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LITHIUM OXALATOMETALLATES OF RARE EARTHS

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The synthesis of fifteen compounds of rare earths with general formula $LiLn(C_2O_4)_2.5H_2O$ is reported. They were characterized by chemical and thermal analysis. Thermal analysis in dry air shows two principal effects. The first one is the dehydration with the probable formation of dihydrate, followed by the oxidation of oxalate ion at temperature around 400°C. X-ray powder diffraction photographs were used for the classification of the isolated compounds into four, internally isostructural, groups.

The reported work is a part of continuous research in our laboratory on oxalates of trivalent cations and oxalatometallates(III) (1). Recently our investigations were extended also to the use of the ions of rare earths. A survey of the literature has not produced any substantial data on oxalatometallates of rare earths with lithium.

Davitashvili, Shelija and Modebadze (2) reported the isolation of $LiGd(C_2O_4)_2.5H_2O$ as well as its thermal decomposition. They also reported the synthesis of the similar row of the compounds, where Gd was replaced by Pr, Tb, Ho and Y (3). A similar paper deals with the compound with the formula $LiSm(C_2O_4)_2.5H_2O$ (4).

In our study three main goals were followed: to determine the conditions of the synthesis, to determine the isostructural groups and to investigate thermal behaviour of all isolated compounds.

EXPERIMENTAL

We have chosen rare earths oxides, guaranteed pure 99,9% referring to the corresponding element from the firm Koch-Light Laboratories, Colnbrook, England, as a source for preparation of corresponding nitrates. All other chemicals used during this study were standard quality for analysis. Compounds were isolated by adding saturated solution of lithium oxalate to 1M solution of $Ln(NO_3)_3$, at room temperature. The precipitate, which appears immediately, was filtered after 24 hours of standing and washed with water. The determination of rare earth was done by standard method (5). This method was controlled in accordnace with some quotations from the literature stating that alkalic ions disturb the determination of rare earth. It was found out, that the above mentioned quotation is questionable when dealing with highly acidic solutions what was the case in our work. Oxalate ions were determined with the standard permanganometrical method.

Powder photographs with Guinier-de Wolf camera with CuKα radiation were taken for all isolated compounds.

The conditions of thermal analysis were as follows: Mettler's thermoanalysator (6) with combined TD1 measuring head, rate of heating 4°C/min, dry air 5 l/h, weight 50 mg and α-Al_2O_3 as the reference material for DTA.

RESULTS AND DISCUSSION

Extensive preliminary investigations were made in order to isolate pure compounds, including also some other univalent cations to establish optimal conditions. Details will not be quoted, however, normal oxalates of elements of rare earths were obtained in acidic solutions. At higher values of pH and when the concentration of oxalate ions is too low, mixtures of normal oxalates with oxalatometallates were detected. According to preliminary investigations, the following conditions were used: pH around 6 and molar ratio $M_2C_2O_4/Ln^{3+}$ not lower than 5. In some cases even higher molar ratio was used. Analytical results are given in the Table 1, together with their calculated values. The percent of H_2O was obtained by thermogravimetrical measurements. The compounds in Table 1 were isolated with the molar ratio $M_2C_2O_4/Ln^{3+} = 5:1$, except in the case of lanthanum, cerium and lutetium, where the molar ratio was raised up to 10:1. A survey over the table leads us to the conclusion that the stoichiometry of $LiLn(C_2O_4)_2.5H_2O$ is the principal. Larger deviations appear only in the case of compounds with lanthanum and cerium. All the samples were extremely dispersive and therefore Guinier diagrams were not very sharp. On the basis of X-ray diffraction patterns all isolated compounds can be divided into following four isostructural groups:

1. La, Ce
2. Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Y
3. Ho, Er, Tm
4. Lu

For more details single crystal structures of the representatives of all four groups will be needed.

In the thermal analysis the first step is the thermal dehydration of compounds and the second is exothermal oxidation of oxalate ion. At the chosen final temperature (only 500°C), either oxide or basic carbonate and lithium carbonate were obtained, depending on element of rare earth. Examples of these types are compounds $LiM(C_2O_4)_2.5H_2O$ (M = Ce, Pr, Ho). Their TG, DTG and DTA curves are given on Figures 1-3. It must be stressed that the course of dehydration proceeds through several steps. In the case of the elements from La to Eu there are three steps, while in the case of the elements from Gd to Yb including Y only two steps were found. However, the first and the second steps of the compounds from La to Eu correspond to formation of dihydrates, while the first step of the compounds from Gd to Yb including Y corresponds also to the formation of dihydrates. The last step of all compounds gave the dehydrated salt. Exothermal oxidation of oxalate occurs at the temperature of 400°C ± 5°C regardless of the rare earth. An exception is the decomposition of cerium, where this maximum is reached at 340°C, probably because of formation of CeO_2. Thermal decomposition at higher temperature was not examined because of great possibility of corrosion of platinum vessels. The compounds of this type present a potential for the synthesis of the binary oxides of lithium and elements of the rare earths.

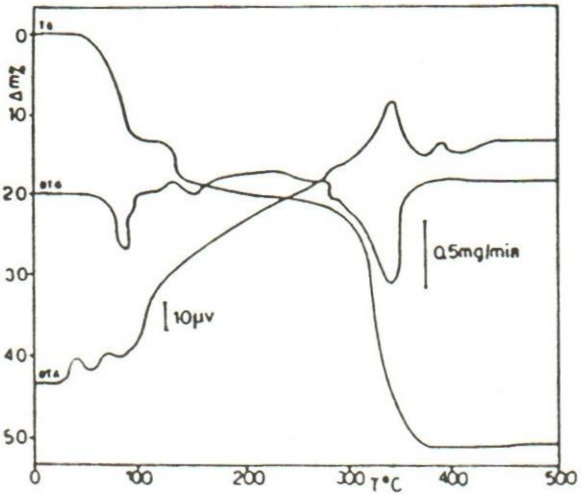

Figure 1. TG, DTG and DTA curves of $LiCe(C_2O_4)_2 \cdot 5H_2O$ in air

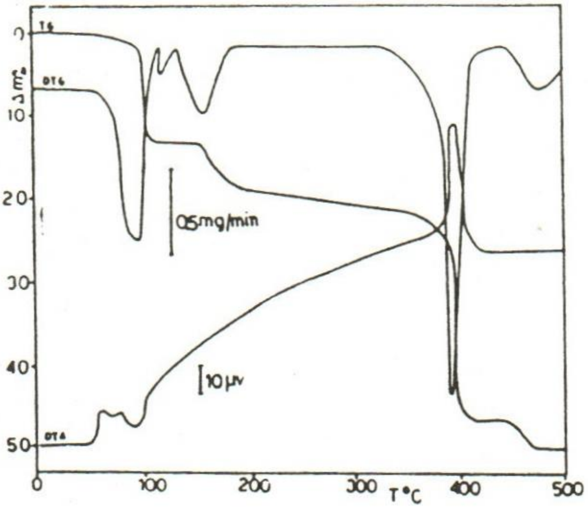

Figure 2. TG, DTG and DTA curves of $LiPr(C_2O_4)_2.5H_2O$ in air

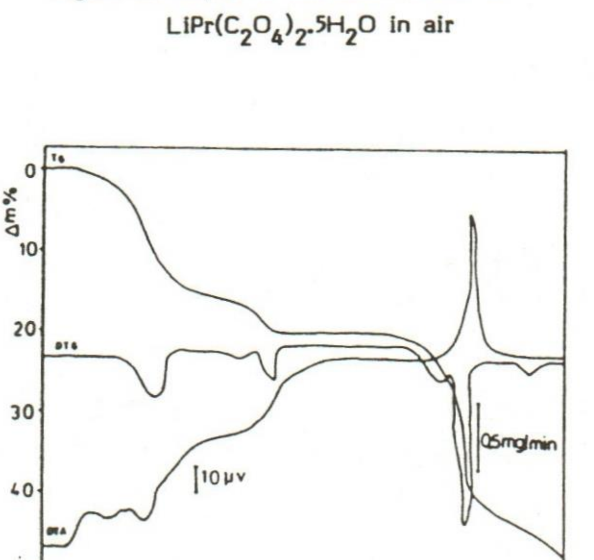

Figure 3. TG, DTG and DTA curves of $LiHo(C_2O_4)_2.5H_2O$ in air

Table 1. Analytical data of isolated compounds and their calculated values

	Found			Calculated			
Compounds	% Ln	% C_2O_4	% H_2O	% Ln	% C_2O_4	% H_2O	%Li
$LiLa(C_2O_4)_2.5H_2O$	32,48	42,08	22,28	33,72	42,74	21,85	1,68
$LiCe(C_2O_4)_2.5H_2O$	34,45	43,89	20,19	33,92	42,61	21,79	1,68
$LiPr(C_2O_4)_2.5H_2O$	34,19	42,44	21,07	34,05	42,53	21,75	1,68
$LiNd(C_2O_4)_2.5H_2O$	34,42	42,19	21,21	34,54	42,19	21,57	1,66
$LiSm(C_2O_4)_2.5H_2O$	35,41	41,43	21,14	35,53	41,57	21,26	1,64
$LiEu(C_2O_4)_2.5H_2O$	34,99	39,89	21,41	35,76	41,42	21,18	1,63
$LiGd(C_2O_4)_2.5H_2O$	36,40	40,81	23,16	36,55	40,91	20,92	1,61
$LiTb(C_2O_4)_2.5H_2O$	36,01	39,99	21,00	36,79	40,75	20,84	1,60
$LiDy(C_2O_4)_2.5H_2O$	37,43	39,83	21,18	37,32	40,42	20,67	1,59
$LiHo(C_2O_4)_2.5H_2O$	36,77	39,79	20,51	37,67	40,19	20,55	1,58
$LiEr(C_2O_4)_2.5H_2O$	38,16	39,95	19,61	37,99	39,98	20,41	1,58
$LiTm(C_2O_4)_2.5H_2O$	37,61	38,45	21,32	38,23	39,83	20,37	1,57
$LiYb(C_2O_4)_2.5H_2O$	37,43	40,53	21,04	38,79	39,46	20,18	1,56
$LiLu(C_2O_4)_2.5H_2O$	39,81	39,35		39,06	39,29	20,09	1,54
$LiY(C_2O_4)_2.5H_2O$	23,87	46,93	24,30	24,57	48,63	24,87	1,92

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POVZETEK

Poročano je o sintezi in karakterizaciji petnajstih spojin redkih zemelj s splošno formulo $LiLn(C_2O_4)_2.5H_2O$ s kemijsko analizo in termično analizo. Termična analiza na zraku kaže dva glavna efekta. Prvi je dehidratacija z verjetno tvorbo vmesnega dihidrata, ki ji sledi oksidacija oksalatnega iona pri temperaturi okrog 400°C. Praškovni difrakcijski diagrami omogočajo razdelitev v štiri izostrukturne skupine.

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