

SYNTHESIS AND THERMAL DECOMPOSITION OF ACID ALKALI METAL HEXAFLUOROALUMINATES

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Acid alkali hexafluoroaluminates of K and Rb were prepared by precipitation of alkali fluoride containing H_3AlF_6 solutions with ethanol. Compounds were characterized by X-ray diffraction, IR spectroscopy, $^1\text{H-NMR}$ and chemical analysis. The constitution is $\text{M}^1(\text{H}_3\text{O})_2\text{AlF}_6$. Lattice parameters were determined.

Dehydration and thermal decomposition were investigated by thermal analysis (TG, DTG, DTA) on a derivatograph-Q and by high temperature X-ray diffraction. Thermal decomposition is accompanied by liberation of H_2O and HF and a condensation of $[\text{AlF}_6]^{3-}$ octahedra forming layer structures. Stable intermediate products are $\text{M}^1\text{AlF}_4 \cdot 0.5\text{H}_2\text{O}$ and M^1AlF_4 . At higher temperatures hydrolysis occurs.

We earlier investigated the thermal decompositions of alkali metal fluorometallate hydrates and their structural changes [1, 2]. By variation of the synthesis methods, we were able to prepare a new type of fluoroaluminate with the analytical composition $\text{M}^1\text{H}_2\text{AlF}_6 \cdot 2\text{H}_2\text{O}$. Well crystallized substances with $\text{M}^1 = \text{K}$ and Rb have been prepared. Potassium can be partly substituted by rubidium and caesium. Aluminium can also be replaced by other M^{III} cations, but only to very slight extents.

Since we are interested in the relations between the nature of the water bonding, the thermal behaviour and the structural changes during thermal treatment, we have investigated these compounds. This paper reports on spectroscopic, X-ray and thermal analytical investigations of acid fluoroaluminates, especially those of potassium and rubidium, and the mixed cationic compound $\text{K}_{0.5}\text{Rb}_{0.5}\text{H}_2\text{AlF}_6 \cdot 2\text{H}_2\text{O}$.

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Experimental

Preparation of the compounds: 1 g Al was dissolved in 50 ml HF solution (40%). A concentrated solution of alkali metal fluoride, chloride or carbonate in HF was added (molar ratio $M^I:Al = 1:1$) to this solution, followed by 50 ml ethanol. After 30 minutes the solution became transparent and crystallization began. The crystals were separated after some hours, washed with ethanol and dried in air. The compounds were analysed for alkali metal with sodium tetraphenylborate, for aluminium with EDTA, and for fluorine by SEEL.

TG, DTG and DTA curves were recorded with a Q-1500 D derivatograph.

Experimental conditions: Pt crucible, sample masses 250–600 mg, heating rate 5 deg/min, N_2 flowing at 25 l/h, $\alpha-Al_2O_3$ as reference substance for DTA. IR spectra were recorded on an Specord IR-75 instrument (KBr pellets) and 1H -NMR spectra on an FKS 176 multi-pulse spectrometer. X-ray powder diffraction patterns were recorded with a Guinier-Lenné camera with a heating device (heating rate 2.5 deg/min, 20–600°).

Results and discussion

Analytical characterization

The atomic ratio given by elemental analysis is $M^I:Al:F:H_2O = 1:1:1:6:2$. Consequently, there are different possibilities for the constitution: it may be an adduct $M^IAlF_4 \cdot 2H_2O$, a hexafluoroaluminate dihydrate $M^IH_2AlF_6 \cdot 2H_2O$, or an oxonium hexafluoroaluminate $M^I(H_3O)_2AlF_6$. In spite of the fact that the specimens are well crystallized, the crystal structure could not be determined, because they show complicated symmetry relations, pointing to a disordered structure.

The IR spectra of all compounds are very similar and rich in absorptions. The position of $\nu_3(Al-F)$ at 535 and 585 cm^{-1} points to the presence of isolated, but not regular $[AlF_6]^{3-}$ octahedra [3]. It is not possible to decide if the crystal structures contain H_3O^+ or H_2O and HF. It can rather be assumed that all the observed absorptions are caused by the interaction of H_2O with H^+ and F^- and by strong hydrogen-bonding.

From 1H -NMR measurements it should be possible to establish if there are water molecules or/and oxonium ions. The room-temperature spectra show a narrow signal, pointing to a high mobility of the protons. The low-temperature spectra (-150°) show a broad signal in the case of the Rb compound. The shape of this is typical of H_3O^+ or both H_3O^+ and H_2O .

Table 1 Lattice parameters of cubic hexafluoroaluminates

Compound	<i>a</i> , pm	Temp., °C	Ref.
(H ₃ O) ₃ AlF ₆ · 3H ₂ O	815.0	- 90	4
K(H ₃ O) ₂ AlF ₆	864.6	20	this work
K _{0.5} Rb _{0.5} (H ₃ O) ₂ AlF ₆	869.5	20	this work
Rb(H ₃ O) ₂ AlF ₆	881.4	20	this work
(NH ₄) ₃ AlF ₆	840.0	20	5
K ₃ AlF ₆	855.0	400	6
Rb ₃ AlF ₆	888.0	400	6

Oellers and Mootz [4] determined the crystal structure of H₃AlF₆ · 6H₂O and found that the constitution corresponds to an oxonium salt hydrate (H₃O)₃AlF₆ · 3H₂O with cubic symmetry. Table 1 shows the lattice parameters of the synthesized compounds determined from powder diffraction patterns. Comparison of the unit cell parameters of the acid fluoroaluminates with those of other alkali metal hexafluoroaluminates and the oxonium hexafluoroaluminate hydrate reveals a great similarity. To summarize all the known experimental results, we tend to assume that the prepared acid fluoroaluminates are alkali metal oxonium hexafluoroaluminates M^I(H₃O)₂AlF₆.

Thermoanalytical and X-ray investigations

Figure 1 shows the complete TG, DTG and DTA curves of the K compound. It can be seen that there are two parts in the TG curve: the first appears between 85

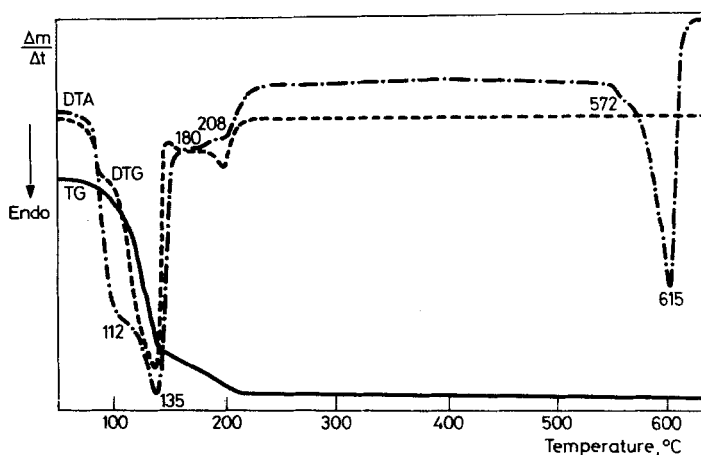


Fig. 1 TG, DTG and DTA curves for the decomposition of K(H₃O)₂AlF₆.

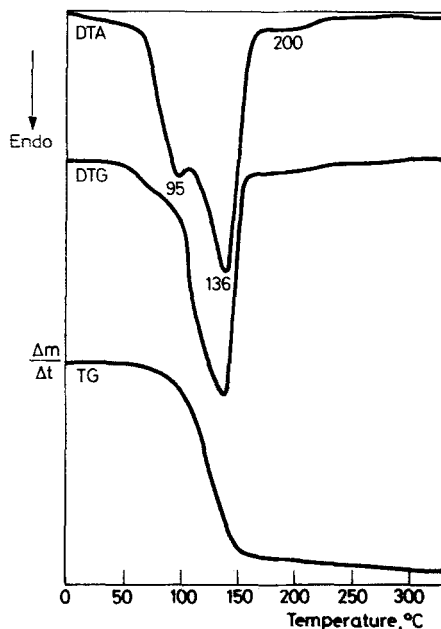


Fig. 2 TG, DTG and DTA curves for the decomposition of (K, Rb) $(\text{H}_3\text{O})_2\text{AlF}_6$

and 140° , and the second from 140 to 210° . The first part corresponds to the loss of 2 mole HF and 1 mole H_2O . The second part corresponds to the loss 0.85 mole H_2O , which means that a small amount of water remains in the structure. The DTA curve shows several endothermic effects, corresponding to a gradual liberation of HF and H_2O . It is not yet possible to give an explanation of the effect at 112° but we tend to assume that there is a chemical reaction before and during the liberation of HF and H_2O . This initial reaction causes the loss of HF and H_2O . As we have not analysed the gaseous phase, we are not able to estimate and separate the temperature ranges of liberation of HF and H_2O . However, it is probable that HF and H_2O are given up essentially simultaneously in the temperature range 85 – 140° .

The liberation of the last mole of H_2O is also a stepwise process, with two DTA effects, at 180 and 208° . Above 210° , no weight loss is detectable. At 615° , a large endothermic effect can be observed, caused by melting of the tetrafluoroaluminate formed.

Figures 2 and 3 show the TG, DTG and DTA curves (up to 300°) of the (K/Rb) compound and the Rb compound. The first part of the weight loss is connected with two DTA effects. As compared with the K compound, the temperature of the initial reaction are lower. Consequently, this temperature should be a characteristic one and a criterion of stability. The second part of the weight loss is not revealed

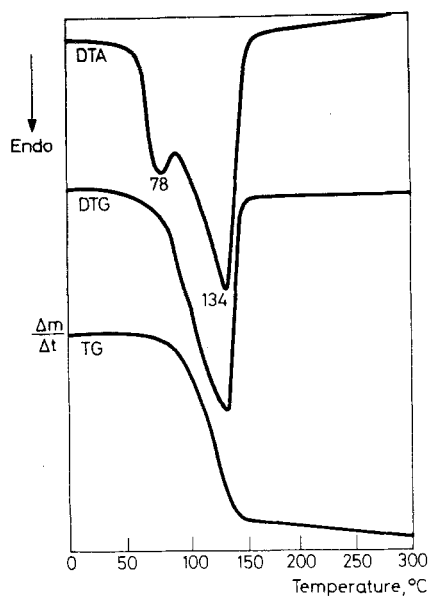


Fig. 3 TG, DTG and DTA curves for the decomposition of $\text{Rb}(\text{H}_3\text{O})_2\text{AlF}_6$

Table 2 High-temperature X-ray investigations of phases dependent on temperature ($^{\circ}\text{C}$)

Phases	$\text{M}^{\text{I}} = \text{K}$	$\text{M}^{\text{I}} = (\text{K}, \text{Rb})$	$\text{M}^{\text{I}} = \text{Rb}$
$\text{M}^{\text{I}}(\text{H}_3\text{O})_2\text{AlF}_6$	20–125	20–120	20– 85
Amorphous phase	125–140	120–205	85–120
$\text{M}^{\text{I}}\text{AlF}_4 \cdot 0.5\text{H}_2\text{O}$	140–345	205–375	120–425
$\text{M}^{\text{I}}\text{AlF}_4$	220–550	285–485	300–500
M_3AlF_6 and product of hydrolysis	370–600	400–600	440–600

distinctly as compared with the second part in the case of the K compound. Consequently, the corresponding DTA effect is very weak. Further, the last quantity of water is liberated over a wide temperature range.

High-temperature X-ray investigations have provided more information about the thermal decomposition and the phases formed during thermal treatment. The results of X-ray analysis are listed in Table 2. It should be noted that the conversion temperatures found by X-ray analysis can not be compared with those of thermal analysis without restriction because there were different conditions. Thermal analysis gives values more exactly, but the effects observed are comparable.

Thermal treatment and the following liberation of HF and H_2O lead to destruction of the crystal lattice and an amorphous phase results. The first crystalline product is a tetragonal phase. The separate synthesis of this phase and

elemental analysis showed the composition $M^IAlF_4 \cdot 0.5H_2O$. Further increase of temperature leads to the tetragonal M^IAlF_4 phases. At higher temperatures ($> 400^\circ$), $M^I_3AlF_6$ and a cubic oxygen-containing phase (the Rb compound has not yet been identified) are traceable, caused by hydrolysis [7]. After cooling, Al_2O_3 is detectable besides the hexafluoroaluminate.

With reference to thermal analysis, the first DTA effect corresponds to the formation of the alkali metal tetrafluoroaluminate hemihydrate. The second, weaker DTA effect is connected with dehydration of the hemihydrate and the formation of M^IAlF_4 . The endothermic effects at 615 , 608 and 590° for the K (K, Rb) and Rb compound, respectively, correspond to the melting points of M^IAlF_4 .

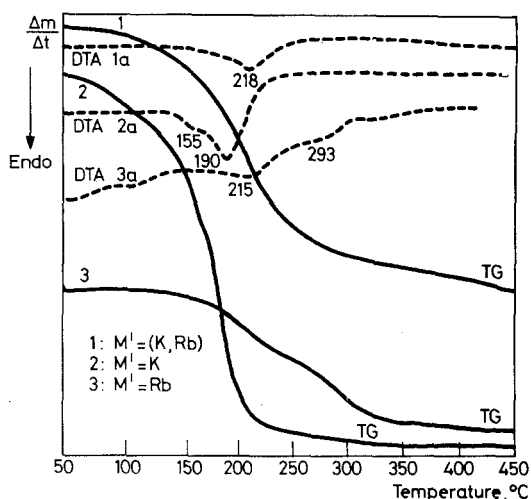
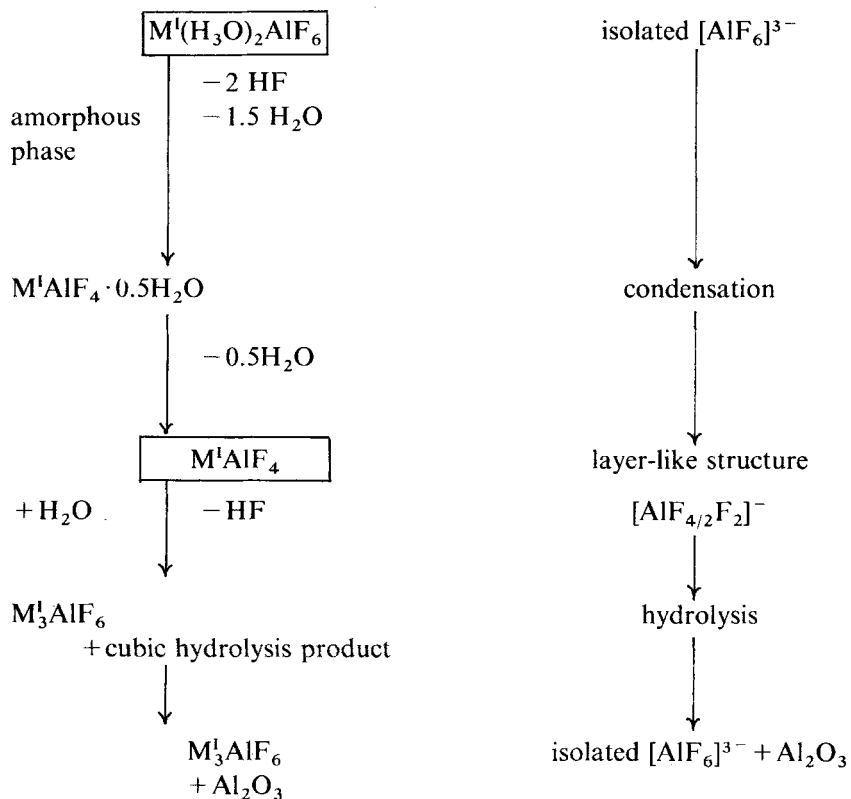


Fig. 4 TG and DTA curves for the dehydration of $M^IAlF_4 \cdot 0.5H_2O$. 1: $M^I = (K, Rb)$, 2: $M^I = K$, 3: $M^I = Rb$

The compounds $M^IAlF_4 \cdot 0.5H_2O$ can be synthesized through the heating of $M^IH_2AlF_6 \cdot 2H_2O$ for about 2–4 h at 100° . TG and DTA curves showing the dehydration of the hemihydrates are presented in Fig. 4. Corresponding to the X-ray investigations [7], only in the case of the K compound is a two-stage process detectable; this leads to the formation of pure $KAlF_4$. For the Rb and (K, Rb) compounds, higher dehydration temperatures have been found. There is a wide temperature range of dehydration causing hydrolysis reactions and consequently no pure tetrafluoroaluminate can be obtained. The thermal decompositions of acid hexafluoroaluminates can be summarized as shown in the following scheme.



All the investigated compounds showed the same thermal behaviour in principle. There are differences in thermal stability and reactivity. The decomposition is a two-stage process involving a structural reconstruction. Especially the Rb-containing compounds are very susceptible to hydrolysis

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Zusammenfassung — Es wurden saure Kalium- und Rubidiumhexafluoroaluminat durch Fällung aus Alkalifluorid enthaltenden H_3AlF_6 -Lösungen mit Ethanol dargestellt. Die erhaltenen Verbindungen wurden chemisch, röntgenographisch, IR- sowie 1H -NMR-spektroskopisch charakterisiert. Die Konstitution der Verbindungen ist $M^I(H_3O)_2AlF_6$. Die Gitterkonstanten wurden aus Röntgendiffraktionsdaten bestimmt. Entwässerung und thermische Zersetzung wurden mittels Heizguiniertechnik und Thermoanalyse (TG, DTG, DTA) an einem Derivatograph-Q untersucht. Bei der thermischen Zersetzung erfolgt eine HF- und H_2O -Abgabe sowie eine Kondensation von AlF_6^{3-} -Oktaedern unter Ausbildung von Schichtstrukturen. Als stabile Zwischenprodukte wurden $M^IAlF_4 \cdot 0.5H_2O$ und M^IAlF_4 nachgewiesen. Bei höheren Temperaturen werden Hydrolysereaktionen beobachtet.

Резюме — Кислые гексафторалюминаты калия и рубидия были получены из растворов фторидов калия и рубидия, содержащих H_3AlF_6 , путем осаждения этанолом. Полученные соединения состава $M^I(H_3O)_2AlF_6$ были охарактеризованы рентгеноструктурным анализом, ИК- и ПМР-спектроскопией и химическим анализом. Определены параметры их кристаллических решеток. Дегидратация и термическое разложение были исследованы методами термического анализа (ТГ, ДТГ, ДТА) на Q-derivатографе, а также высокотемпературным рентгеноструктурным анализом. Термическое разложение сопровождается выделением воды и фтористого водорода и конденсацией октаэдров $[AlF_6]^{3-}$ с образованием слоистых структур. Установлено образование устойчивых промежуточных продуктов типа $M^IAlF_4 \cdot 0.5H_2O$ и M^IAlF_4 . При более высоких температурах происходит гидролиз.