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STUDY OF THE THERMAL BEHAVIOUR OF $[Cr(NH_3)_6]MF_6$ (M = Cr, Al, Fe, Ga and In) and $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$

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Abstract

The thermal behaviour of the hexamminechromium hexafluorometallates and $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ was investigated by non-reciprocal quasi-isobaric thermal analysis, X-ray diffraction and i.r. spectroscopy. Reduction of chromium(III) was not observed, neither during the decomposition $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ nor during the decomposition of any of the title hexamminechromium hexafluorometallates. Obviously this reduction is not promoted by the coördinative Cr–N bonds, neither these in the starting materials nor those in the intermediately formed phases. Under non-reciprocal quasi-isobaric conditions, hexamminechromium hexafluorometallates are ideal precursors for preparing mixed cationic fluorides both in the rhombohedral modification and in the modification of the hexagonal tungsten bronze type structure.

Keywords: fluorides with HTB structure, hexamminechromium hexafluorometallates, mixed cationic fluorides, quasi-static thermal analysis, thermal analysis

Introduction

Fluorometallates, $[Cr(NH_3)_6]MF_6$ (M = Al, Ga, In, Sc, Ti, V, Fe, Rh), were described and structurally characterized by Wieghardt and Siebert [1]. These compounds crystallize in the cubic system, space group Pa3. On the thermal behaviour of these compounds nothing is known so far. Only Shevchenko *et al.* [2] investigated the thermal dissociation of $[Co(NH_3)_6]F_3$ and $[Cr(NH_3)_6]F_3$. The reaction scheme of Shevchenko *et al.* [2] (also Fig. 5) summarizes the thermogravimetric results and analytical characterization of the intermediates and is based on a stepwise generation of NH_3.

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Investigations of the thermal decomposition of the hexamminechromium hexafluorometallates are interesting for two reasons. Because of the stoichiometric composition of the hexafluorometallates, one could expect fluorides of the composition $Cr_{0.5}M^{III}_{0.5}F_3$ to be available in an elegant way by thermal decomposition of hexamminechromium hexafluorometallates. The ferroelastic properties of the mixed fluorides were described by Guelin *et al.* [3]. Secondly, knowledge of the thermal behaviour of compounds with coordinatively bonded NH_3 is important in order to understand side reactions of the thermal decomposition of ammonium halogenometallates [4–6]. Especially, the importance of these compounds for the reduction of the central atom of the halogenometallates is not clear yet. Meyer and Möller [4] have observed $(NH_4)_2[RhCl_5(NH_3)]$ as an intermediate during formation of metallic Rh by thermal induced reduction of $(NH_3)_2RhCl_6{\cdot}H_2O$. Irmler, Möller and Meyer pointed out that the electron transfer and consequently the reduction should be promoted by the direct interaction of nitrogen and the central atom in such kinds of compounds [5]. Intermediates with coordinatively bonded NH_3, namely $CrF_3{\cdot}xNH_3$ [6], are formed in the decomposition process of $(NH_4)_3CrF_6$ before a partial reduction to Cr_2F_5 takes place. On the other hand, Shevchenko *et al.* did not observe any reduction during the thermal decomposition of $[Cr(NH_3)_6]F_3$ [2]. This is in contrast to the discussion given above.

For our investigations we selected the compounds $[Cr(NH_3)_6]MF_6$ with M = Cr, Al, Fe, Ga and In. In completion of the studies by Shevchenko *et al.* [2] we extended the investigations by including $[Cr(NH_3)_6]F_3{\cdot}HF{\cdot}H_2O$, which was first described by Birk and Bilz in 1926 [7].

Experimental

The thermal analysis was carried out on a Derivatograph Q1500D modified for analyzing high reactive substances [6] and coupled with a computer MC80. Non-reciprocal quasi-static conditions were obtained using a Q-crucible [8] in which the partial pressure of the gaseous reaction products reaches 70 kPa (self-generated atmosphere). The following parameters were used: sample mass: 200–400 mg; dynamic heating rate: 5 deg·min^{-1}; atmosphere: dry N_2, pumping rate 8 l/h; reference: Al_2O_3; material of the crucibles: Pt.

The mass spectrometric investigations were carried out on a MS Q300, the equipment and the experimental conditions correspond to those given by Heide *et al.* [13].

The samples were prepared and characterized as described in the references [1, 7].

Intermediates and final products of the decomposition reactions were characterized by X-ray (Guinier-method, CuK$_\alpha$-radiation) and by i.r. spectroscopy (Specord, KBr-technique) after cooling to room-temperature.

Results and discussion

Hexamminechromium hexafluorometallates

The thermal decomposition starts above 200°C if the thermal decomposition of the hexamminechromium hexafluorometallates is carried out in an open crucible and dry N_2 atmosphere. Under these conditions the dissociation takes place simultaneously with hydrolysis reactions caused by traces of water and hy-

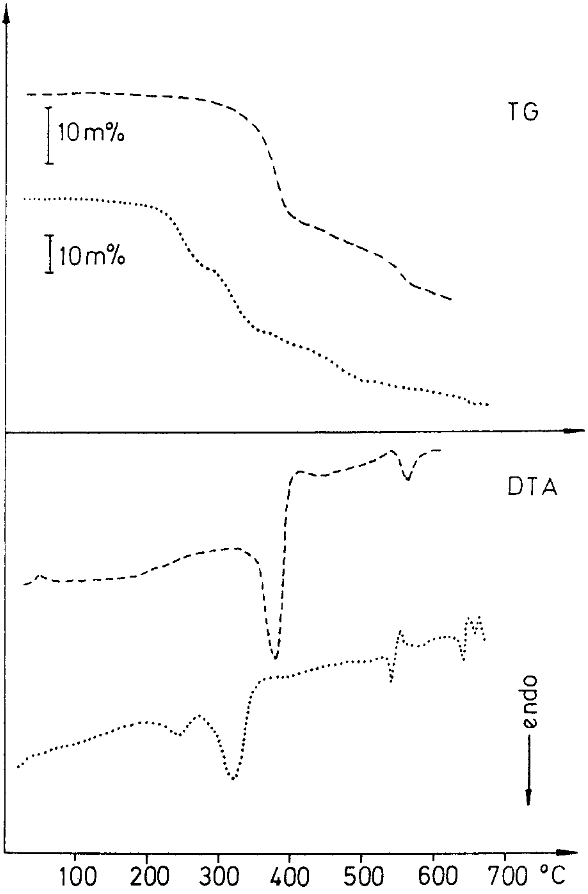


Fig. 1 The thermal decomposition of hexamminechromium hexafluorochromate – thermal analysis, ---- dynamic conditions,····· non-reciprocal quasi-isobaric conditions

Table 1 Results from the thermal decomposition of hexamminechromium hexafluorometallates $[Cr(NH_3)_6]MF_6$

	1st step (–4 NH_3)			2nd step (–5 NH_3)			3rd step (–6 NH_3)		
M	temp./	Δm_{exp} /	Δm_{cal} /	temp./	Δm_{exp} /	Δm_{cal} /	temp./	Δm_{exp} /	Δm_{cal} /
	°C	%		°C	%		°C	%	
Al	300–390	25.2	23.1	390–			580	35.5	34.6
Cr	310–410	21.6	21.3	410–510	27.1	26.6	510–680	33.3	31.9
Fe	280–360	26.1	21.0			formation of FeF_2			
Ga	290–380	22.0	20.2	380–445	27.9	25.2	445–650	34.9	30.2
In	300–370	18.8	17.8	370–430	23.3	22.3	430–650	26.5	26.6

droxides in the starting material. This has been proved by mass spectrometric investigations. In the whole temperature range investigated HF is a main product. An assignment of thermogravimetric steps to single reaction steps is not possible as the thermal decomposition is overlaid by hydrolysis.

In such cases it is advantageous to use quasi-static thermoanalytical methods in order to characterize the thermal decomposition. We have shown the possibility to suppress hydrolysis reactions using non-reciprocal quasi-isobaric conditions, i.e. thermal analysis under a constant pressure of the gaseous reaction products ($p>70$ kPa, self-generated atmosphere) [8]. This method has been successful in the present investigations, too.

Although the thermal decomposition here starts at higher temperatures and the total mass loss corresponds to the generation of 6 mol NH_3 per mol $[Cr(NH_3)_6]MF_6$. In Fig. 1 the dependence of decomposition reactions on partial pressure is shown for the hexafluorochromate sample.

The following considerations refer only to investigations in self-generated atmosphere to allow the comparison of the different compounds.

The hexamminechromium hexafluorometallates dissociate in three steps. The results of the thermoanalytical investigations are given in Table 1.

The thermal stability of $[Cr(NH_3)_6]MF_6$ decreases in the order M = In>Ga>Fe>Al>Cr (criterion: DTA maximum of the first step). The approximate compositions of the intermediates deduced from the mass losses are $CrM(NH_3)_2F_6$ and $CrM(NH_3)_6F_6$. The given formulas agree with the i.r. spectra (Fig. 2). The bands typically for complex bonded NH_3 always dominate ($\rho(NH_3)$: 814...710 cm^{-1}; $\delta_s(NH_3)$: 1315, 1324...1290 cm^{-1}; $\delta_e(NH_3)$: 1656, 1609 cm^{-1}; $\nu(NH)$: 3260...3250, 3320 cm^{-1} [6]). However, the reduction of intensities due to increased temperature has to be taken into consideration. Ammonium compounds are formed intermediately as side products of the decomposition, visible for appropriate i.r. band ($\nu_4(NH_4^+)$: 1420 cm^{-1}). The decomposition products are all amorphous. Only during the decomposition of $[Cr(NH_3)_6]InF_6$ NH_4InF_4 was identified as a crystalline phase.

Final products of the decomposition are rhombohedral fluorides $Cr_{0.5}M_{0.5}F_3$. The found lattice constants correspond to the values given by Guelin *et al.* [3].

A formation of Cr(II)-compounds was not observed by X-ray measurements in any of the cases. Nor the investigations of the decomposition reaction by mass spectrometry gave any indication for reduction reactions. These reactions occurring in addition to the generation of NH_3 would be recognized by a simultaneous increase of intensities of the masses of 14 (N^+), 28 (N_2^+), and 20 (HF^+) [9].

Only during the decomposition of the fluoroferrates a reduction occurs, to Fe^{2+}. In this case, the final products are CrF_3 and FeF_2.

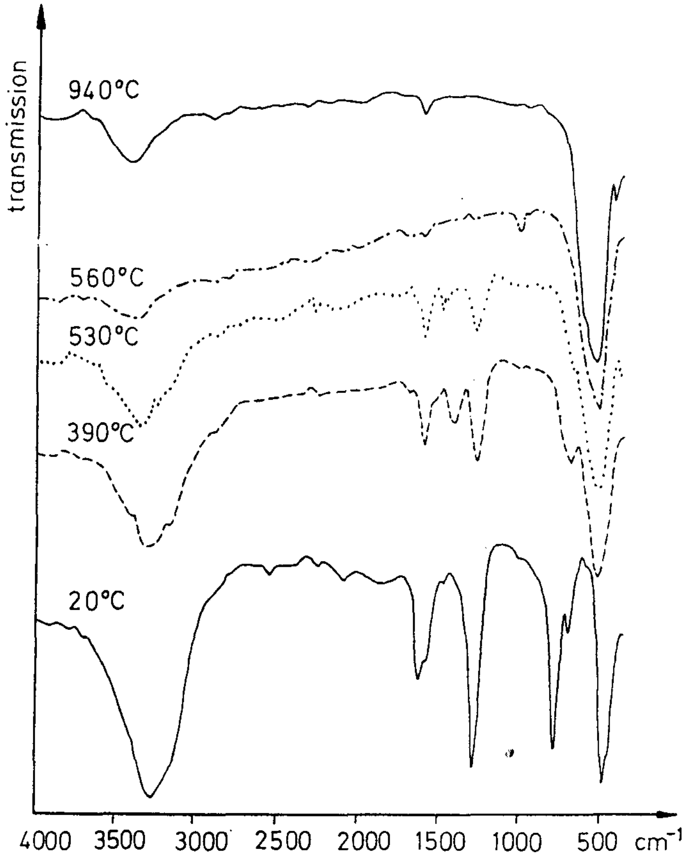


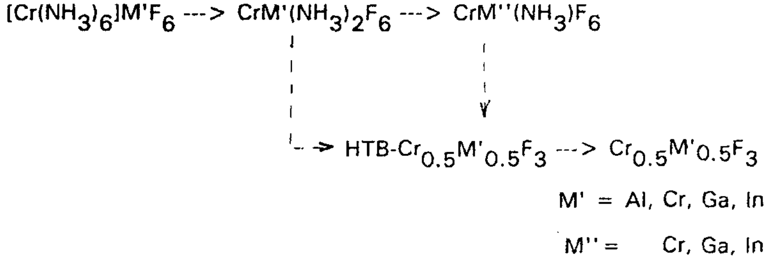
Fig. 2 I.r. spectroscopic characterization of the thermal decomposition of hexamminechromium hexafluorochromate

The generation of 6 NH_3 does not lead directly to the expected rhombohedral fluorides $Cr_{0.5}M_{0.5}F_3$. First, an orthorhombic intermediate is formed as during the decomposition of ammonium fluorometallates [6]. The intermediate of the decomposition of the $[Cr(NH_3)_6]CrF_6$ was identified by powder pattern as the orthorhombic modification of CrF_3 with the hexagonal tungsten bronze type-structure (HTB-CrF_3) determined by de Pape *et al.* [10]. The decomposition of the other hexamminechromium hexafluorometallates leads obviously to compounds isostructural to HTB-CrF_3. The X-ray photographs show the weak and diffuse reflexes of all hkl values calculated after [10] with relative intensities higher than 10%, and the lattice constants correspond to Vegard's rule and are given in Table 2. The transformation into the final products is irreversible.

Table 2 Lattice constants of the orthorhombic fluorides $Cr_{0.5}$ $M'_{0.5}F_3$ (HTB structure)

Compound	Lattice constants in pm			Reference
	a	b	c	
AlF3	693.1	1200.2	713.4	[11]
CrF3	727.6	1248.0	736.4	[10]
GaF3	721.0	1339.8	733.3	[11]
InF3	787.5	1349.9	795.6	[11]
$Al_{0.5}$ $Cr_{0.5}F_3$	710.0	1224.0	725.0	This paper
$Cr_{0.5}$ $Ga_{0.5}F_3$	724.0	1244.0	735.0	This paper
$Cr_{0.5}$ $In_{0.5}F_3$	758.0	1299.0	766.0	This paper

The thermal dissociation can be described as in the following scheme:



The reaction step according to the decomposition of the intermediates $CrM''(NH_3)F_6$ is especially accented if the starting material is derived from fluorides forming ammoniates themselves (*M''* = Cr, Ga, In) [6, 12].

An exception from this scheme is $[Cr(NH_3)_6]FeF_6$, where the formation of ammonium compounds dominates, due to the reduction of Fe^{3+}.

$[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$

Contrary to the hexamminechromium hexafluorometallates, an immediate structural reconstruction of the solid phase occurs during the thermal decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$. Figure 3 shows the stepwise decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$. The decomposition starts with generation of HF and H_2O accompanied by a complete change of the solid phase leading to the formation of crystalline $(NH_4)_3CrF_6$ and amorphous products (exothermal effect at 120°C). I.r. spectroscopic (Fig. 4) and X-ray diffraction investigations of the intermediates confirm this. Figure 4 shows the changes in the solid phase during the decomposition process. Between 1500 and 1200 cm^{-1} the vibration

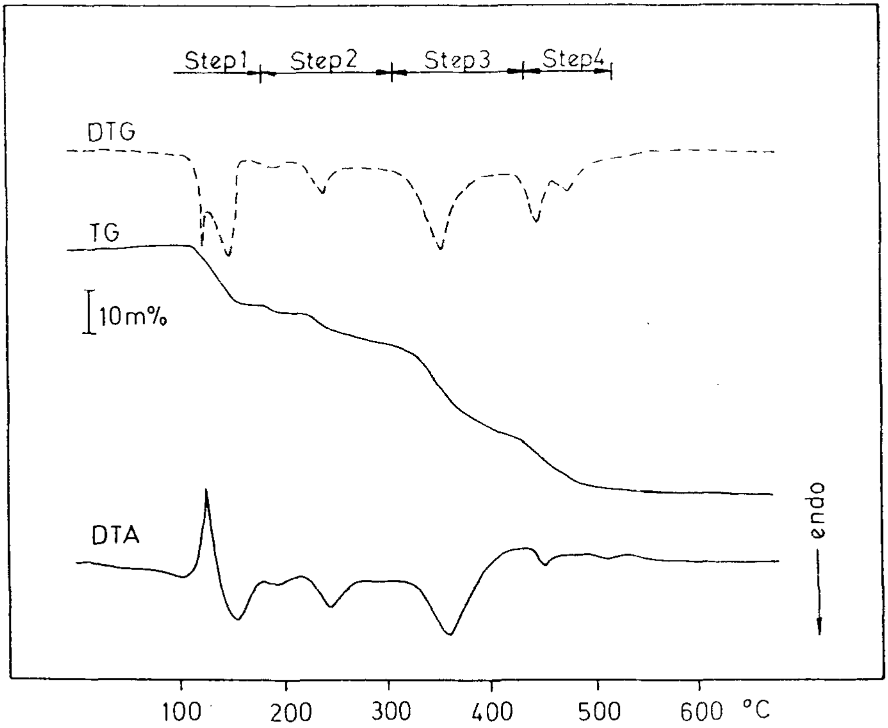


Fig. 3 The thermal decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ under non-reciprocal quasi-isobaric conditions – thermal analysis

bands assigned to HF_2^- have disappeared but the typical NH_4^+ vibrations are visible. As described for the hexamminechromium hexafluorometallates, coordinative NH_3 bonds – or with other words chromiumfluoride ammoniates $CrF_3 \cdot xNH_3$ (bands at 1610, 1290, 710 cm^{-1}) [6] still remain within the amorphous phases during this decomposition process, too. The further course of the decomposition reactions is determined by the decomposition of the amorphous chromiumfluoride ammoniates and the stepwise dissociation of $(NH_4)_3CrF_6$. Therefore the investigation of the thermal decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ is especially suitable for studying the effect of the presence of chromiumfluoride ammoniates on the thermal decomposition of ammonium fluorochromates.

Using the information about the thermal behaviour of $(NH_4)_3CrF_6$ [6] and $[Cr(NH_3)_6]F_3$ [2], the several reactions can be correlated to the thermogravimetric curves (Fig. 5). The comparison of the mass losses, calculated from this scheme and measured, respectively, shows a good coincidence (Table 3). It is noteworthy that no reduction products were detectable despite of the – in com-

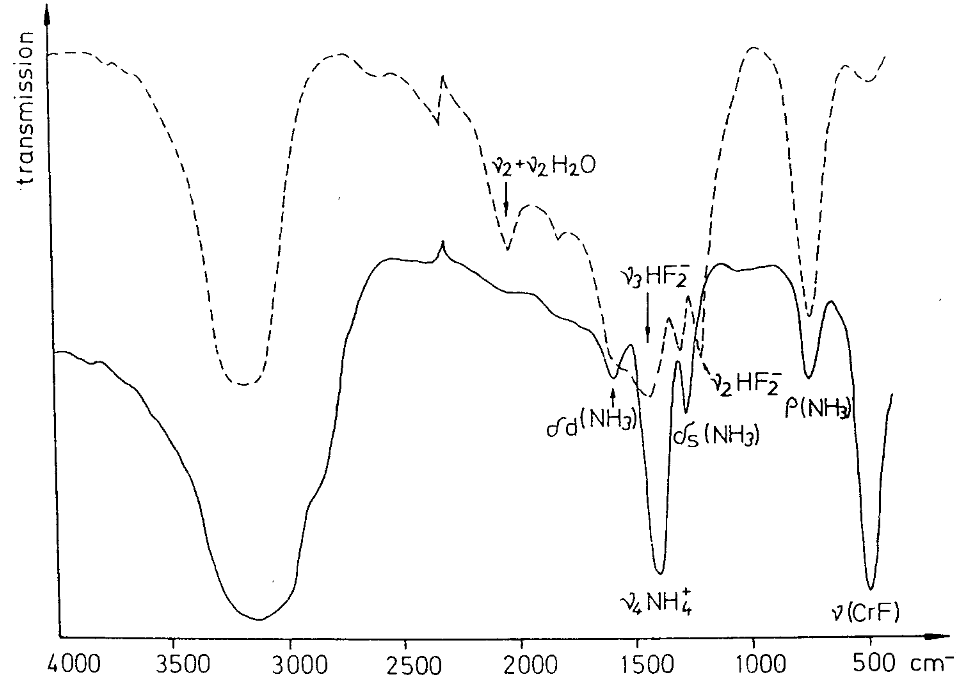


Fig. 4 I.r. spectroscopic characterization of the thermal decomposition $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ ---- starting material, — residue at 120°C

Table 3 Comparison of calculated[a] and experimentally determined mass losses

Reaction step (see Fig. 5)	Calculated[a] mass loss Δm / %	Experimentally determined	
		mass loss Δm / %	temperature range/°C
1	14.0	14.7	25-220
2	23.1	23.5	220-320
3	44.8	44.8	320-440
4	56.2	56.8	440-550

[a] from the reactiom scheme in Fig. 5

parison with the decomposition of pure ammonium fluorochromates – clearly increased concentration of the ammoniate $CrF_3 \cdot xNH_3$ in the solid phase.

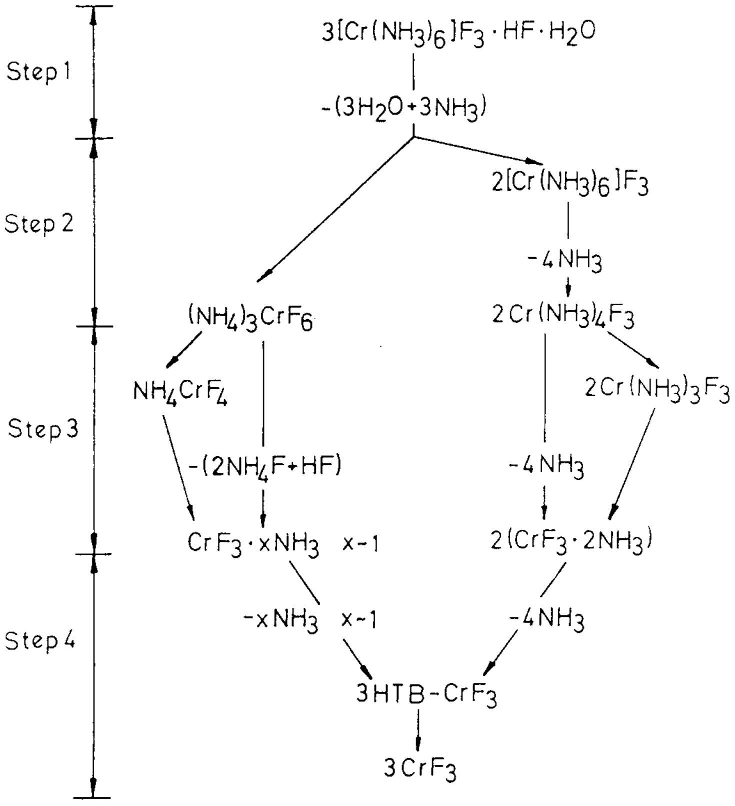


Fig. 5 Reaction scheme of the thermal decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$

Conclusions

Corresponding to the results of Shevchenko *et al.* [2] a reduction of chromium(III) was not observed, neither during the decomposition of $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ nor during the decomposition of hexamminechromium hexafluorometallates. Obviously this side reaction is promoted neither by the coordinative Cr–N bonds in the starting materials nor by those in the intermediate phases.

Hexamminechromium hexafluorometallates are ideal precursors for the preparation of mixed cationic fluorides. Because the decomposition is completed below 700°C, not only mixed cationic fluorides of rhombohedral modification are available. It is also possible to produce mixed cationic fluorides with HTB-structure by a controlled thermal decomposition.

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References

1 K. Wieghardt and H. Siebert, J. Mol. Struct., 7 (1971) 305.

2 Yu. N. Shevchenko, N. K. Davidenko and K. B. Yatsimirskii, Zh. Neorg. Khim., 20 (1975) 406.

3 J. Guelin, A. Yacoubi, J. Ravez and J. Grannec, Z. Anorg. Allg. Chem., 557 (1988) 225.

4 G. Meyer and A. Möller, Proceed. GEFTA TA-Symposium 3.–10. 1990, Karlsruhe.

5 M. Irmler, A. Möller and G. Meyer, Z. Anorg. Allg. Chem., 604 (1991) 7.

6 D.-H. Menz and U. Bentrup, Z. Anorg. Allg. Chem., 613 (1992) 108.

7 E. Birk and W. Bilz, Z. Anorg. Allg. Chem., 153 (1926) 125.

8 D.-H. Menz, J. Thermal Anal., 38 (1992) 321.

9 D.-H. Menz and D. Becker, unpublished.

10 R. de Pape, A. Le Bail, F. Lubin and G. Ferey, Rev. Chim. Miner., 24 (1987) 545.

11 A. Le Bail, C. Jacoboni, M. Leblanc, R. de Pape, H. Duroy and J. L. Fourquet, J. Solid State Chem., 77 (1988) 96.

12 S. A. Polishchuk, S. P. Kozerenko and Yu. V. Gagarinskii, J. Less Common Met., 27 (1972) 45.

13 K. Heide, E. Hartung, H. G. Schmidt and I. Ottlinger, Glastechn. Ber., 59 (1986) 59.

Zusammenfassung — Das thermische Verhalten von Hexamminchromium-hexafluorometallaten und $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ wurde mittels nicht-reziproker quasi-isobarer Thermoanalyse, röntgenographisch und IR-spektroskopisch untersucht. Weder bei der thermischen Zersetzung von Hexamminchromium-hexafluorometallaten noch bei der thermischen Zersetzung von $[Cr(NH_3)_6]F_3 \cdot HF \cdot H_2O$ wurde eine Reduktion von Chromium(III) beobachtet. Offensichtlich wird diese Nebenreaktion nicht durch die in den Ausgangsstoffen bzw. Zwischenprodukten vorliegenden Cr–N-Bindungen begünstigt. Unter nicht-reziproken quasi-isobaren Bedingungen sind Hexamminchromium-hexafluorometallate ideale precursor für die Herstellung gemischt-kationischer Fluoride. Dabei sind sowohl die rhomboedrischen Modifikationen als auch die Fluoride mit hexagonaler Bronzestruktur zugänglich.