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DIFFERENCES IN THE THERMAL DECOMPOSITION OF DOUBLE  
SULPHATES OF RARE EARTHS WITH METHYLAMMONIUM  
IONS IN AIR OR ARGON

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The thermal decomposition of some double sulphates of rare earths with  $\text{CH}_3\text{NH}_3^+$ ,  $(\text{CH}_3)_2\text{NH}_2^+$ ,  $(\text{CH}_3)_3\text{NH}^+$  and  $(\text{CH}_3)_4\text{N}^+$  ions from 20 to 700°C in atmospheres of air and argon was studied by methods of TG, DTG and DTA. The weight losses are greater in an atmosphere of argon than in air. This is probably due to further decomposition of rare earth sulphates because of the presence of carbon.

Double sulphates of rare earths with classical monovalent ions have been much cited in the literature. We have extended such studies to non-classical ions such as monomethylammonium, trimethylammonium and tetramethylammonium cations /1/. Although our primary interest was crystal structure determination, all the compounds were characterized by thermoanalytical methods. The crystal structure of the isostructural

series  $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Ln = Tb - Ln and Y) /2/, together with thermoanalytical results have already been published /3/. In the above compounds some differences in thermal behaviour in atmospheres of air and argon were observed. In the present paper we report and discuss these differences in the temperature range from 25 to 700°C for some double sulphates of rare earths containing the above monovalent, non-classical cations.

$\text{Ln}_2(\text{SO}_4)_3$  are stable in the temperature range 25 - 700°C. Bukovec et al. /4/ reported that thermal decomposition of  $\text{Ln}_2(\text{SO}_4)_3$  (La - Lu and Y) in atmosphere of air begins above 932°C under dynamic conditions. Nathans and Wendlant /5/ concluded that thermal decomposition of  $\text{Ln}_2(\text{SO}_4)_3$  following the equation  $\text{Ln}_2(\text{SO}_4)_3 \longrightarrow \text{Ln}_2\text{O}_2\text{SO}_4 + 2\text{SO}_2 + \text{O}_2$  is noticeable from 855-946°C (where Ln is a rare earth). Erämetsä and Niinisto /6/ reported that thermal decomposition of  $\text{Sm}_2(\text{SO}_4)_3$  takes place at temperatures higher than 850°C.

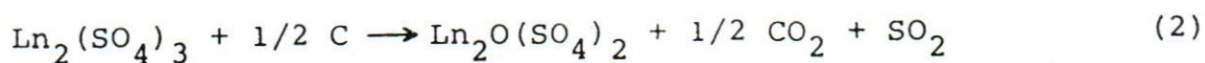
## EXPERIMENTAL

The methods of preparation of double rare earth sulphates with the above cations are essentially the same as described earlier /3/. Thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermal analysis (DTA) data were obtained simultaneously by means of a Mettler thermoanalyser with Pt/Pt-Rh thermocouples and Pt crucibles (TD1). Measurements were carried out in a dynamic atmosphere ( $5 \text{ l h}^{-1}$ ) of dry air and argon at a heating rate of  $4^\circ\text{C min}^{-1}$  and with sample masses of 100 mg. Inert alumina was used as reference material for DTA.

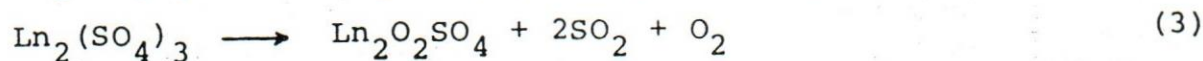


## RESULTS AND DISCUSSION

TG, DTG and DTA curves are shown in Fig. 1-10. Experimental weight losses in a atmospheres of air or argon are given in Table 1. Calculated weight losses for different tentative end products of decomposition are given in Table 2. As can be seen from Table 1, the weight losses for all compounds are greater in argon than in air. Figures 1-10 show there are no differences in the dehydration of double sulphates for either atmosphere under the same conditions in the first stage of thermal decomposition. But decomposition of anhydrous double sulphates proceeds in a different way. The DTA peaks of these compounds (in the second stage of thermal decomposition) show exothermic effects in air (Fig. 1, 3, 5, 7, 9), but in an atmosphere of argon there are no exothermic effects. That means that in the second stage of thermal decomposition in an atmosphere of air, oxidation of methylammonium ions takes place. In an atmosphere of argon a third stage of thermal decomposition appears. It is quite possible that above 550°C in an atmosphere of argon released carbon causes the reaction:



It is also possible that the release of oxygen by the reactions:



is greater in argon than in air.

It can be seen from Table 1 that thermal decomposition of  $\text{Pr}_2(\text{SO}_4)_3$  in argon in the case of  $[(\text{CH}_3)_3\text{NH}]_3\text{Pr}(\text{SO}_4)_3 \cdot 4.5\text{H}_2\text{O}$  takes place according to equation 2. But in the case of  $(\text{CH}_3)_4\text{NNd}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  the thermal decomposition of  $\text{Nd}_2(\text{SO}_4)_3$

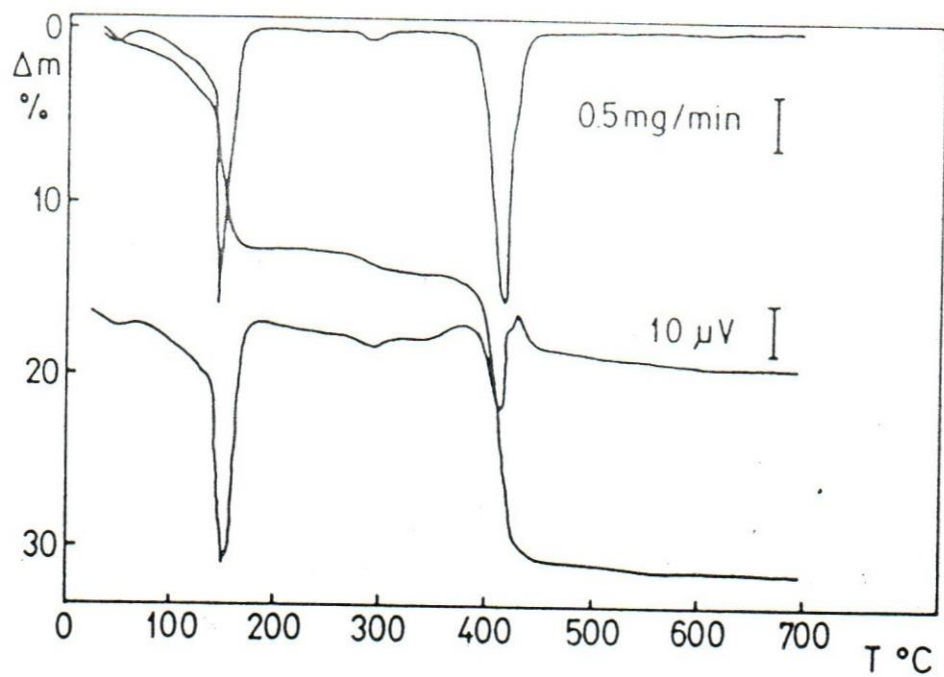


Figure 1. TG, DTG and DTA Curves  
of  $\text{CH}_3\text{NH}_3\text{Er}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Air

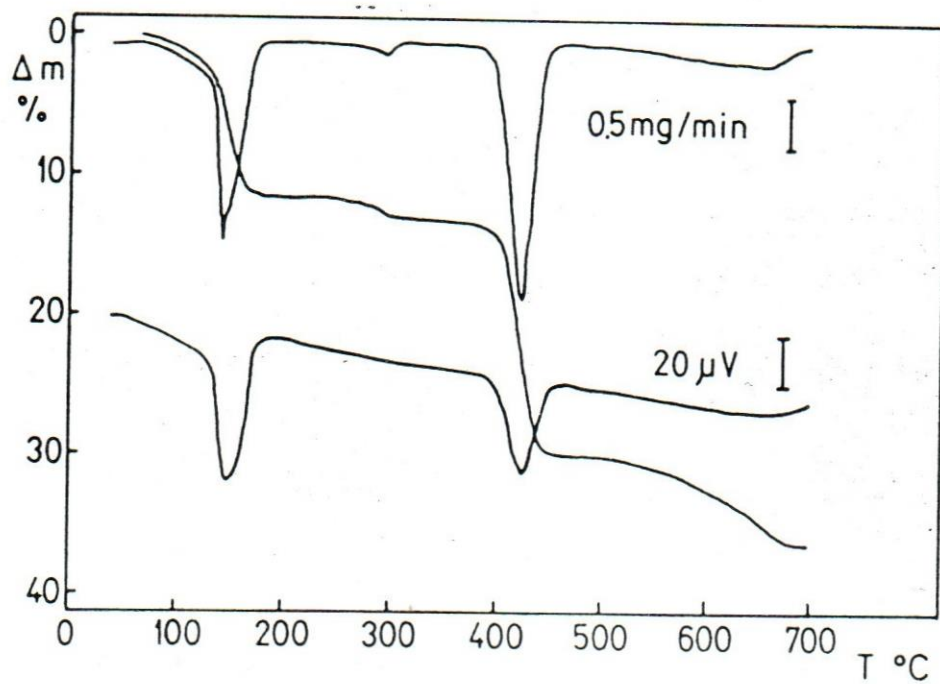


Figure 2. TG, DTG and DTA Curves  
of  $\text{CH}_3\text{NH}_3\text{Er}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Argon

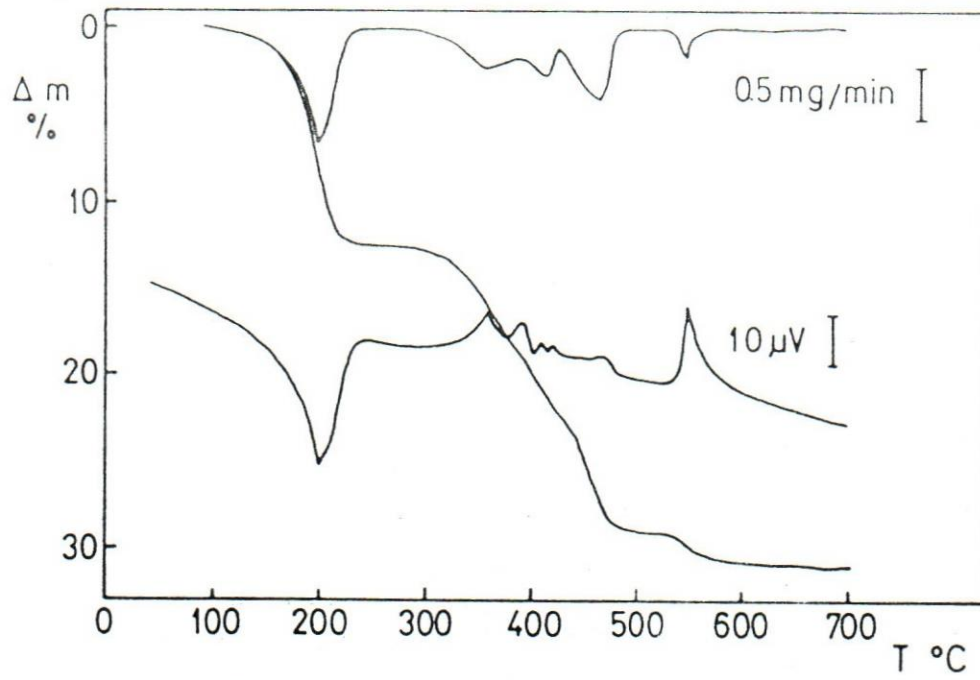


Figure 3. TG, DTG and DTA Curves  
of  $\text{CH}_3\text{NH}_3\text{Sm}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Air

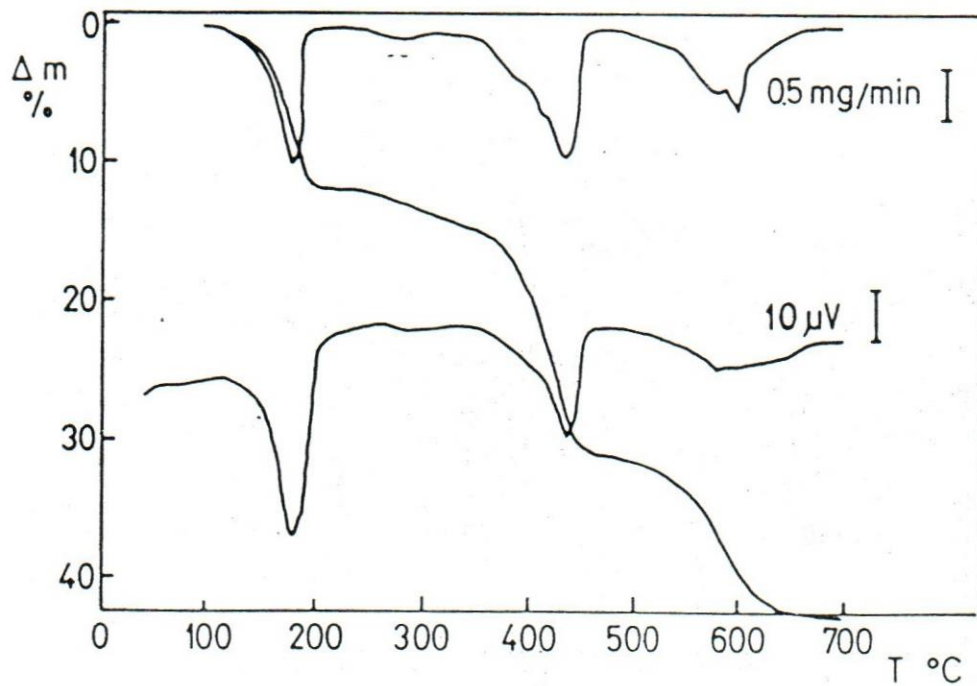


Figure 4. TG, DTG and DTA Curves  
of  $\text{CH}_3\text{NH}_3\text{Sm}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Argon

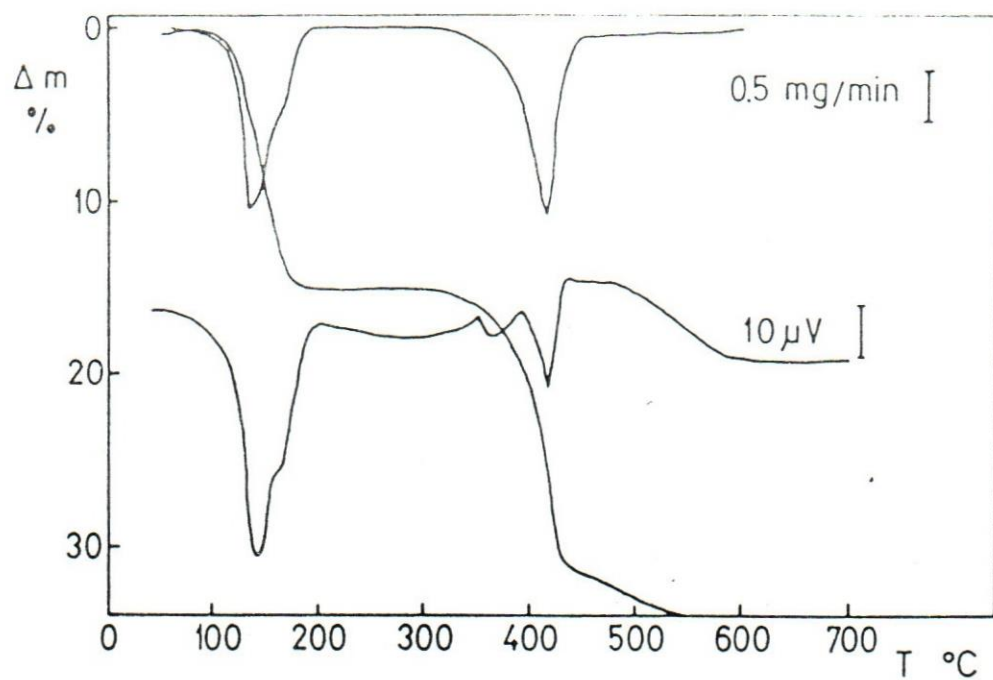


Figure 5. TG, DTG and DTA Curves  
of  $(\text{CH}_3)_2\text{NH}_2\text{Er}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in Air

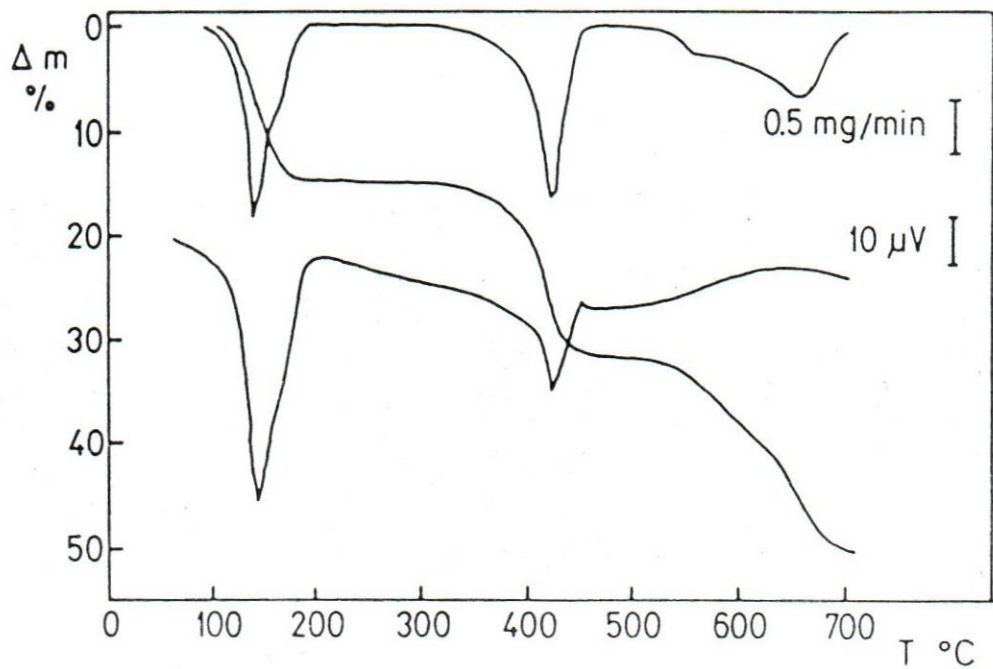


Figure 6. TG, DTG and DTA Curves  
of  $(\text{CH}_3)_2\text{NH}_2\text{Er}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in Argon



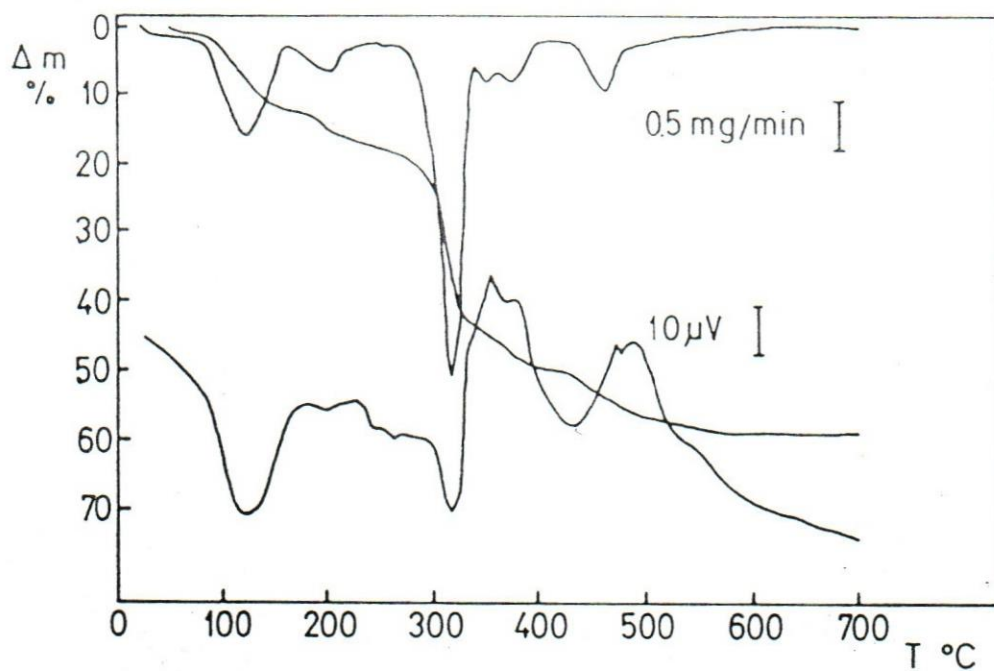


Figure 7. TG, DTG and DTA Curves  
of  $[(\text{CH}_3)_3\text{NH}]_3\text{Pr}(\text{SO}_4)_3 \cdot 4,5 \text{H}_2\text{O}$  in Air

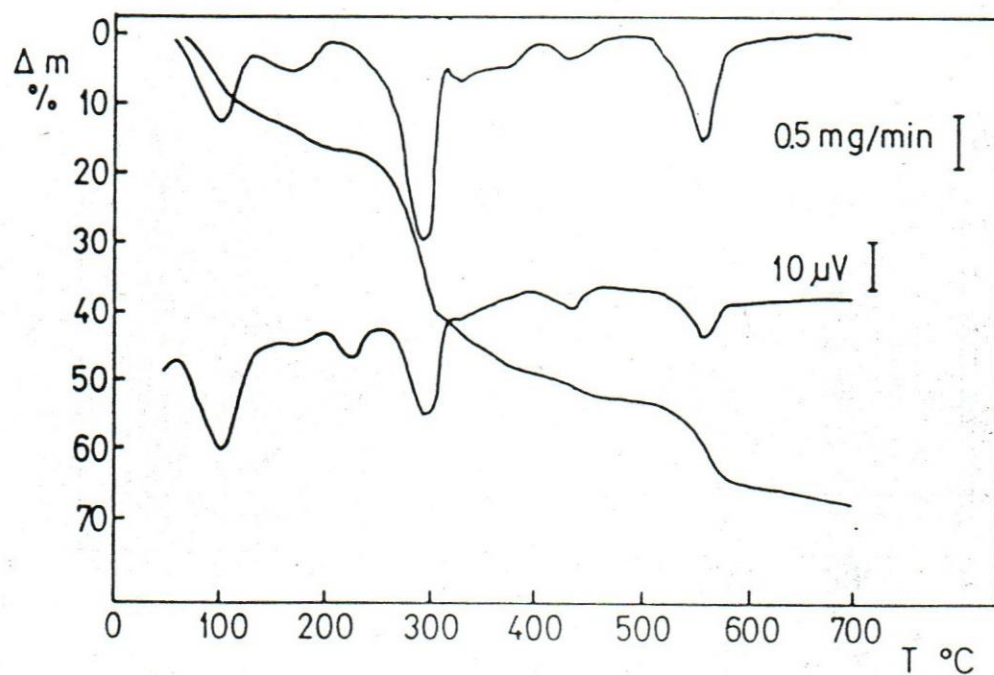


Figure 8. TG, DTG and DTA Curves  
of  $[(\text{CH}_3)_3\text{NH}]_3\text{Pr}(\text{SO}_4)_3 \cdot 4,5 \text{H}_2\text{O}$  in Argon

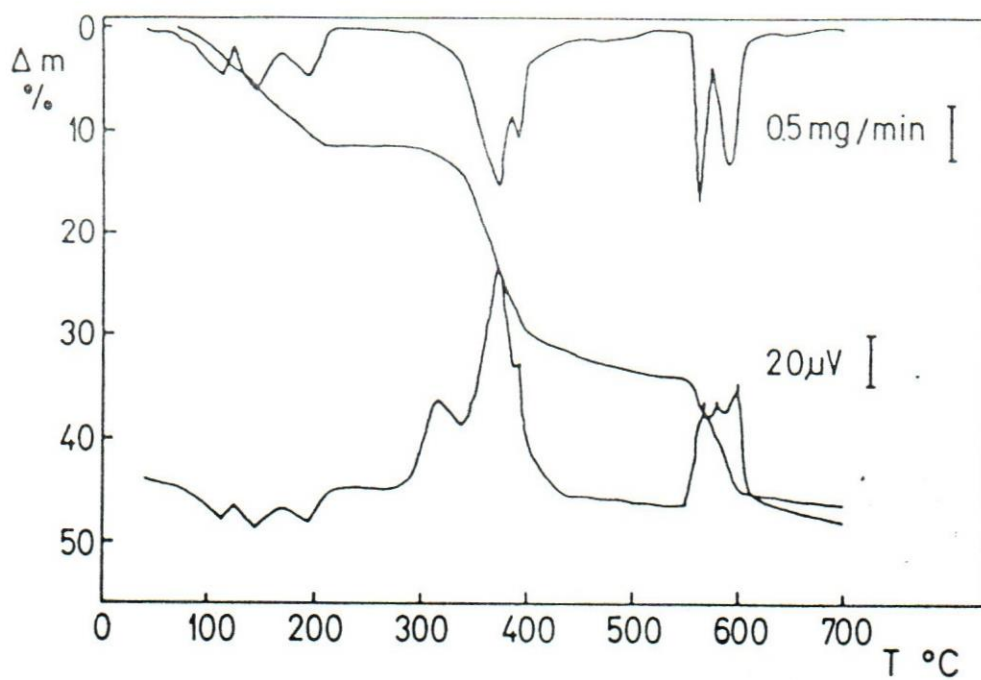


Figure 9. TG, DTG and DTA Curves  
of  $(\text{CH}_3)_4\text{NND}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Air

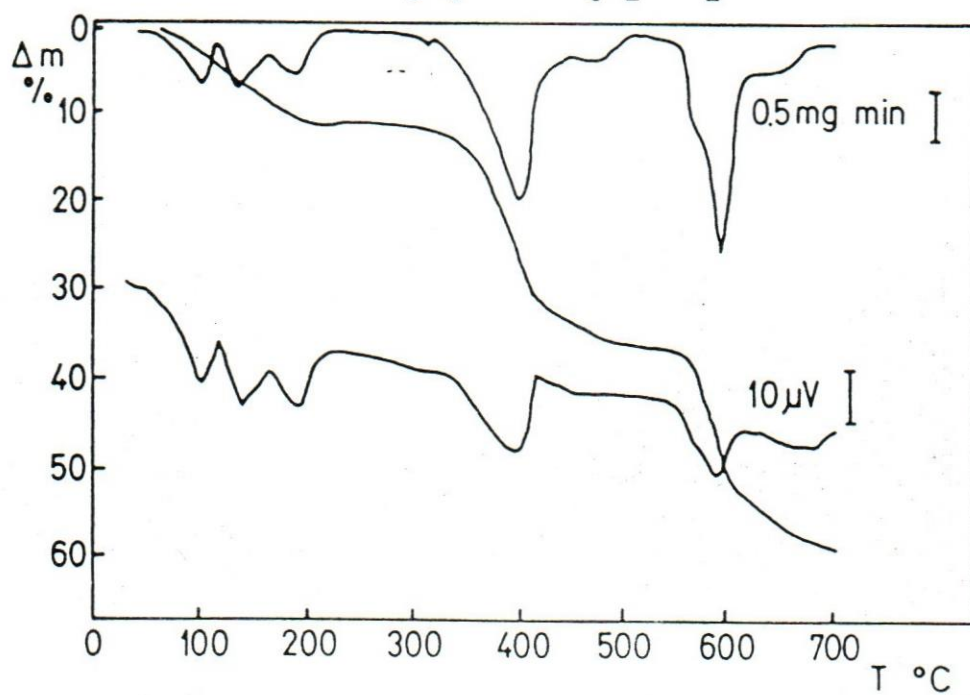


Figure 10. TG, DTG and DTA Curves  
of  $(\text{CH}_3)_4\text{NND}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in Argon



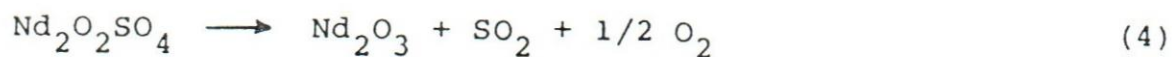
Table 1. Experimental weight losses obtained from TG curves

Compound/formula mass/	in air %	in argon %
1. $\text{CH}_3\text{NH}_3\text{Er}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (445.49)	31.18	36.58
2. $\text{CH}_3\text{NH}_3\text{Sm}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (428.63)	30.93	42.80
3. $(\text{CH}_3)_2\text{NH}_2\text{Er}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (477.53)	34.53	50.59
4. $[(\text{CH}_3)_3\text{NH}]_3\text{Pr}(\text{SO}_4)_3 \cdot 4.5\text{H}_2\text{O}$ (690.51)	58.48	68.80
5. $(\text{CH}_3)_4\text{N}\text{Nd}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (472.28)	49.76	59.04

Table 2. The theoretical values for weight losses if the residue is

$\text{Ln}_2(\text{SO}_4)_2$	$\text{Ln}_2\text{O}(\text{SO}_4)_2$	in %	$\text{Ln}_2\text{O}_2\text{SO}_4$	$\text{Ln}_2\text{O}_3$
1. 30.11	38.70			
2. 31.30	40.66			
3. 34.48	43.20		51.58	59.05
4. 58.73	69.55			
5. 37.94	47.44		55.91	64.38

in air goes to  $\text{Nd}_2\text{O}(\text{SO}_4)_2$  /Eq. 2/. Perhaps also another reduction process occurs. In an atmosphere of argon decomposition proceeds to  $\text{Nd}_2\text{O}_2\text{SO}_4$  /Eq. 3/, and partially to  $\text{Nd}_2\text{O}_3$  following equation 4:



Thus in Fig.10 in the 3rd stage, two steps of thermal decomposition can be seen, but in the case of  $(\text{CH}_3)_2\text{NH}_2\text{Er}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , the decomposition of  $\text{Er}_2(\text{SO}_4)_3$  in the 3rd stage takes place according to equation 3.

#### ACKNOWLEDGEMENT

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#### LITERATURE

- /1/ V.Jordanovska, Ph.D.Thesis, Ljubljana, 1981
- /2/ A.Arhar, L.Golič, V.Jordanovska and J.Šiftar, Vestn. Slov.Kem.Drus., 28, 311 (1981).
- /3/ V.Jordanovska, J.Šiftar, J.Therm.Anal., 31, 1049 (1986).
- /4/ N.Bukovec, P.Bukovec, J.Šiftar, Vestn.Slov.Kem.Drus., 22, 5 (1975).
- /5/ M.W.Nathans, W.W.Wendlandt, J.Inorg.Nucl.Chem., 24, 869 (1962).
- /6/ O.Krämetza and L.Niinisto, Suomen Kemistilehti B, 207 (1971).

## POVZETEK

Raziskovan je bil termični razkroj nekaterih dvojnih sulfatov redkih zemelj s  $\text{CH}_3\text{NH}_3^+$ ,  $(\text{CH}_3)_2\text{NH}_2^+$ ,  $(\text{CH}_3)_3\text{NH}^+$  in  $(\text{CH}_3)_4\text{N}^+$  od 20 do  $700^\circ\text{C}$  v zraku in argonu s termoanaliznimi metodami (TG, DTG in DTA). Zguba mase brezvodnih sulfatov redkih zemelj je večja v argonu kot v atmosferi zraka in jo je verjetno pripisati predvsem redukciji z ogljikom, ker so ostali pogoji isti.

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