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SYNTHESIS AND INVESTIGATION OF SOME RARE EARTHS(III) ANTHRANILATES

Abstract: The rare earths(III) anthranilates were obtained as crystal products, from an aqueous mixture of sodium anthranilate and rare earth(III) sulphate in molar ratio 6 : 1 at pH 6.5. After filtration, the crystal products were dried on air and investigated by the methods of X-ray powder diffraction, IR spectroscopy, thermal analysis and elemental analysis. The results of the thermal and elemental analysis showed that the compounds obtained have the general formula $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot \text{H}_2\text{O}$ (where Ln = Y, Gd, Dy, Ho, Er). Also, from the X-ray powder diffraction patterns and the IR spectra, it can be concluded that the compounds obtained are isomorphous.

Introduction

Recently, great interest has been shown in the synthesis and the investigation of the physico-chemical properties of rare earths complexes with organic acids. Anthranilic acid, an important precursor of the aminoacid triptophan, because of its formation of stable, very sparingly soluble complexes with di- and trivalent metal ions, appears as an important reagent in analytical chemistry.

A survey of the literature shows that there are some data on anthranilate and p-aminobenzoate of Sc [1]. It was found that their empirical formulae are ScR_3 and $\text{ScOHR}_2 \cdot \text{H}_2\text{O}$ respectively (R = organic acid anion).

Thermal decomposition of the complexes of Sc with some m-derivatives of benzoic acid and m-aminobenzoic acid with the empirical formula $\text{Sc}[\text{NH}_2\text{C}_6\text{H}_4\text{COO}]_3$ has been investigated by Brzyska et al. [2]. It was found that m-aminobenzoate of Sc decomposes in one step from 320 to 810 °C. Recently, Rzaczyńska Z. and Brzyska W. have presented the results of the synthesis, thermal behavior and IR spectra of the complexes of Y, La and other lanthanides with m-aminobenzoic acid [3].

The synthesis of p-aminobenzoates of rare earths, with the empirical formula $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot n\text{H}_2\text{O}$, their IR spectra and thermal behavior, have been investigated by Efremova et al. in order to determine their

structure [4]. They have found two types of compounds: one from La to Eu with $n = 1$ and another from Gd to Lu, with $n = 2$.

The thermodynamic parameters for Eu(III) and La, Sm, Dy, Ho, Er, Yb and Lu as monoanthranilate complexes and a discussion of the role of amino group are reported [5].

Carasev et al. [6] have investigated the complexes of Tb with anthranilic acid and some neutral ligands (pyridine, dimethylpyridine, dimethylformamide, dimethylsulphoxide). By X-ray diffraction and luminiscence analysis they have found a difference in the structure of the complexes of the types: $Tb(\text{Ant})_3 \cdot \text{H}_2\text{O}$ and $Tb(\text{Ant})_3 \cdot \text{H}_2\text{O} \cdot \text{D}$ (D = neutral ligand, Ant = anthranilate anion).

Stability constants of some lanthanides and actinide ions with anthranilic acid are given by Majid Yehya A. et al. [7]. Anthranilates of some lanthanides with the general formula $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot n\text{H}_2\text{O}$ where $n = 0$ for Ln = La, Ce, Pr, Nd, Sm; $n = 1$ for Ln = Eu and Gd, and $n = 2$ for Ln = Y are obtained by the reaction of Ln(III) hydroxide and anthranilic acid [8]. These compounds are examined by IR-spectroscopy, X-ray powder diffraction and derivatographic measurements. On the basis of the X-ray powder diffraction patterns the authors have discovered that rare earths(III) anthranilates are isostructural in the groups: La-Sm and Eu, Gd and Y.

Continuing our work on the salts of rare earths, in this work we have presented the results of the synthesis, thermal behavior, IR spectra and X-ray powder diffraction patterns of some rare earths(III) anthranilates for which we have not found any evidence in the literature about the synthesis and investigation in the solid state.

Experimental

Materials

Rare earths sulfates were used as starting compounds. A solution of sodium anthranilate was used, obtained by neutralization of anthranilic acid with an aqueous solution of sodium hydroxide to pH = 6.5.

Procedure

Rare earths(III) anthranilates were obtained as crystal products from a concentrated mixture of sodium anthranilate and rare earth(III) sulfate in the molar ratio of 6 : 1. After filtration, the crystal products were dried on air and examined by the methods of X-ray powder diffraction, IR spectroscopy, TG and DTA, and elemental analysis.

Methods

The thermoanalytical curves were obtained on thermoanalyser NETZSCH SPA409 in a flow of dry air. Experimental conditions: sample

mass about 100 mg, reference substance for DTA determinations α -Al₂O₃; TG macrosamples holder with Pt-crucibles; heating rate 5 °C/min; temperature range from 20–800 °C; flow velocity 5 l/h.

For X-ray powder diffraction patterns JEOL X-ray diffractometer was used with Cu_{K α} -radiation, Ni filtered.

IR spectra were done on PERKIN-ELMER 520 IR spectrophotometer in KBr pellets.

Elemental analysis of C and H was carried out by Liebigs methods on CARBON-HYDROGEN ANALYZER COLEMAN MODEL 33, and N by Dumas method.

Results and discussion

The anthranilates of La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er and Y were synthesized by the method described in the experimental part. On the basis of the IR spectra and the X-ray powder diffraction patterns, as well as from the results of the elemental analysis, it was found that the anthranilates of La, Ce, Pr, Nd, Sm, Gd are identical with those presented by Brzyska et al. [8]. Since we have found no evidence about anthranilates of Dy, Ho and Er and because for Y anthranilate we have established monohydrate, only the results of the investigations of these anthranilates are presented. For comparison, the results of Gd anthranilate are given, as well.

Table I

The results of the elemental and thermal analysis of
Ln(C₆H₄NH₂COO)₃ · H₂O

Ln(C ₆ H ₄ NH ₂ COO) ₃ · H ₂ O		%H ₂ O	%C	%N	%H
Y* Mr = 515.31	theor.	3.50	48.95	8.15	3.91
	exper.	2.94	49.54	7.62	4.21
Gd Mr = 583.65	theor.	3.08	43.21	7.20	3.45
	exper.	3.28	44.12	6.42	3.55
Dy Mr = 588.91	theor.	3.06	42.83	7.13	3.42
	exper.	2.93	42.79	6.53	4.04
Ho Mr = 591.34	theor.	3.05	42.65	7.11	3.41
	exper.	3.16	42.76	6.76	3.70
Er Mr = 593.67	theor.	3.03	42.49	7.07	3.40
	exper.	3.41	42.45	6.22	3.42

* Y was determined gravimetrically (theoretical value 17.18%, experimental, 17.52%).

The results of the elemental and thermal analysis (Table I), as well as the X-ray powder diffraction patterns (Fig. 1), show that the obtained anthranilates of Y, Gd, Dy, Ho and Er, have the empirical formula $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot n\text{H}_2\text{O}$.

These results are in agreement with the results for Eu and Gd anthranilates given by Brzyska et al. [8], but not for Y-anthranilate. Namely, from the X-ray powder diffraction patterns (Fig. 1) it is clearly evident that all compounds are isomorphous. Also, the TG analysis for mass losses in the first stage of dehydration process (Fig. 2) shows that there is only one water molecule in the formula unit.

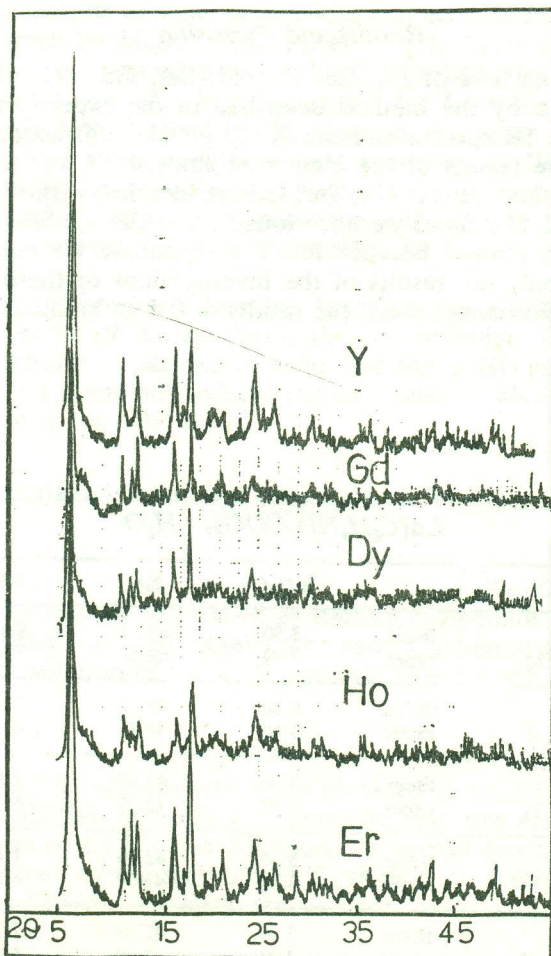


Fig. 1 - X-ray powder diffraction patterns of $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot \text{H}_2\text{O}$

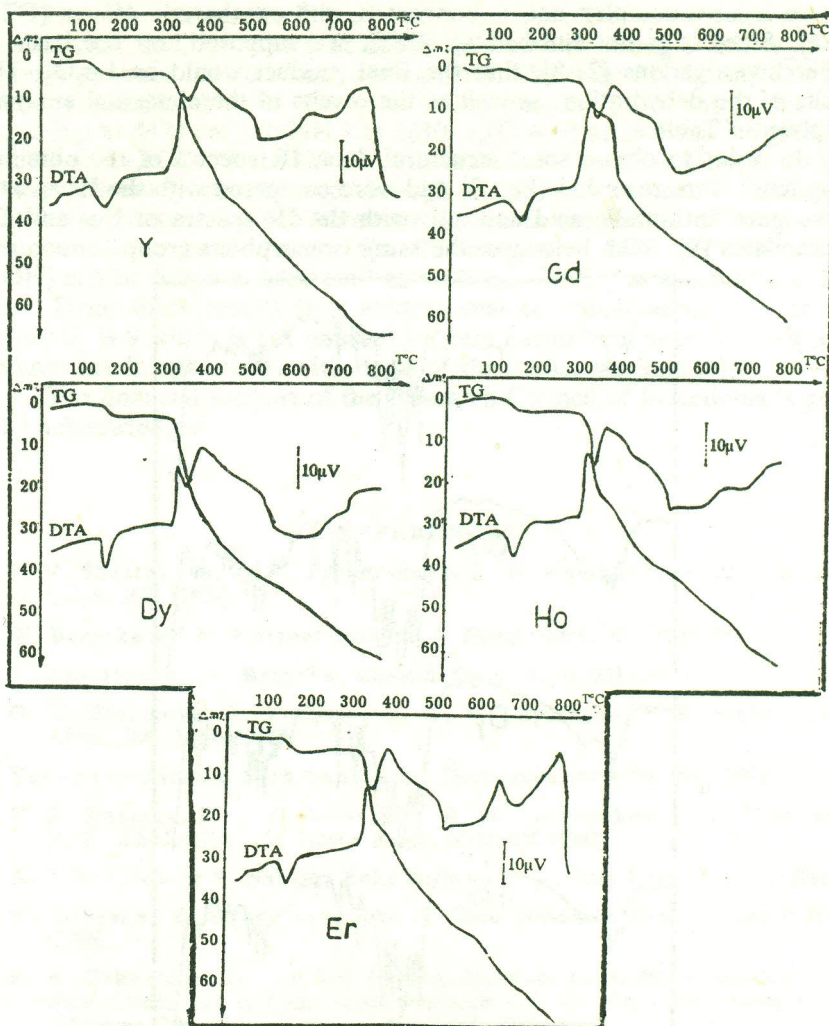


Fig. 2 - TG and DTA curves of $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot \text{H}_2\text{O}$

Thermal decomposition of the rare earth(III) anthranilates monohydrates takes place in two clearly separated stages (Fig. 2). In the first stage, a dehydration process appears at a temperature higher than 120 °C. So, on the DTA curve, an endothermic peak at 160 °C for Gd and Ho compounds, at 150 °C for Dy and Y compounds and at 140 °C for Er compound can be seen.

The second stage, which is connected with the thermal decomposition of the anhydrous salts, begins at a temperature higher than 300 °C. This

process is very complex and is connected with exothermic effects (DTA curve). Since it is not finished at 800°C, we supposed, on the basis of earlier investigations [2, 8], that the final product would be Ln_2O_3 . The results of the dehydration, as well as the results of the elemental analysis, are given in Table I.

In order to obtain some structural data, IR spectra of the obtained compounds were recorded (Fig. 3) and were compared with the IR spectra of the pure anthranilic acid and also with the IR spectra of Eu- and Gd anthranilates [8] which belong to the same isomorphous group.

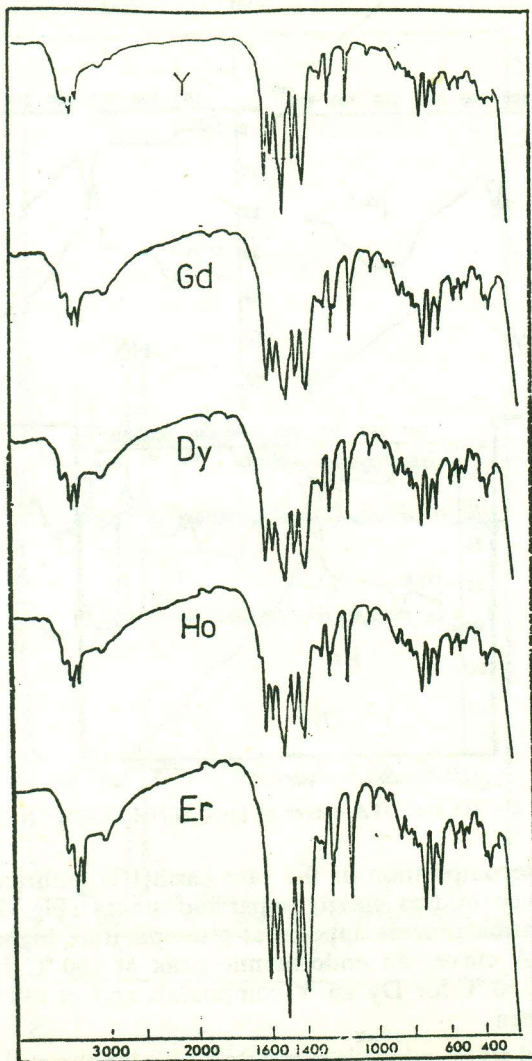


Fig. 3 - IR spectra of $\text{Ln}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_3 \cdot \text{H}_2\text{O}$

From the IR spectra it can be seen that $\nu_{as}(\text{COO}^-)$ absorption appears at 1508 cm^{-1} and $\nu_s(\text{COO}^-)$ at about 1395 cm^{-1} as strong bands. $\nu_{as}(\text{NH}_2)$ appears at about 1610 cm^{-1} as a strong band. The shifted NH_2 - and COO^- -vibrations compared with the same vibrations in pure anthranilic acid ($\nu_{as}(\text{NH}_2)$ at 3470 cm^{-1} , $\delta(\text{NH}_2)$ at 1610 , $\nu_s(\text{C}=\text{O})$ at 1670 cm^{-1} , $\nu_{as}(\text{COO}^-)$ at 1585 and $\nu_s(\text{COO}^-)$ at 1420 cm^{-1}) indicated that rare earth(III) is probably simultaneously coordinated through amino and carboxylic groups and that the carboxylate ion is a bidentate ligand. In the spectra of the obtained compounds the band due to $\text{C}=\text{O}$ vibration at 1680 cm^{-1} disappears. $\nu(\text{OH})$ can be found at 3480 cm^{-1} as weak and $\delta(\text{OH})$ as a shoulder at 1680 cm^{-1} . From these results it is evident that coordination number of rare earth(III) is 9 which is not unusual for rare earths complexes [9]. All these findings are in agreement with those of the earlier workers [8].

The financial support of the Research Council of Macedonia is gratefully acknowledged.

REFERENCES

1. T. V. Shestakova, Z. N. Prozorskaya, L. N. Komissarova, *Zh. Anal. Khim.*: 19(10), 2671 (1974).
2. W. Brzyska and R. Kurpiel-Gorgol, *J. Therm. Anal.*, 32, 671 (1987).
3. Z. Rzaczyńska, W. Brzyska, *Monatsh. Chem.*, 12(3), 231 (1987).
4. G. H. Efremova, R. T. Buchova, A. V. Lapickaya, S. B. Pirkes, *Koord. Khim.*, 3(8), 1184 (1977).
5. Young Inn Kim and Sock Sung Yuu, *Thermochim. Acta*, 59, 299 (1982).
6. V. E. Karasev, N. I. Steblevskaya, R. N. Shchelokov, I. V. Shchukina, N. F. Zhelokina, *Zh. Neorg. Khim.*, 26(2), 350 (1981).
7. A. Yehia, Majid S. Nabila, Zeki Al Muddaris, *Iraqi J. Sci.*, 23(4), 515 (1982).
8. W. Brzyska, Z. Rzaczyńska, *Pol. J. Chem. (Formerly Roczniki Chemii)*, 60, 27 (1986).
9. K. A. Gshneider, Jr., Le Roy Eyring, *Handbook on the Physics and Chemistry of Rare Earths*, Vol 3, Nonmetallic compounds - 1, 234-237, (1979), North Holland Publishing Company, Amsterdam, New York, Oxford.

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СИНТЕЗА И ИСПИТУВАЊЕ НА АНТРАНИЛАТИ НА НЕКОИ РЕТКИ ЗЕМЈИ

(Резиме)

Антранилатите на некои лантаниди беа добиени од смеса на водени раствори на натриум антранилат и сулфат на соодветниот лантанид. Издвоените кристали беа сушени на воздух, а потоа испитувани со методите на рендгенска прашковна дифракција, термичка анализа, инфрацрвена спектроскопија и елементарна ана-

лиза. Резултатите од термичката и елементарната анализа покажаа дека добиените соединенија имаат емпириска формула $Ln(C_6H_4NH_2COO)_3 \cdot H_2O$ (каде $Ln = Y, Gd, Dy, Ho, Er$). Од рендгенските прашковни дифрактограми, како и од инфрацрвените спектри, може да се заклучи дека добиените соединенија се меѓусебно изоморфни.

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