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THERMAL DECOMPOSITION OF HEXAMMINOCOBALT(III) HEXAFLUOROMETALLATES(III)

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ABSTRACT

The compounds of general formula $[Co(NH_3)_6]MF_6$ have been prepared in aqueous solutions of the corresponding fluorides. Thermal decomposition of the complexes has been investigated by simultaneous thermogravimetry and differential thermal analysis. X-ray powder measurements and infrared spectra have been employed to characterize the intermediate and final products. The compounds with M-Al,Ga,V,Cr,Fe give intermediate phases of composition NH_4CoMF_6 with cubic unit cells. The final products are mixtures of CoF_2+MF_3 or CoF_2+MF_2.

INTRODUCTION

The thermal decomposition of numerous transition metal ammine complexes has been studied in recent years (1). $[Co(NH_3)_6]X_3$, where X=Cl,Br,J. decompose through several steps with the reduction of Co(III) to Co(II) to yield CoX_2 (2,3). With X=F the decomposition sequence is $[Co(NH_3)_5F]F_2$, $[Co(NH_3)_4F_2]F$,$[Co(NH_3)_3F_3]$ and finally CoF_2 (4). The dissociation of complexes other than halogenides take place similarly (5). In the presence of oxidizing groups such as NO_3^-, Co_2O_3 has been obtained (2).

The thermal decomposition of fluorometallates has already been studied in our laboratory in order to elucidate the stoichiometry of the reactions as well as to synthesize new inorganic compounds (6-10). In this work we extended our studies from ammonium and hydrazinium to the hexammincobalt(III) fluorometallates.

EXPERIMENTAL

The complexes have been precipitated in aqueous hydrogen fluoride solutions containing $[Co(NH_3)_6]Cl_3$ and metal trifluorides. TG and DTA curves have been obtained simultaneously by means of a Mettler thermoanalyzer with Pt crucibles. Measurements have been carried out in a dynamic atmosphere ($51h^{-1}$) of dry argon at heating rate of 6 $Kmin^{-1}$ and sample masses of 100 mg. Inert alumina has been used as reference material for DTA. Intermediate phases have

been obtained by heating the initial compounds at a heating rate of 6 $Kmin^{-1}$ to the desired temperatures and cooling the samples.

Infrared spectra have been measured using a Model 521 Perkin Elmer grating spectrometer (4000-250 cm^{-1}). Crystallographic powder spectra have been obtained with a Guinier-de Wolff camera using CuKα radiation.

RESULTS AND DISCUSSION

The TG and DTA curves of hexammincobalt(III) hexaflurometallates are given in Figure 1, and the other decomposition data in Table 1. The thermal decomposition of $[Co(NH_3)_6]MF_6$, M=Sc,Mn takes place in one step to give finally CoF_2+ScF_3 and CoF_2+MnF_2 respectively. The reduction of Co(III) to Co(II) and Mn(III) to Mn(II) in the presence of ammonia has already been observed in previous studies (1-5,10). For both cases the intermediate phase is a mixture of the initial complex and residual fluorides. Infrared spectra of intermediates exibit no absorption bands characteristic for ammonium ion. The number of DTA effects (1 for Sc, 2 for Mn) can be correlated to the reduction of Co(III) in Sc compound and to the reduction of Co(III) and Mn(III) in Mn complex.

In the next group there are $[Co(NH_3)_6]MF_6$, M=Al,Ga,V,Cr,Fe, which all decompose in two steps. In the first stage the reduction of Co(III) to CO(II) takes place to yield intermediate composition NH_4CoMF_6. These phases are cubic and isostructural to a series of compounds $M^{I}M^{II}M^{III}F_6$ (11). The cell parameters together with the other data are given in Table 2. There appeared also a characteristic absorption band of ammonium ion at ca. 1420 cm^{-1} (12). The decomposition reaction could be described as:

$$6\,[Co(NH_3)_6]MF_6 \longrightarrow 6NH_4CoMF_6 + N_2 + 28NH_3$$

Further decomposition of NH_4CoMF_6, M=Al,Ga,V,Cr proceeds by giving off NH_4F and leaving a mixture of both trifluorides. The calculated weight loss for the decomposition of $[Co(NH_3)_6]FeF_6$ to $CoF_2 + FeF_2$ agrees very well with the observed one, however those lines in the X-ray powder pattern which do not belong to CoF_2 couldn't be ascribed to known modifications of FeF_2.

The thermal decomposition of $[Co(NH_3)_6]InF_6$ takes place in two stages. X-ray powder pattern of the intermediate phase is different from all patterns observed in this study. The final product is again a mixture of the trifluorides, however the observed mass loss

exceeds considerably the calculated value.

TABLE 1. Thermal decomposition data for $[Co(NH_3)_6]MF_6$

$[Co(NH_3)_6]MF_6$ M	DTA peak temp. (°C)	% mass loss abs.	% mass loss calc.	residual X-ray
Al	297, 425	41.50	40.11	CoF_2+AlF_3
Ga	305, 460, 500	36.87	36.75	CoF_2+GaF_3
In	325, 400	38.87	31.08	CoF_2+InF_3
Sc	363	37.52	37.86	CoF_2+ScF_3
V	265, 400	40.33	40.45	CoF_2+VF_3
Cr	360, 530	37.98	37.05	CoF_2+CrF_3
Mn	305, 365	42.40	42.47	CoF_2+MnF_2
Fe	290, 355, 465	42.15	42.56	CoF_2+FeF_2

TABLE 2. Data for intermediate phases NH_4CoMF_6

$[Co(NH_3)_6]MF_6$ M	% mass loss obs.	% mass loss calc.	a (Å)	$\nu_4(NH_4^+)$ (cm^{-1})
Al	28.71	28.07	10.00	1420
Ga	26.24	26.32	10.23	1420
V	28.50	29.68	10.34	1420
Cr	26.65	25.72	10.23	1415
Fe	26.15	25.42	10.32	1420

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FIG 1 TG AND DTA CURVES OF $[Co(NH_3)_6]MF_6$