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SYNTHESIS AND THERMAL DECOMPOSITION OF $(NH_4)_2[M^{III}F_5(H_2O)$ (M = Al, Fe AND Cr)

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Ammonium pentafluorometallate monohydrates were prepared by different methods and characterized by chemical analysis, IR spectrometry and X-ray diffraction. Unit cell parameters were determined for the Fe and Cr compounds, which were found to be isostructural with the known Al compound. The IR spectra, X-ray diffraction patterns and lattice data on the compounds are very similar, and point to the existence of isolated $[M^{III}F_5(H_2O)]^{2-}$ octahedra. The water is coordinated to the M^{III} cation.

Dehydration and thermal decomposition were investigated by thermal analysis (TG, DTG, DTA) on the Q-derivatograph and by high-temperature X-ray diffraction. Different dehydration temperatures and products were found, depending on the nature of the M^{III} cation. NH_4F is liberated in several steps (Al or Fe) or continuously (Cr), leading to the formation of M^{III} fluorides.

Alkali metal pentafluorometallate monohydrates exist in two structure types. Type A is characterized by corner-connected $[MF_6]^{3-}$ octahedra, forming $[MF_4F_{2/2}]^{2-}$ chains; the alkali metal cations and water are situated between the chains. Type B is characterized by isolated $[MF_5(H_2O)]^{2-}$ octahedra, i.e. the water is coordinated to the M^{III} cation. We are interested in studies of the relations between the water bonding and the thermal behaviour of such hydrates, and especially of the ammonium compounds.

Only the crystal structure of the Al compound is known [1] to belong in type B. From IR data, it has been concluded that the Fe and Cr compounds also have the same structure type [2, 3]. Since the described synthesis methods could not be reproduced and no X-ray data have been published on the Fe and Cr compounds, we have developed suitable synthesis methods and determined the lattice parameters of these compounds.

The thermal behaviour of the ammonium pentafluorometallate monohydrates of Al, Fe and Cr has not been investigated previously. We also set out to investigate the structural changes occurring during the dehydration and to characterize the phases formed during the thermal treatment. There are two possibilities. During

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dehydration either a condensation process takes place leading to the formation of $(NH_4)_2MF_5$, or, if this phase is unstable, dismutation process leads to the formation of NH_4MF_4 and $(NH_4)_3MF_6$.

Experimental

The described compounds were analysed for ammonium according to Kjeldahl, fluorine according to Seel [4], aluminium with EDTA, iron as Fe_2O_3 and chromium as Ag_2CrO_4 after oxidation with persulfate.

TG, DTG and DTA curves were recorded by means of a Q–1500 D derivatograph. Experimental conditions: Pt crucibles, sample mass 150–300 mg, heating rate 5 deg min^{-1}, N_2 flowing at 50 l h^{-1}, α-Al_2O_3 as reference substance for DTA.

IR spectra were recorded on a Specord IR–75 (KBr pellets). X-ray powder diffraction patterns were taken by using a Guinier camera with a heating device (heating rate 2.5 deg min^{-1}, 20–600°).

Results and discussion

$(NH_4)_2[AlF_5(H_2O)]$: We could not obtain a pure compound by following the method described in [1]. The best products is high yields were obtained by precipitation from Al-containing HF solutions with gaseous NH_3 [5]. The results of elemental analysis were in good agreement with the theoretical values. The positions of the very strong ν_3 (Al–F) vibration and the strong lib (H_2O) vibration in the IR spectrum (Table 1) are characteristic of coordinated water [6]. X-ray investigations during programmed heating (Table 3) showed that no $(NH_4)_2AlF_5$ exists; rather, a dismutation process takes place during thermal treatment, leading

Table 1 IR data of $(NH_4)_2[M^{III}F_5(H_2O)]$—wave numbers ($cm^{-1}$), intensities and assignments

M / Assignments	Al	Fe	Cr
ν_3 (M–F)	510 s, 570 vs	455 vs	520 vs
lib (H_2O)	740 s, 855 sh	725 s, 830 sh	730 s, 865 sh
ν (N–H)	1440 vs	1435 vs	1430 vs
δ (H–O–H)	1615 vw	1620 vw	1615 vw
ν (O–H)	3090 s, br	3080 s, br	3055 s, br
ν (N–H)	3250 s, br	3225 s, br	3245 s, br

vs – very strong; s – strong; vw – very weak; sh – shoulder; br – broad.

Table 2 Unit cell parameters (in pm) of orthorhombic $(NH_4)_2M^{III}F_5(H_2O)]$

M	*a*	*b*	*c*
Al	1019.2	803.7	784.4*
Cr	1043.3	806.7	797.4**
Fe	1048.3	808.9	797.1**

* Knop et al.

** own results: calculated from powder pattern

Table 3 High temperature X-ray diffraction investigation of $(NH_4)_2[M^{III}F_5(H_2O)]$—phases in dependence on temperature

M	Temperature interval of detectability, °C		
Phases	Al	Fe	Cr
$(NH_4)_2[M^{III}F_5(H_2O)$	20–190	20–115	20–220
$(NH_4)_2M^{III}F_5$	—	65–220	—
$(NH_4)_3M^{III}F_6$	70–225	—	—
$(NH_4\ddot{u}_3M^{III}F_4$	70–330	100–280	—
$M^{III}F_3$	155–550	—	385–600
M_2O_3	—	440–600	—

Table 4 Thermogravimetric investigation of $(NH_4)_2[M^{III}F_5(H_2O)]$—decomposition temperatures (°C) and weight losses

M	1. step dehydration	2. step formation of $NH_4M^{III}F_4$	3. step formation of MF_3
Fe	82–110 8.7%	228–321 18.0%	321–461 20.1%
Al	111–152 10.6%	175–310 20.4%	310–463 20.8%
Cr*	188–286 11.7%	286–496 26.2%	496–625 11.0%

* Continuous weight loss, steps are not separated, temperatures are given where the weight loss corresponds to the formulated steps.

to NH_4AlF_4 and $(NH_4)_3AlF_6$. Further heating causes the liberation of NH_4F, and γ-AlF_3 is detectable. From these result, all the effects in the TG and DTA curves can be interpreted. The first step (Table 4, Fig. 1) corresponds to dehydration and confirmed that a mixture of equal proportions of tetra- and hexafluoroaluminate is formed. It should be noted that the conversion temperatures found by X-ray

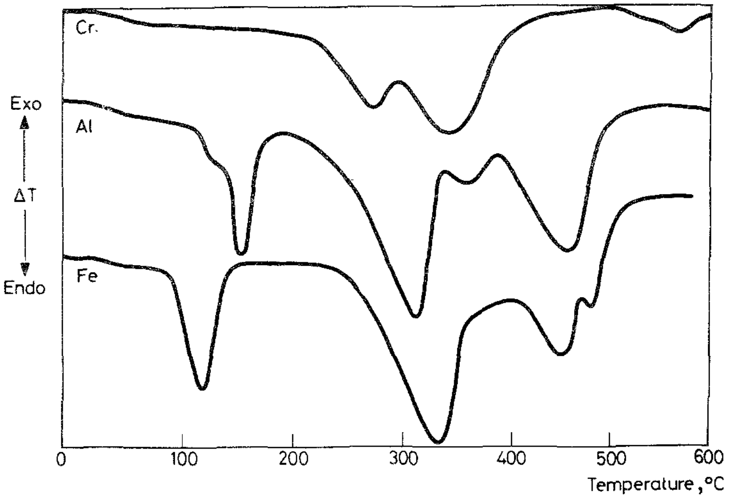

Fig. 1 DTA curves of $(NH_4)_2[M^{III}F_5(H_2O)]$

analysis were not strinctly comparable with those of thermal analysis, because the experimental conditions differed. However, the observed effects are comparable. The next steps correspond to the decomposition of $(NH_4)_3AlF_6$ and NH_4AlF_4, respectively. The temperature ranges are comparable with the published results [7, 8]. The exothermic effects at about 337° and 375° correspond to the reactions of NH_4F with Al–O species formed in side-reactions [9].

$(NH_4)_2[FeF_5(H_2O)]$: An appropriate method for preparation of the Fe compound is precipitation with methanol from a solution containing Fe and NH_4F (molar ratio 1 : 4) and excess HF. The results of elemental analysis were in good agreement with the theoretical values. The X-ray patterns are similar to those of the Al compound; the calculated lattice parameters are given in Table 2. The IR spectrum is comparable with that of the Al compound (Table 1). Consequently, it can be stated that the water is coordinately bound to the Fe^{III} cation.

Dehydration proceeds at lower temperatures than for the Al compound (Tables 3 and 4, Fig. 1). A new phase is formed which has not yet been characterized. Elemental analysis indicated the composition $(NH_4)_2FeF_5$. At higher temperatures, the formation of NH_4FeF_4 can be observed. On X-ray analysis, no crystalline FeF_3 could be detected, but only Fe_2O_3 (formed via hydrolysis). The results of thermal analysis are in good agreement with those of X-ray investigations (endothermic peaks at 307°, 422° and 453° correspond to the conversion to NH_4FeF_4, FeF_3 and Fe_2O_3, respectively) and with published observations [7].

$(NH_4)_2[CrF_5(H_2O)]$: A good synthesis has been described in [2]. We are able to report two further methods. The first one is to reduce an NH_4F-containing

$(NH_4)_2Cr_2O_7$ solution (molar ratio $Cr:NH_4F = 1:2$) with ethanol. The $CrF_3 \cdot 3H_2O$ is then separated off, and the fluorochromate is precipitated with methanol. Another way is to reduce such solutions with fomaldehyde. A further preparation was performed according to [2]. The results of elemental analysis were in good agreement with the theoretical values. The IR spectrum and lattice parameters (Tables 1 and 2) are similar to those of the Al and Fe compounds. Therefore, we presume that the Cr compound is of the same structure type. However, the thermal behaviour is different. In contrast with the Al and Fe compounds a continuous weight loss was observed (Table 4, Fig. 1). Dehydration takes place at essentially(higher temperatures and is associated with the liberation of NH_4F. No crystalline phase was detected by X-ray diffraction (Table 3). At higher temperatures, CrF_3 was obtained. No pure $(NH_4)_2CrF_5$ or NH_4CrF_4 were detected as intermediates. Similar behaviour has been described for the decomposition of $(NH_4)_3CrF_6$ [10]. $_6$ [10].

To summarize it can be stated that, in spite of the identical structure type, the different behaviour of the ammonium pentafluoroaluminate hydrates of Al, Cr and Fe can be observed. There are differences as regards the dehydration temperatures and the reaction products. Further investigations must be performed to clarify the reasons for the different properties of these compounds.

References

1 O. Knop, T. S. Cameron, S. P. Deraniyagala and D. Adhikesavalu, Can. J. Chem., 63 (1985) 516.
2 M. K. Chaudhuri and N. Roy, Synth. React. Inorg. Met.-Org. Chem., 12 (1982) 879.
3 E. N. Deichman, Yu. Ya. Kharitonov and A. A. Schachnasarjan, Zh. Neorg. Khim., 16 (1971) 3271.
4 F. Seel, E. Steigner and J. Burger, Angew. Chem., 76 (1964) 532.
5 DD-patent WP CO1F 284070/5, 10. 12. 1985.
6 U. Bentrup, R. Stodolski and L. Kolditz, Z. Chem., 26 (1986) 187.
7 D. B. Shinn, D. S. Crocket and H. M. Haendler, Inorg. Chem., 5 (1966) 1927.
8 P. Bukovec and J. Siftar, Therm. Anal., Proc. 3rd Int. Conf., 1971, 2, p. 321.
9 publication in preparation.
10 P. Bukovec and J. Siftar, Monatsch. Chem., 105 (1974) 510.

Zusammenfassung — Ammoniumpentafluormetallat-monohydrate $(NH_4)_2MeF_5 \cdot H_2O$ (M = Fe, Al, Cr) wurden nach verschiedenen Methoden präpariert und durch chemische Analyse, IR-Spektren und Röntgenbeugung charakterisiert. Die Elementarzellen-Parameter der mit der Al-Verbindung isostrukturellen Fe- und Cr-Verbindung wurden ermittelt. IR-Spektren, Röntgenbeugungsdiagramme und Gitterdaten aller drei Verbindungen sind einander sehr ähnlich und beweisen das Vorliegen isolierter $[M^{III}F_5(H_2O)]^{2-}$-Oktaeder, in denen Wasser mit dem Kation koordiniert ist. Entwässerung und thermische Zersetzung wurden durch simultane TG–DTG–DTA und durch Hochtemperatur-Röntgenbeugung untersucht. Abhängig vom Kation M^{III} werden unterschiedliche Reaktionsprodukte und -temperaturen gefunden. Unter kontinuierlicher (M = Cr) oder schrittweiser Freisetzung von NH_4F (Fe, Al) wird das jeweilige Fluorid $M^{III}F_3$ gebildet.

Резюме — Полученные различными методами моногидраты пентафторметаллатов аммония, были охарактеризованы химическим и рентгенофазовым анализом и ИК спектроскопией. Для соединений железа и хрома, изоструктурных известному соединению алюминия, были определены параметры кристаллической ячейки. ИК спектры, данные рентгенофазового анализа и параметры решетки были подобны для всех соединений. Установлено наличие изолированного октаэдра $[M^{III}F_5(H_2O)]^{2-}$, в котором вода координирована с катионом M^{III}. Дегидратация и термическое разложение были исследованы на Q-дериватографе методами ТГ, ДТГ и ДТА, а также высокотемпературным рентгенофазовым анализом. Определены различные температуры и продукты дегидратации, зависящие от природы катиона M^{III}. В случае алюминий и железосодержащих соединений, фторид аммония выделяется в несколько стадий, а в случае хромсодержащих соединений — выделяется непрерывно, приводя во всех случаях к образованию фторидов трехвалентных металлов.