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SYNTHESIS AND THERMAL DECOMPOSITION OF HYDRAZINIUM (1 +) NEODYMIUM SULFATE MONOHYDRATE

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ABSTRACT

The thermal decomposition of $N_2H_5Nd(SO_4)_2 \cdot H_2O$ has been studied by simultaneous TG and DSC and by isothermal weight change determination. The final product and the intermediate phases have been identified by chemical analysis, X-ray powder patterns and infrared spectroscopy. The solid phases in the decomposition sequence are: $N_2H_5Nd(SO_4)_2 \cdot H_2O \rightarrow N_2H_5Nd(SO_4)_2 \rightarrow NH_4Nd(SO_4)_2 \rightarrow Nd_2(SO_4)_3$. The reactions overlap under dynamic conditions, isothermally, however, $NH_4Nd(SO_4)_2$ can be obtained by 200°C.

INTRODUCTION

Studies on double sulfates with hydrazinium and metal cations are rare. The compounds of general formula $(N_2H_5)_2M(SO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) have been prepared from aqueous solutions of the corresponding sulfates and studied by several spectroscopic techniques [1]. Patil et al. [2] prepared double sulfates of composition $(N_2H_5)_2M(SO_4)_2 \cdot 3N_2H_4$ (M = Fe, Co, Ni) and $N_2H_5Al(SO_4)_2 \cdot 6N_2H_4$ by the reaction between metal ammonium sulfates and hydrazine hydrate. To the author's knowledge there are no studies on the thermal properties of these materials. The simple salts $N_2H_6SO_4$, $(N_2H_5)_2SO_4$ and $N_2H_5HSO_4$ decompose by disproportionation to give N_2, $(NH_4)_2SO_4$ and/or NH_4HSO_4, NH_3, H_2S, SO_2 and, in the case of $N_2H_6SO_4$, also S [3].

In this work, which is the continuation of a study on rare earth sulfates [4,5], the preparation and thermal decomposition of $N_2H_5Nd(SO_4)_2 \cdot H_2O$ is reported.

EXPERIMENTAL

The compound $N_2H_5Nd(SO_4)_2 \cdot H_2O$ was prepared by isothermal evaporation (95°C) of an aqueous solution containing neodymium sulfate

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and hydrazinium sulfate in the molar ratio 1:3. Found: N_2H_5, 8.50; Nd, 37.35; SO_4, 50.99; H_2O, 4.35%. Calc. for $N_2H_5Nd(SO_4)_2 \cdot H_2O$: N_2H_5, 8.53; Nd, 37.23; SO_4, 49.59; H_2O, 4.65%. The composition was also proved by single crystal structure analysis [6].

The simultaneous TG and DSC measurements were performed by means of a Mettler thermoanalyser (TA 2000C). Experimental conditions: TG–DSC sample holder, flat platinum crucibles, 7 mm in diameter; sample masses, 20 mg; heating rate, 2 K min^{-1}; inert alumina as reference material for DSC; atmosphere of dry air with 30 ml min^{-1} flow rate.

Intermediate phases were obtained isothermally in the thermoanalyser at 220, 230 and 240°C, as well as by heating the initial compound for two months at 200°C in a dynamic atmosphere in a tube furnace.

Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer (4000–250 cm^{-1}) as Nujol and fluorolube mulls. Crystallographic powder spectra were obtained with a Guinier-de Wolff camera using Cu$K\alpha$ radiation.

RESULTS

The thermal decomposition of $N_2H_5Nd(SO_4)_2 \cdot H_2O$ (Fig. 1) begins at about 200°C and proceeds in three stages which overlap. The first step is the dehydration with an endothermal DSC peak at 285°C. The inflection point by 4.6% mass loss theoretically corresponds to one molecule of water. However, it was impossible to isolate the anhydrous compound as it was too unstable.

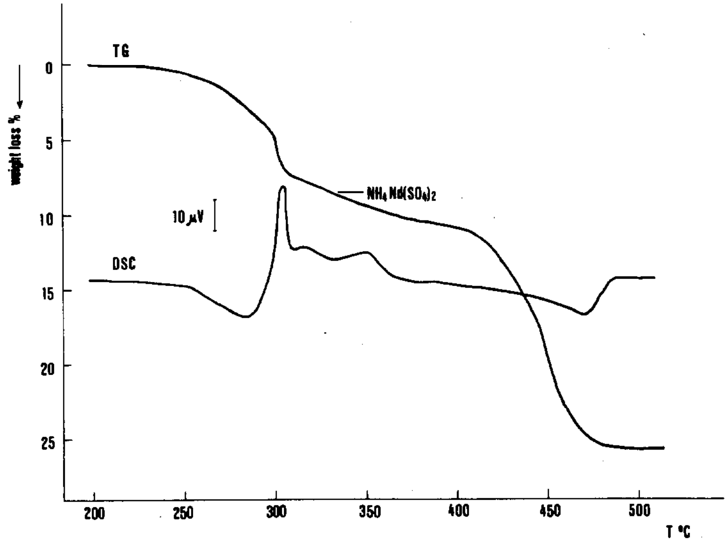

Fig. 1. TG and DSC curves of $N_2H_5Nd(SO_4)_2 \cdot H_2O$.

In the next step the hydrazinium cation disproportionates to give ammonia and nitrogen. This reaction has already been observed by the decomposition of similar compounds [3,7]. Under the dynamic experimental conditions used in this study, the disproportionation takes place between 280 and 350°C. There is an inflection on the TG curve at about 8.5% mass loss, which is in good agreement with the theoretical value of 8.52%.

The intermediate compound $NH_4Nd(SO_4)_2$ decomposes in the temperature range 350–480°C to give finally $Nd_2(SO_4)_3$. The experimental mass loss of 25.5% agrees well with the calculated value (25.57%).

The decomposition reactions could therefore be described as

$$N_2H_5Nd(SO_4)_2 \cdot H_2O = N_2H_5Nd(SO_4)_2 + H_2O \tag{1}$$

$$3N_2H_5Nd(SO_4)_2 = 3NH_4Nd(SO_4)_2 + NH_3 + N_2 \tag{2}$$

$$2NH_4Nd(SO_4)_2 = Nd_2(SO_4)_3 + 2NH_3 + SO_3 + H_2O \tag{3}$$

Isothermal measurements have also been used to elucidate the course of the decomposition and to find out whether the intermediate phases could be isolated.

Isothermal runs at 220, 230 and 240°C, made up to mass losses of 9.4% (calc. for $NH_4Nd(SO_4)_2$, 8.5%), show no plateaux at these temperatures. Chemical analysis of the samples gave 2.2–3.0% $N_2H_5^+$ and infrared spectra exhibit a strong deformation band of NH_4^+ at 1415 cm^{-1}, beside weak bands of $N_2H_5^+$. The ammonium compound therefore decomposed further before the disproportionation of hydrazinium was complete.

The next isothermal measurement was carried out at 230°C up to a mass loss of 5.67%. Assuming only reactions (1) and (2) with a weight change of 5.67%, the calculated amount of $N_2H_5^+$ in the sample should be 6.49%. Chemical analysis revealed 6.66% $N_2H_5^+$ proving that reaction (3) has not yet begun.

The final isothermal run was made at 200°C until the mass of the sample remained constant. After two months a mass loss of 8.7% had been achieved as compared to the calculated value of 8.52% for reaction (2). Chemical analysis showed 4.97% NH_4^+ and 0.00% $N_2H_5^+$; calc. for $NH_4Nd(SO_4)_2$: 5.07% NH_4^+.

X-ray powder patterns of all the intermediate phases are similar but very diffuse. The best pattern has been obtained for the phase heated for two months.

Infrared absorption frequencies of $N_2H_5Nd(SO_4)_2 \cdot H_2O$ and the intermediate phase $NH_4Nd(SO_4)_2$ obtained by isothermal weight change at 200°C are listed in Table 1. The assignments of the bands have been made on the basis of earlier work [3,8–10]. The most obvious distinguishing features between the two compounds are the deformation modes of NH_4^+ at 1415 cm^{-1} and of $N_2H_5^+$ between 1650 and 1265 cm^{-1}.

TABLE 1

IR spectra of initial and intermediate compounds (cm^{-1})[a]

$N_2H_5Nd(SO_4)_2 \cdot H_2O$	Assignment[b]	$NH_4Nd(SO_4)_2$	Assignment
3375 s, br	$\nu(H_2O)$	3260 vs	$\nu_3 NH_4$
3270 s	$\nu(NH_2)_2$	3065 s	$\nu_2 + \nu_4 NH_4$
3160 m, br			
3110 m, br	$\nu(NH_3^+)_s$	2865 m, sh	$2\nu_4 NH_4$
2995 m, br			
		1415 vs	$\nu_4 NH_4$
1650 w-m	$(NH_2)_d$		
		1170 vs, sh	
		1115 vs	$\nu_3 SO_4$
1610 w-m		1040 s	
1585 m	$(NH_3^+)_d$		
1540 m			
		985 m	$\nu_1 SO_4$
		970 m	
1395 w	$(NH_2)_d$		
1265 w			
		640 s	
		625 s	$\nu_4 SO_4$
1180 sh		600 s	
1150 vs			
1120 sh	$\nu_3 SO_4$		
1100 vs			
1085 vs			
1060 sh			
1032 vs			
1012 w-m	$(N–N)_s$		
995 w-m	$\nu_1 SO_4$		
670 m, br			
650 m			
635 w	$\nu_4 SO_4$		
620 w-m			
595 s			

[a] s = strong, m = medium, w-m = weak to medium, w = weak, sh = shoulder, b = broad and v = very.

[b] d = deformation, s = stretching.

CONCLUSION

There are at least three reactions characteristic of the thermal decomposition of $N_2H_5Nd(SO_4)_2 \cdot H_2O$. Two of them, the dehydration and the disproportionation of $N_2H_5^+$, begin at about 200°C and the third one, the decomposition of ammonium sulfate, part of the intermediate double sulfate, begins at approximately 220°C. Due to competition between these processes, the overall decomposition reaction heavily depends upon the experimental conditions. As the reactions proceeded in the narrow temperature range only one intermediate phase could be isolated.

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