Thermochimica Acta, 97 (1986) 215–218
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF HEXAMMINCOBALT(III) NEODYMIUM SULFATE TRIHYDRATE

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(Received 24 June 1985)

ABSTRACT

The thermal decomposition of $[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O$ has been studied by simultaneous TG and DSC, isothermal weight change determination, magnetic susceptibility measurements and X-ray powder diffractometry. In the first part of the decomposition, which is completed at about 500°C, dehydration and deammination, together with the reduction $Co(III) \rightarrow Co(II)$ take place. The intermediate phase consisting of β-$CoSO_4$ and $Nd_2(SO_4)_3$ is stable up to ~ 750°C. In air the mixture of both sulfates decomposes further to give first Co_3O_4 and then $Nd_2O_2SO_4$. In an inert atmosphere CoO is the final product instead of Co_3O_4.

INTRODUCTION

The thermal decomposition of hexammincobalt(III) compounds has been thoroughly studied by Wendlandt et al. [1–5]. A stepwise departure of ammonia together with the reduction of Co(III) to Co(II) are general characteristics of the thermal decomposition of these materials. For hydrated complexes the dehydration began below 100°C and progressed by replacing the departing H_2O molecules by anions [5]. The resulting TG curves showed badly resolved stages due to overlapping reactions. Recently, the synthesis together with the thermal dehydration of $[Co(NH_3)_6]La(SO_4)_3 \cdot H_2O$ have been reported [6]. In this work we studied the thermal decomposition of $[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O$.

EXPERIMENTAL

The compound $[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O$ was prepared from aqueous solutions of the corresponding sulfates as described elsewhere [7]. TG and DSC curves were recorded using a Mettler thermoanalyser (TA 2000C). Experimental conditions: TG–DSC sample holder, flat platinum crucibles 7

0040-6031/86/$03.50

mm in diameter; sample masses, 20 mg; heating rates, 2 K min^{-1}; reference material for DSC, inert alumina; atmosphere, dry air and argon at a 30 ml min^{-1} flow rate.

Powder spectra were obtained with Guinier-de Wolff camera using Cu$K\alpha$ radiation.

For magnetic measurements, the Faraday method was used. Experiments were performed at 22°C on a modified Newport Instruments apparatus, calibrated by $Hg[Co(CNS)_4]$. The samples for magnetic measurements were prepared by heating the initial substance up to the desired temperatures and cooling intermediate phases. The susceptibility of each phase was measured at six different magnetic fields.

RESULTS AND DISCUSSION

The thermal decomposition of $[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O$ (Fig. 1) begins at ~ 90°C and proceeds in two stages. The first step up to ~ 510°C is complicated and consists of a number of reactions which overlap. The dehydration has two endothermal DSC peaks at 108 and 133°C overlap with the next stage, where the decomposition of the hexammincobalt(III) ion takes place. The main endothermal DSC effect appears at 280°C. Additionally, there is a number of smaller peaks at 220, 260, 311, 327, 359 and 490°C. All attempts to isolate the anhydrous compound isothermally failed.

Wendlandt and Smith [2] found that the reduction of cobalt in $[Co(NH_3)_6]_2(SO_4)_3$ began at ~ 166°C and finished at 345°C. We have

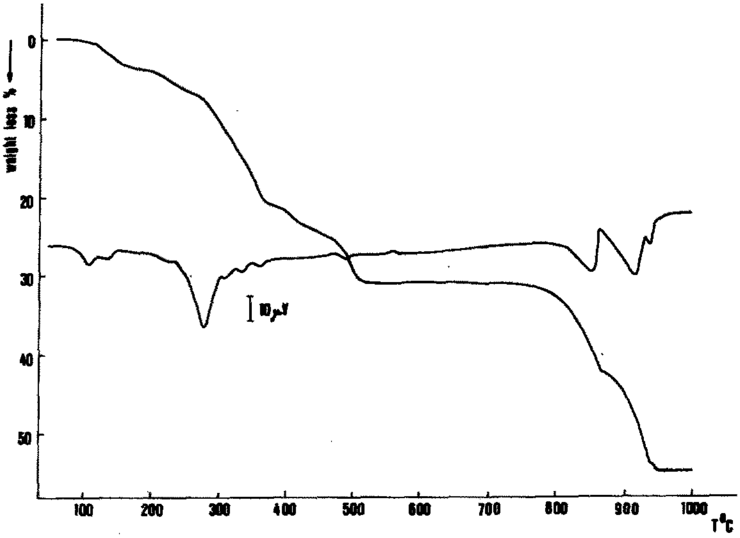

Fig. 1. TG and DSC curves of $[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O$ recorded in air.

TABLE 1

Magnetic susceptibilities of intermediate phases with standard deviations in parentheses

T (°C)	200	250	280	350
χ (emu g^{-1})	6.93 (5)	13.67 (10)	29.56 (56)	33.02 (39)

followed the reduction of cobalt by measuring the magnetic susceptibility at room temperature of samples isolated at 200, 250, 280 and 350°C. The magnetic susceptibilities per gram are given in Table 1. The sample isolated at 200°C is paramagnetic due to Nd(III), the strong increase in magnetic susceptibility up to 350°C accounts for the reduction of diamagnetic Co(III) to paramagnetic Co(II). The temperature range of the reduction is the same as that of other hexammincobalt(III) complexes [2]. The samples isolated at 200, 250, 280 and 350°C are amorphous, however, in the powder spectra of the sample isolated at 350°C, the first very diffuse lines of β-$CoSO_4$ occur [8].

The first step of the thermal decomposition is completed at ~ 510°C. The intermediate phase is stable up to 750°C. The X-ray powder pattern of the intermediate phase obtained at 630°C contains the lines of β-$CoSO_4$ and $Nd_2(SO_4)_3$ [8,9]. The observed mass loss of 31.10% agrees very well with the calculated one (31.54%) for the first step of the decomposition

$$6[Co(NH_3)_6]Nd(SO_4)_3 \cdot 3H_2O \rightarrow 6CoSO_4 + 3Nd_2(SO_4)_3 + N_2 + 34NH_3$$
$$+ 3SO_2 + 3/2O_2 + 21H_2O$$

This equation is tentative as we did not analyse the gaseous decomposition products.

At ~ 750°C, the thermal decomposition of the mixture $2CoSO_4 + Nd_2(SO_4)_3$ proceeds to give, finally, Co_3O_4 and $Nd_2O_2SO_4$ as proved by X-ray powder photography [8,10]. The observed and calculated mass losses of 55.57 and 55.44%, respectively, agree with the X-ray data. There are two relatively well-defined steps on the TG and DSC curves with a smaller additional effect at the very end (DSC peaks at 856, 920 and 939°C). An intermediate phase obtained on heating the initial compound up to 865°C shows the lines of Co_3O_4 and $Nd_2(SO_4)_3$ in its X-ray powder spectrum. Obviously, $CoSO_4$ decomposes before $Nd_2(SO_4)_3$. It has already been shown that the thermal decomposition of $CoSO_4$ in an inert atmosphere gives CoO. In air, however, CoO instantaneously oxidizes to Co_3O_4 [11]. By carrying out the decomposition in argon we also found CoO and $Nd_2O_2SO_4$ as final products. It has already been mentioned [11] that it is impossible to detect the oxidation of CoO to Co_3O_4 from the TG curves, as the mass losses in oxidizing and inert atmosphere are too close. In our case the corresponding calculated weight changes are 55.44 and 56.27%, respectively.

ACKNOWLEDGEMENTS

We wish to thank Dr. Drago Lutar from the Institute Jozef Stefan for magnetic measurements. The financial support of the Research Community of Slovenia is gratefully acknowledged.

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