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THERMAL DECOMPOSITION OF DOUBLE SULFATES OF Pr(III) AND Nd(III) WITH BENZYLAMMONIUM CATION

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Abstract

The double sulfates of Pr(III) and Nd(III) with benzylammonium were obtained as crystalline products by evaporation of aqueous mixture of rare earth(III) sulfate and benzylammonium sulfate in molar ratio 1:6. The isolated product was investigated by means of elemental analysis and TG, DTG and DTA from room temperature up to 1000 ^{o}C. It was established that they have identical empirical formula:
$Ln_2(C_6H_5CH_2NH_3)_4(SO_4)_5 \cdot 4H_2O$
The double sulfates of Ln(III) with above stoichiometry are known with other monovalent cations. The dehydration of above complexes takes place on a same way and it suggests that the water molecules are bonded on an identical manner in both compounds.

Introduction

For the double sulfates of rare earths(III) with monovalent cations with an empirical formula **$MTr(SO)_4 \cdot xH_2O$** there is plenty of data [1], but few data concerning double sulfates of Ln(III) and M(I) with other stoichiometry. There are investigations about synthesis and crystal structure of anhydrous double sulfates of potassium with rare earths as: **$K_3Ln(SO_4)_3$**, **$K_7Ln_3(SO_4)_8$**, **$K_4Ln_2(SO_4)_5$**, **$K_6Ln_4(SO_4)_9$**, **$K_5Ln(SO_4)_4$**, and **$K_8Ln_2(SO_4)_7$**; of ammonium : **$(NH_4)_3Ln(SO_4)_3$** and **$(NH_4)_5La(SO_4)_4$**; rubidium: **$Rb_3Ln(SO_4)_3$**, **$Rb_4Ln_2(SO_4)_5$** and **$Rb_3Ln_3(SO_4)_7$**; cesium: **$Cs_3Ln(SO_4)_3$**. The above compounds are obtained by: isothermal evaporation of aqueous solutions, dehydration of crystalohydrates, solid-solid hydrothermal reaction, or synthesis in the presence of sulfuric acid [2]. There are also data about the dehydration of double sulfates crystalohydrates with general formula **$K_6Ln_4(SO_4)_9 \cdot 8H_2O$** [2]. Recently, results of the synthesis and thermal decomposition of double sulfates of some rare earths with dimethylamonium-, with a general formula **$[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$** [3], as well as with trimethylammonium monovalent cation with a general formula **$[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$** have been reported [4]. It was found that these compounds have been obtained only in a high molar ratio. Also the double sulfates of Pr and Ce with tetramethyl ammonium cation with an empirical formula **$[(CH_3)_4N]_4Ln_2(SO_4)_5 \cdot 10H_2O$** are synthesized and identified with the methods of thermal decomposition, **X**-ray powder diffraction patterns and elemental analysis [5]. Double sulfates crystalohydrates with a general formula **$HOCH_2CH_2NH_3M(SO_4)_2.xH_2O$** of Al(III) and Fe(III) with ethanolammonium have been synthesized and characterized with **X**-ray powder diffraction patterns, TG and DTA analysis [6].Continuing our work on double sulfates of M(III) with different nonclassical monovalent cations, in this paper we present the results of synthesis, identification and thermal behavior of double sulfates of

Pr(III) and Nd(III) with Benzylammonium monovalent cation, as a part of our investigations of double sulfates of lanthanides and ytrium with above monovalent cation for which we have found no data in the literature.
These investigations were performed to confirm the possibility of synthesis of double sulfates of Ln(III) with large monovalent cations.

Material and Methods

Benzylamine (purum, Merck); $Ln_2(SO_4)_3 \cdot 8H_2O$; sulfuric acid (p.a. Merck)
Double sulfates of Ln (Pr and Nd) are obtained by evaporation at ambient temperature of a concentrated aqueous solution of lanthanide(III) sulfate and benzylammonium sulfate in a molar ratio 1:6. The products were characterized by elemental analysis.
Benzylammonium sulfate solution was obtained by neutralization of Benzylamine with 1:1 sulfuric acid with permanent external cooling in ice-water bath up to pH 3-4.
TG, DTR and DTA were performed on a Cahn Q Derivatograph(MOM, Hungary) in static air atmosphere at a heating rate of 10 K/min, on samples of about 100 mg, in Pt crucibles. The reference substance was pure alumina.
Elemental analyses of carbon and hydrogen were carried out on a Coleman Model 33 instrument by Liebig's method and nitrogen was determined by the Dumas method.

Results and Discussion

The obtained crystal products are with some lighter color than the starting lanthanide sulfates of Pr and Nd e.g. light green or light violet. From the results of elemental analysis and from the mass losses (TG curves), the following general formula is proposed:
$\mathbf{(C6H_5CH_2NH_3)_4Ln_2(SO_4)_5 \cdot 4H_2O}$ (Ln = Pr or Nd)
The main point of our investigation was the thermal decomposition of investigated compounds in static air atmosphere. The thermal decomposition up to 1000 ^oC takes place with clearly differentiated four steps (Fig-s 1 and 2). This fact help us to determine the empirical formula of the investigated complexes with greater accuracy. Generally, in the first step (up to about 150 and 170 oC for Nd- and Pr- compound) dehydration of the compounds occurs, in the second, third and fourth steps decomposition of anhydrous sulfates up to $Nd_2O_2SO_4$ and $Pr_2O(SO_4)_2$ takes place. TG, DTG and DTA curves of both complexes are alike and point at a simillar crystal structure (the investigations are in progress).
The thermal decomposition of the investigated compounds could be expressed in the equatations, where R= $C_6H_5CH_2$:

1. Stage, from room temperature up to 170 ^oC (Pr) and 150 ^oC (Nd)
   $Ln_2(RNH_3)_4(SO_4)_5.4H_2O \rightarrow Ln_2(RNH_3)_4(SO_4)_5 + 4H_2O(g)$
   Mass losses in % : Pr/5.6% (5.69%); Nd/5.5% (5.66%)
2. Stage, for Pr-compound, 170-310 ^oC
   $Pr_2(RNH_3)_4(SO_4)_5 \rightarrow Pr_2(SO_4)_3.2SO_3 + 4RNH_2(g) + 2H_2O(g)$
   Mass loss 36.8% (36.63%)
3. Stage, 310-490 ^oC

$Pr_2(SO_4)_3.2SO_3 \rightarrow Pr_2(SO_4)_3 + 2SO_3(g)$
Mass loss 11.84% (12.64%)
4. Stage, 490-1000 oC
$Pr_2(SO_4)_3 \rightarrow Pr_2O(SO_4)_2 + SO_3(g)$
Mass loss 7,89% (6.32%)
Total mass loss 62.13% (61.28%)

2. Stage for Nd compound, 150-400 ^oC
$Nd_2(RNH_3)_4(SO_4)_5 \rightarrow Nd_2(SO_4)_3.SO_3 + 4RNH_2(g) + SO_3(g) + 2H_2O$
Mass loss 43.3% (42.78%)
3. Stage, 400-450 ^oC
$Nd_2(SO_4)_3.SO_3 \rightarrow Nd_2(SO_4)_3 + SO_3(g)$
Mass loss 6.2% (6.29%)
5. Stage 450-1000 ^oC
$Nd_2(SO_4)_3 \rightarrow Nd_2O_2SO_4 + 2SO_3(g)$
Mass loss 10.99% (12.58%)
Total mass loss 66.07% (67.31%)
The teorethical values are given in brackets.
As could be seen, the thermal decomposition of Nd-compound takes place at lower temperature.

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