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SYNTHESIS AND DEHYDRATION OF DOUBLE OXALATES OF RARE EARTHS(III) WITH SOME MONOVALENT METALS

I. Synthesis and thermal behaviour of $KLn(C_2O_4)_2{\cdot}nH_2O$

O. Genčova[1] *and J. Šiftar*[2]

[1]Institute of Chemistry, Faculty of Science, 'St. Cyril and Methodius' University, 91000 Skopje, Macedonia
[2]Department of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

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Abstract

The synthesis of double oxalates of rare earths(III) and potassium with empirical formulae $K_4Ln_2(C_2O_4)_5{\cdot}10H_2O$ (*Ln*=La, Ce) and $KLn(C_2O_4)_2{\cdot}nH_2O$ (where *n*=4 for Pr–Dy and *n*=4.5 for Ho–Lu, Y) is described. The compounds obtained were studied by TG, DTG and DTA over the temperature interval 25–500°C and by X-ray powder diffraction and chemical analysis. Three structurally different groups were recognized. It was found that either rare earth oxide or basic carbonate ($Ln_2O_2{\cdot}CO_3$) and potassium carbonate were obtained as final product at 500°C, depending on the rare earth element. The thermal decomposition takes place in two well-resolved stages.

Keywords: double oxalates, potassium, rare earths (lanthanons)

Introduction

Double oxalates of rare earths(III) and classical monovalent cations or ammonium have been the subject of many investigations: the synthesis and thermal decomposition of double oxalates with lithium [1–5], sodium [6–8], rubidium [9, 10], caesium [2, 4, 8–10] and ammonium [2–4, 9, 11, 12] have been reported.

Double oxalates of rare earths(III) and potassium, with general empirical formulae $KYb(C_2O_4)_2{\cdot}4H_2O$ [2], $KSm(C_2O_4)_2{\cdot}3.5H_2O$ [2], $KGd(C_2O_4)_2{\cdot}4H_2O$ [13] and $K_4Ce_2(C_2O_4)_5{\cdot}9H_2O$ [11], have been prepared. Double oxalates of rare earths(III) with empirical formulae $K_3LnOx_3{\cdot}nH_2O$ (*Ln*=La–Tb) and $K_8LnOx_7{\cdot}14H_2O$ (*Ln*=Tb–Yb, Y) [14] and $K_3[LnOx_3{\cdot}H_2O]{\cdot}H_2O$ (*Ln*=Nd, Sm, Eu, Gd, Tb) [15] too have been prepared, and the crystal structures of the compounds containing Nd and Gd have been determined at room temperature by single-crystal X-ray diffraction methods. The compounds are triclinic with space group $P_{\bar{1}}$ and 1=2. It was found

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that Tb forms a monoclinic complex $K_8TbOx_7 \cdot 14H_2O$ and a triclinic complex $K_3TbOx_3 \cdot 3H_2O$.

As a continuation of the work on the synthesis of double oxalates of lanthanons and monovalent cations [16], we present here the results of the synthesis, chemical analysis and thermal analysis of double oxalates of rare earths(III) and potassium, with general empirical formulae $KLn(C_2O_4)_2 \cdot 4H_2O$, $KLn(C_2O_4)_2 \cdot 4.5H_2O$ and $K_4Ln(C_2O_4)_5 \cdot 10H_2O$, obtained from a starting mixture with a 1:5 molar ratio of rare earth(III) nitrate and potassium oxalate.

Experimental

Extensive preliminary investigations were made in order to isolate pure compounds, including the use of some other univalent cations, in order to establish optimal conditions. Details will not be given here, however. Normal oxalates of the rare earths were obtained in acidic solutions.

On the basis of the preliminary research, we chose a molar ratio of $Ln(NO_3)_3:K_2C_2O_4=1:5$, at a *pH* around 6; at lower ratios, mixtures of normal oxalates with oxalatometallates were detected. The compounds were isolated by adding a saturated solution of potassium oxalate to a 1 *M* solution of $Ln(NO_3)_3$, at room temperature. The rare earth was determined by a standard method [17].The oxalate group was determined permanganometrically.

The thermoanalytical curves were obtained on a Mettler Thermoanalyzer in dynamic dry air: flow velocity 5 l h^{-1}; Pt/Pt–Rh thermocouple; Pt crucibles (TDl and TDMa), sample mass approximately 50 mg; heating rate 4°C min^{-1}. The reference for DTA determinations was α-Al_2O_3, in the temperature range 20–500°C.

Results and discussion

From the X-ray powder diffraction patterns, it was possible to identify three structurally different groups of double oxalates. Group 1 involves those of La and Ce, group 2 those from Pr to Dy, and group 3 those from Ho to Lu and Y. From TG and the results of quantitative analyses of Ln and the C_2O_4 group (Table 1), the following general empirical formulae were found for the three groups:

1. $K_4Ln(C_2O_4)_5 \cdot 10H_2O$ (*Ln*=La, Ce)
2. $KLn(C_2O_4)_2 \cdot 4H_2O$ (*Ln*=Pr–Dy)
3. $KLn(C_2O_4)_2 \cdot 4H_2O$ (*Ln*=Ho–Lu, Y)

The first thing to be stressed as concerns Table 1 is the 2:5 stoichiometry for Ln^{3+}: C_2O_4 in the cases of La and Ce. Šterba-Böhm *et al.* [11] reported a similar ratio only for sodium and cerium: $Na_4Ce_2(C_2O_4)_5 \cdot 10H_2O$. For all the other rare earths, the ratio Ln^{3+}: C_2O_4 was found to 1:2.

The TG, DTG and DTA curves (Figs 1(a)–(h)) reveal that the thermal decomposition is similar in each isomorphous group and takes place in two well-resolved stages. In the first stage, associated with the dehydration, the water is evolved at different rates and two DTA endothermic peaks appear for all three isostructural

Table 1 Analytical and calculated data on the compounds

Compound	Found/%			Calculated/%			
	Ln	C_2O_4	H_2O	Ln	C_2O_4	H_2O	K
$K_4La_2(C_2O_4)_5 \cdot 10H_2O$	26.85	42.05	16.75	26.35	41.73	17.10	14.89
$K_4Ce_2(C_2O_4)_5 \cdot 10H_2O$	26.24	41.55	16.75	26.52	41.64	17.04	14.80
$KPr(C_2O_4)_2 \cdot 4H_2O$	33.27	40.99	17.15	32.92	41.12	16.82	9.14
$KNd(C_2O_4)_2 \cdot 4H_2O$	33.27	41.07	16.49	33.43	40.80	16.70	9.06
$KSm(C_2O_4)_2 \cdot 4H_2O$	33.96	40.81	16.37	34.36	40.23	16.47	8.94
$KEu(C_2O_4)_2 \cdot 4H_2O$	33.66	39.09	16.09	34.60	40.08	16.41	8.90
$KGd(C_2O_4)_2 \cdot 4H_2O$	36.02	40.28	15.67	35.38	39.61	16.21	8.79
$KTb(C_2O_4)_2 \cdot 4H_2O$	36.07	40.27	15.60	35.62	39.46	16.15	8.76
$KDy(C_2O_4)_2 \cdot 4H_2O$	35.82	38.66	16.62	36.14	39.15	16.02	8.69
$KHo(C_2O_4)_2 \cdot 4.5H_2O$	35.93	39.20	17.50	35.77	38.18	17.57	8.48
$KEr(C_2O_4)_2 \cdot 4.5H_2O$	35.92	38.54	17.56	36.09	37.98	17.48	8.44
$KTm(C_2O_4)_2 \cdot 4.5H_2O$	35.33	38.33	16.94	36.32	37.85	17.42	8.41
$KYb(C_2O_4)_2 \cdot 4.5H_2O$	36.61	37.46	16.98	36.88	37.51	17.28	8.33
$KLu(C_2O_4)_2 \cdot 4.5H_2O$	36.92	37.41		37.13	37.36	17.21	8.29
$KY(C_2O_4)_2 \cdot 4.5H_2O$	22.88	46.51	20.83	23.09	45.71	21.05	10.15

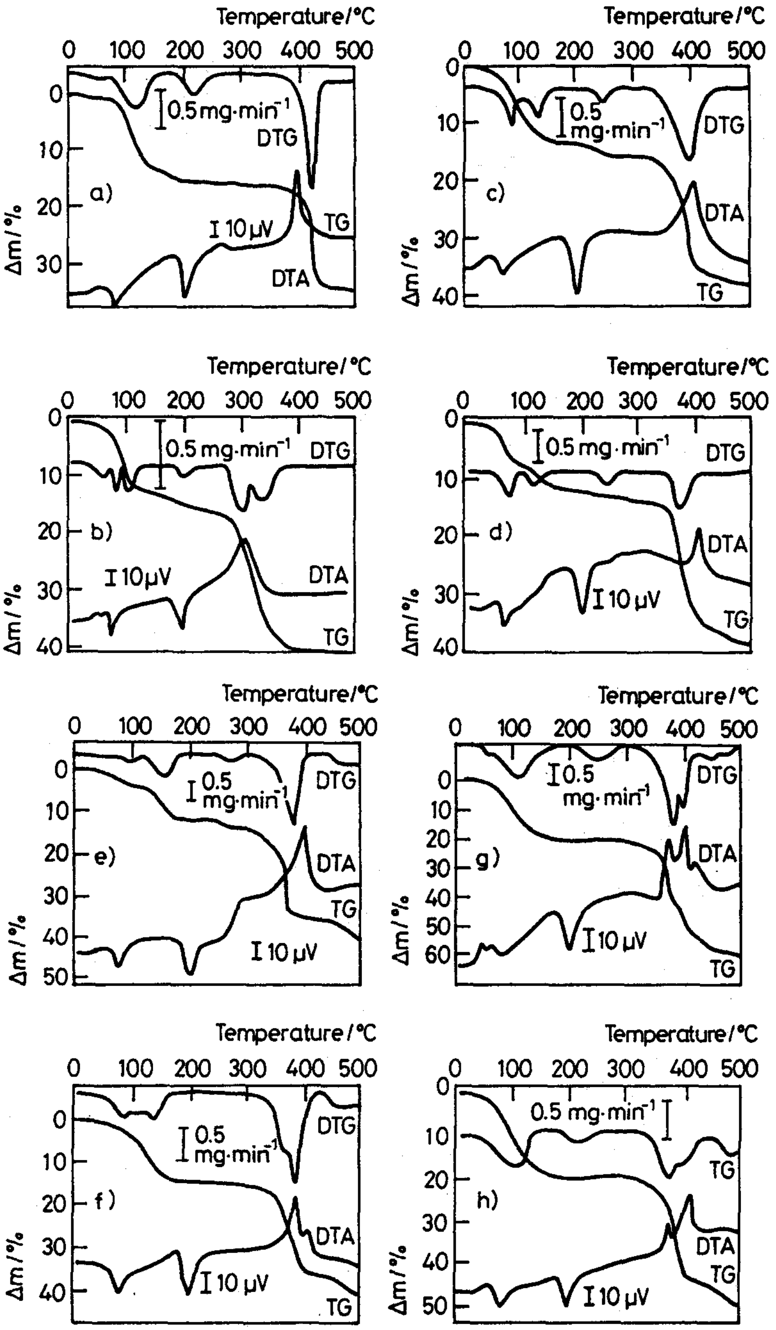

Fig. 1 TG, DTG and DTA curves of: $K_4Ln_2(C_2O_4)_5\cdot 10H_2O$ (La (a), Ce (b)), $KLn(C_2O_4)_2\cdot 4H_2O$ (Nd (c), Sm (d), Dy (e)) and $KLn(C_2O_4)_2\cdot 4.5H_2O$ (Ho (f), Er (g), Y(h))

Table 2 TG analysis of $KLn(C_2O_4)_2 \cdot nH_2O$ at 500°C

Compound	Fragmentation products	$\Delta m_{exp.}$/%	$\Delta m_{calc.}$/%
$K_4La_2(C_2O_4)_5 \cdot 10H_2O$	$2K_2CO_3 + La_2O_2 \cdot 2CO_3$	34.52	34.42
$K_4Ce_2(C_2O_4)_5 \cdot 10H_2O$	$2K_2CO_3 + 2CeO_2$	40.77	40.74
$KPr(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Pr_2O_2 \cdot CO_3$	40.33	40.18
$KNd(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Nd_2O_2 \cdot CO_3$	38.94	39.87
$KSm(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Sm_2O_2 \cdot CO_3$	39.31	39.31
$KEu(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Eu_2O_2 \cdot CO_3$	39.00	39.17
$KGd(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Gd_2O_2 \cdot CO_3$	38.65	38.71
$KTb(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Tb_2O_2 \cdot CO_3$	38.55	38.49
$KDy(C_2O_4)_2 \cdot 4H_2O$	$K_2CO_3 + Dy_2O_2 \cdot CO_3$	37.50	38.25
$KHo(C_2O_4)_2 \cdot 4.5H_2O$	$K_2CO_3 + Ho_2O_2 \cdot CO_3$	40.12	39.26
$KEr(C_2O_4)_2 \cdot 4.5H_2O$	$K_2CO_3 + Er_2O_3$	43.90	43.81
$KTm(C_2O_4)_2 \cdot 4.5H_2O$	$K_2CO_3 + Tm_2O_3$	42.80	43.65
$KYb(C_2O_4)_2 \cdot 4.5H_2O$	$K_2CO_3 + Yb_2O_3$	43.00	43.27
$KY(C_2O_4)_2 \cdot 4.5H_2O$	$K_2CO_3 + Y_2O_3$	54.65	54.02

groups, at 75±10°C and 200°C (Figs 1(a)–(h)). In the first step, the double oxalates evolve 3 moles of water, and in the second step 1 or 1.5 moles of water. The first and the second steps for the compounds from Pr to Dy correspond to the formation of monohydrates, and for the compounds from Ho to Lu and Y to the formation of sesquihydrates.

The second stage of thermal decomposition, which begins at about 300°C and ends at about 500°C, involves the thermal decomposition of the anhydrous double oxalates at about 400±5°C, with exothermic effects caused by the oxidation of oxalate ion. An exception is the decomposition of cerium, where this maximum is reached at 300°C, probably because of the formation of CeO_2. On the basis of the total mass losses (Δm), which are in agreement with the theoretical values (Table 2), it is proposed that final product formed at 500°C is a mixture of potassium carbonate and either the basic carbonate ($Ln_2O_2CO_3$), for the double oxalates from La to Ho (an exception is the cerium compound, where CeO_2 and K_2CO_3 were obtained), or K_2CO_3 and Ln_2O_3, for the elements from Er to Yb and Y.

The report by Kahwa *et al.* [15] is interesting because of the method of synthesis of the double oxalatometallates of lanthanons and potassium. The main difference is that they worked with hot solutions, whereas our double oxalates were obtained at room temperature.

References

1 E. G. Davitashvili, N. G. Sheliya and M. E. Modebadze, Zh. Neorg. Khim., 14 (1969) 917.
2 E. G. Davitashvili, M. E. Modebadze and N. G. Sheliya, Zh. Neorg. Khim., 16 (1971) 655.
3 Zh. Sh. Kublashvili and E. G. Davitashvili, Zh. Neorg. Khim., 17 (1972) 262.

4 E. G. Davitashvili, N. G. Sheliya and M. E. Modebadze, Issled. Obl. Khim. Kompleksn. Prostykh soed. Nekot. Perekh. Red. Met., 2 (1974) 205, Chem. Abstr., 82 (1975) 25294e .
5 E. G. Davitashvili and M. E. Modebadze, Issled. Obl. Khim. Kompleksn. Prostykh Soed. Nekot. Perekh. Red. Met., 3 (1978) 89, Chem. Abstr., 90 (1979) 214498a.
6 I. M. Koelthoff and R. Elmquist, J. Am. Chem. Soc., 53 (1931) 1232.
7 E. G. Davitashvili, N. G. Sheliya, S. G. Kurashvili and N. A. Dzhabishvili, Kompleksn. Soedin. Nekot. Perkh. Red. Elem., 89 (1966), Chem. Abstr., 69 (1968) 5646z.
8 Zh. Sh. Kublashvili and E. G. Davitashvili, Zh. Neorg. Khim., 16 (1971) 1526.
9 M. E. Modebadze, N. G. Sheliya and L. N. Kargareteli, Issled. Obl. Khim. Kompleksn. Prostykh Soed. Nekot. Perekh. Red. Met., 3 (1978) 121, Chem. Abstr., 90 (1979) 214499b.
10 E. G. Davitashvili, M. E. Modebadze and N. G. Sheliya, Soobskh. AN GRUZ SSR, 73 (1974) 65, Chem. Abstr., 80 (1974) 103355a.
11 J. Šterba-Böhm and A. Pisariček, Collekt. Czech. Chem. Commun., 2 (1930) 244.
12 T. R. R. McDonald and J. M. Spink, Acta Crystallogr., 23 (1967) 944.
13 P. B. Sarkar, Bull. Soc. Chim. Fr., 39 (1926) 1390.
14 I. A. Kahwa and J. Selbin, J. Thermal Anal., 28 (1983) 359.
15 I. A. Kahwa, F. R. Fronczek and J. Selbin, Inorg. Chim. Acta, 82 (1984) 161.
16 O. Genčova and J. Šiftar, J. Thermal. Anal., 44 (1995) 1171.
17 W. R. Schoeller and A. R. Powell, the Analysis of Minerals and Ores of the Rare Elements, 3rd Ed., Hafner, New York, 1955, p. 105.