an octahedron in the center of the unit cell with different orientation. The isolated octahedra are connected with hydrogen bridges (O-H···F and N-H···F) with NH_3OH^+ ions and as a result of the hydrogen bonds, the octahedra are slightly destorted. The atomic coordinates and equivalent displacement factors are given in Table 1, some selected bond lengths and angles can be found in Table 2.

$(NH_3OH)_3CrF_6$ is isostructural to the known hydoxylammonium fluorogallate[16] with the formula $(NH_3OH)_3GaF_6$, which also crystallizes triclinic with cell parameters: a = 6.539(1) Å, b = 6.924(1) Å, c = 9.403(1) Å, α = 87.01(1)°, β = 83.98(1)°, γ = 70.28(1)°, V = 398.5(1) Å^3, Z = 2. Both structures consist of isolated MF_6^{3-} octahedra (M = Cr, Ga) on the corners and in the center of the unit cell with different orientation of the octahedron in the center.

Table 1. Fractional coordinates and Equivalent Displacement Parameters ($Å^2$) for $(NH_3OH)_3CrF_6$. $^*U = U_{eq} = 1/3\ \Sigma_i\Sigma j U_{ij} a_i^* a_j^* a_i a_j$.

	x/a	y/b	z/c	U_{eq}
Cr(1)	1/2	1/2	1/2	* 0.0122(2)
Cr(2)	0	0	0	* 0.0126(2)
F(1)	0.1940(2)	0.6114(3)	0.4941(2)	* 0.0243(5)
F(2)	0.4697(3)	0.2734(2)	0.6174(2)	* 0.0208(5)
F(3)	0.4770(3)	0.6540(2)	0.6672(2)	* 0.0242(5)
F(4)	0.1474(3)	-0.0393(3)	0.1692(2)	* 0.0238(5)
F(5)	-0.0965(3)	0.2883(2)	0.0275(2)	* 0.0239(5)
F(6)	0.2602(2)	0.0109(2)	-0.1113(2)	* 0.0206(5)
O(1)	-0.2102(4)	0.9538(3)	0.5462(2)	* 0.0263(7)
O(2)	-0.0125(4)	0.5819(3)	0.2196(2)	* 0.0263(7)
O(3)	0.5726(3)	-0.3189(3)	-0.0506(2)	* 0.0249(7)
N(1)	-0.1951(4)	0.9568(4)	0.3959(2)	* 0.0209(8)
N(2)	0.0822(4)	0.3848(3)	0.2767(2)	* 0.0187(7)
N(3)	0.5523(4)	-0.3174(4)	0.1002(3)	* 0.0218(8)
H(11)	-0.280(8)	1.068(8)	0.360(5)	0.03(1)
H(12)	-0.249(7)	0.866(7)	0.365(4)	0.024(9)
H(13)	-0.07(1)	0.93(1)	0.369(7)	0.06(2)
H(14)	-0.301(7)	1.059(7)	0.577(4)	0.020(8)
H(21)	0.086(6)	0.293(6)	0.217(4)	0.015(7)
H(22)	0.218(7)	0.373(6)	0.293(4)	0.018(8)
H(23)	0.002(7)	0.369(7)	0.356(5)	0.03(1)
H(24)	0.044(8)	0.604(7)	0.143(6)	0.03(1)
H(31)	0.433(8)	-0.250(7)	0.132(5)	0.03(1)
H(32)	0.639(8)	-0.263(7)	0.126(5)	0.03(1)
H(33)	0.576(9)	-0.437(9)	0.127(6)	0.04(1)
H(34)	0.484(9)	-0.218(9)	-0.082(6)	0.04(1)

The measured bond lengths and angles for the CrF_6^{3-} octahedra are in good agreement with literature data for similar fluorochromates, where bond lengths from 1.852 Å to 1.937 Å and angles from 87.66° to 93.27° are reported.[1-4] Measured O-N distances are also in good agreement with values, reported earlier[15-17,19,20] for other hydroxylammonium fluorometallates, which range from 1.396 to 1.42 Å.

The lengths of the O-H···F hydrogen bonds in the structure of $(NH_3OH)_3CrF_6$ (described in Table 3) are comparable to most of the reported hydroxylammonium fluorometallates, where bond lengths O-H···F varied from 2.503 Å–2.661 Å. On the

Table 2. Bond lengths (Å) and angles (°) of $(NH_3OH)_3CrF_6$.

Cr (1) - F(1)	1.894(1)	O (2) - N (2)	1.400(3)
Cr (1) - F(2)	1.923(2)	O (2) - H (24)	0.80(5)
Cr (1) - F(3)	1.915(2)	N (2) - H (21)	0.86(4)
Cr (2) - F(4)	1.909(2)	N (2) - H (22)	0.89(5)
Cr (2) - F(5)	1.907(2)	N (2) - H (23)	0.89(5)
Cr (2) - F(6)	1.923(2)	O (3) - N (3)	1.411(3)
O (1) - N (1)	1.406(3)	O (3) - H (34)	0.81(5)
O (1) - H (14)	0.82(4)	N (3) - H (31)	0.80(4)
N (1) - H (11)	0.86(4)	N (3) - H (32)	0.85(6)
N (1) - H (12)	0.89(5)	N (3) - H (33)	0.82(6)
N (1) - H (13)	0.82(7)		
F (1) - Cr (1) - F (2)	89.16(7)	H (24) - O (2) - N (2)	115(3)
F (1) - Cr (1) - F (3)	89.94(7)	H (21) - N (2) - O (2)	111(2)
F (2) - Cr (1) - F (3)	90.43(7)	H (22) - N (2) - O (2)	107(2)
F (4) - Cr (2) - F (5)	89.05(7)	H (23) - N (2) - O (2)	109(3)
F (4) - Cr (2) - F (6)	90.50(7)	H (34) - O (3) - N (3)	110(3)
F (5) - Cr (2) - F (6)	89.07(7)	H (31) - N (3) - O (3)	112(3)
H (14) - O (1) - N (1)	110(3)	H (32) - N (3) - O (3)	108(3)
H (11) - N (1) - O (1)	113(3)	H (33) - N (3) - O (3)	106(4)
H (12) - N (1) - O (1)	111(3)		
H (13) - N (1) - O (1)	106(5)		

Table 3. Hydrogen bond lengths (Å) and angles (°).

A-H···B	Distance A-H	Distance B-H	Distance A-B	Angle A-H···B	Symmetry operations of B
O(1)-H(14)···F(2)	0.82(4)	1.74(4)	2.546(2)	168(5)	x-1, 1+y, z
N(1)-H(11)···F(3)	0.86(4)	1.95(4)	2.782(3)	164(5)	-x, 2-y, 1-z
N(1)-H(12)···F(2)	0.89(5)	1.98(5)	2.793(4)	151(3)	-x, 1-y, 1-z
N(1)-H(13)···F(4)	0.82(7)	2.26(7)	2.929(3)	139(6)	x, 1+y, z
O(2)-H(24)···F(5)	0.80(5)	1.78(5)	2.561(3)	163(4)	-x, 1-y, -z
N(2)-H(21)···F(5)	0.86(4)	2.26(4)	2.934(3)	135(3)	x, y, z,
N(2)-H(22)···F(3)	0.89(5)	2.02(5)	2.909(3)	180(3)	1-x, 1-y, 1-z
N(2)-H(23)···F(1)	0.89(5)	1.78(5)	2.656(3)	168(4)	-x, 1-y, 1-z
O(3)-H(34)···F(6)	0.81(5)	1.79(5)	2.586(2)	167(4)	x, y, z
N(3)-H(31)···F(4)	0.80(4)	1.95(4)	2.736(3)	165(4)	x, y, z
N(3)-H(32)···F(6)	0.85(6)	2.05(6)	2.801(4)	147(4)	1-x, -y, -z
N(3)-H(33)···F(3)	0.82(6)	2.45(6)	3.148(3)	143(5)	1-x, -y, 1-z

other hand, the N-H···F bond lengths show some significant differences and range from relatively short values (2.656 Å) to rather long bonds of 2.934 Å. The reported N-H···F bond lengths in hydroxylammonium fluorometallates range from 2.666 Å to 2.738 Å with the exception of the hydrated compounds,[17,20] $(NH_3OH)_2TiF_6 \cdot 2H_2O$ and $(NH_3OH)_2SiF_6 \cdot 2H_2O$, with N-H···F lengths 2.856 Å – 2.921 Å.

Experimental

Synthesis. Chromium powder (Aldrich), 40% HF (Merck) and hydroxylammonium chloride (Merck) were used for the synthesis of $(NH_3OH)_3CrF_6$. Hydroxylammine was isolated in ethanolic solution by the reaction of solid hydroxylammonium chloride with sodium ethylate.[22] By adding HF, white crystals of NH_3OHF were obtained,[23] filtered off, dried and the product was used for further synthesis. Two methods of synthesis were applied. In the first method, 0.1 g (1.92 mmol) of Cr powder was dissolved in excess amounts (2-3 mL) of hot 40% HF. After the solution cooled down to room temperature, solid NH_3OHF was added in different molar ratios (the ratio NH_3OHF:Cr varied from 2:1 to 3.5:1). In the second method, $Cr(OH)_3 \cdot H_2O$ was synthesized by the reaction between Cr powder and 40% HF, filtered, dried, characterized by X-ray powder diffraction and used for further synthesis. Saturated solutions of $Cr(OH)_3 \cdot H_2O$ in 20% HF were prepared and calculated amounts of NH_3OHF were added (the molar ratios NH_3OHF:$Cr(OH)_3 \cdot H_2O$ varied from 2:1 to 3:1). In both cases a solid, green microcristalline phase has been obtained after evaporation of the solvent at room temperature. Single crystals were isolated by recrystallisation of the microcristalline phase from 40% HF.

Methods. Hydroxylammonium was determined by titration[24] with $KMnO_4$ and fluorine with a combination fluoride electrode by direct calibration,[25] using the TISAB IV buffer to provide constant background ionic strength, decomplex fluoride and adjust solution pH. Chromium was determined by electrothermal atomic absorption spectrometry (ETAAS). The chemical analysis of a typical product was: 37.8% NH_3OH^+ (calc. 38.1%), 19.7% Cr (calc. 19.4%), 42.6% F^- (calc. 42.5%). Thermal analysis (TG and DSC) was carried out on a METTLER TA 4000 system in the temperature range

30 °C–700 °C (TG) and 30 °C–600 °C (DSC) in a nitrogen stream of 200 mL/min with different heating rates (10 K/min or less), using platinum (TG) and gold crucibles (DSC).

X-Ray powder diffraction data for the products of the thermal decomposition was 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 $10° < 2\Theta < 60°$. The diffraction data have been analyzed using the EVA program and the PDF Datafile.[26]

The magnetic susceptibility measurements were performed in the temperature range 80–290 K using a DSM-8 magneto/susceptometer, working on the principle of a pendule in a calibrated magnetic field. The unit was calibrated with $Gd_2(SO_4)_3 \cdot 8H_2O$ exhibiting a room temperature magnetic susceptibility $\chi = 52.41 \times 10^{-3}$ cm^3/mol. About 50 mg of the finely ground sample were placed in a teflon beaker. The measured magnetic susceptibility of the beaker and the sample was independent of the applied magnetic field, no ferromagnetic impurities were present.

X–Ray structure analysis. Diffraction data for the single crystals of $(NH_3OH)_3CrF_6$ have been collected on a Nonius Kappa CCD diffractometer at room temperature with MoK_α radiation and graphite monochromator. Further details of crystal data, data collection and refinement can be found in Table 4.

A full-matrix least-squares refinement on F was employed with anisotropic temperature factors for all non-hydrogen atoms and isotropic for hydrogen atoms, using the weighting function: $w = 2.45 \times W_f \times W_s$, where W_f ($|F_o| < 2.3$) = ($|F_o|/2.3$), W_f ($|F_o| > 16.0$) = ($16.0/|F_o|$), W_f ($2.3 \leq |F_o| \leq 16.0$) = 1 and W_s ($\sin\theta < 0.51$) = $(\sin\theta/0.51)^2$, W_s ($\sin\theta > 0.56$) = $(0.56/\sin\theta)^4$, W_s ($0.51 \leq \sin\theta \leq 0.56$) = 1. Xtal 3.4 system[27] of programs was used for the correlation and reduction of data, structure refinement and interpretation. Graphics were produced using ORTEPII program.[28] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe (FIZ), D-76344 Eggenstein-Leopoldshafen, Germany, with the deposition number CSD 413130.

Table 4. Crystal data, data collection and refinement summary.

$(NH_3OH)_3CrF_6$	$Z = 2$
$M_r = 268.10$	$D_x = 2.228$ mg m^{-3}
Triclinic, *P*-1, No.: 2	Mo $K\alpha$ radiation
$a = 6.5461(2)$ Å	Cell parameters from 1773
$b = 6.9347(2)$ Å	reflections
$c = 9.4072(3)$ Å	$\theta = 2.91$ - 27.48°
$\alpha = 86.772(1)°$	$\mu = 1.528$ mm^{-1}
$\beta = 83.804(1)°$	$T = 293(1)$ K
$\gamma = 70.283(1)°$	Irregular form green
$V = 399.57(2)$ Å^3	$0.40 \times 0.25 \times 0.25$ mm
$F_{(000)} = 270$	
Nonius Kappa CCD diffractometer	$R_{int} = 0.045$
ω scan	θ range = 3.12 – 27.5°
Multiscan absorption correction	$h = -8 \rightarrow 8$
3347 measured reflections	$k = -8 \rightarrow 8$
1821 unique reflections	$l = -12 \rightarrow 12$
1650 reflections with $I>2.5\sigma(I)$	
Refinement on *F*	Empirical weighting scheme
R (on F_{obs}) = 0.030	Zachariasen's extinct. coeff. =$2.6 \cdot 10^3$
wR (on F_{obs}) = 0.041	$(\Delta/\sigma)_{max} = 0.00109$
$S = 1.009$	$(\Delta/\sigma)_{ave} = 0.00012$
170 parameters	$\Delta\rho_{max} = 0.496$ eÅ^{-3}
H-atoms refined with isotropic displacement parameters	$\Delta\rho_{min} = -0.444$ eÅ^{-3}

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Povzetek

Raziskovali smo reakcije v sistemu Cr–NH_3OHF–HF–H_2O. Iz vodne raztopine smo izločili zelene kristale nove spojine in s kemijsko analizo določili formulo $(NH_3OH)_3CrF_6$. Spojina kristalizira triklinsko, *P*-1, s parametri osnovne celice: a = 6.5461(2) Å, b = 6.9347(2) Å, c = 9.4072(3) Å, α = 86.772(1)°, β = 83.804(1)°, γ = 70.283(1)°. Iz meritev magnetne susceptibilnosti v območju 80-290 K smo izračunali efektivni magnetni moment, μ_{ef} = 3.82 BM. S termogravimetričnimi in diferencialno termičnimi meritvami smo spremljali termični razkroj spojine. $(NH_3OH)_3CrF_6$ nad temperaturo 125 °C razpada v treh stopnjah, pri čemer smo končni preostanek identificirali z rentgenskimi praškovnimi meritvami kot α – Cr_2O_3.