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SPECTRAL AND THERMAL STUDIES OF RARE EARTH ELEMENT 3-METHYLGLUTARATES

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Abstract

Conditions for the formation of rare earth element (Y, La–Lu) 3-methylglutarates were studied and their quantitative composition and solubilities in water at 293 K were determined (10^{-2} mol dm^{-3}). The IR spectra of the prepared complexes with general formula $Ln_2(C_6H_8O_4)_3{\cdot}nH_2O$ (n=3–8) were recorded and their thermal decomposition in the air were investigated. During heating the hydrated 3-methylglutarates are dehydrated in one step and next anhydrous complexes decompose to oxides Ln_2O_3 with intermediate formation $Ln_2O_2CO_3$ (Y, La, Nd–Gd) or directly to the oxides, Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 (Ce, Pr, Tb–Lu).

Keywords: DTA, IR spectra, 3-methylglutarates, synthesis, TG

Introduction

3-Methylglutaric acid $C_4H_8(COOH)_2$ is a crystalline solid soluble in hot water, ethanol and ether, and sparingly soluble in benzene and chloroform [1]. Compounds of 3-methylglutaric acid with metal ions are little known. The complexes of Ag(I) and Pb(II) were prepared as solids sparingly soluble in water, and those of Na(I), NH_4(I) and Ca(II) as soluble in water. Rare earth complexes with 3-methylglutaric acid has not been studied so far.

The aim of our work was to study some physico-chemical properties and thermal decomposition of rare earth 3-methylglutarates prepared under same conditions and to determine the changes of the thermal data in the lanthanides series.

Experimental

The complexes of 3-methylglutaric acid with Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by dissolving freshly precipitated metal(III) hydroxides in a hot 0.1 M solution of 3-methylglutaric acid. The precipitates formed (in conversion reaction) were heated in mother liquor for 0.5 h at 343–353 K, filtered off, washed with water and dried at 303 K to a constant mass.

The carbon and hydrogen contents in the prepared complexes were determined by elemental analysis using Perkin Elmer CHN 2400. Contents of rare earth elements were

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determined from TG curve by ignition of the prepared complexes to oxides at 1273 K. The content of crystallization water molecules were calculated from TG curves and by heating of the complexes at a suitable temperature. The experimental results confirm the calculated data.

IR spectra of the complexes, and spectra of 3-methylglutaric acid and its sodium salt were recorded as KBr discs of FT-IR 1725x Perkin Elmer spectrophotometer (range 4000–400 cm^{-1}). The solubilities in water were determined at 293 K, preparing the saturated solutions isothermally. The concentrations of rare earth ions were determined by spectroscopic method using arsenazo III.

The thermal stabilities of the prepared complexes were studied by means of TG, DTG and DTA techniques. Measurements were made with OD-102 derivatograph at a heating rate of 10 K min^{-1} for full scale. Samples of 100 mg mass were heated in platinum crucibles in air atmosphere to 1273 K at sensitivity: TG=100 mg, DTG-500 μV, DTA-500 μV. The products of decomposition were calculated from TG curves and were determined by IR spectra and X-ray patterns. Al_2O_3 was used as standard material.

Results and discussion

Rare earth(III) 3-methylglutarates were prepared as solids with molar ratio of metal to organic ligand of 2:3 and general formula $Ln_2(C_6H_8O_4)_3\cdot nH_2O$, where Ln=Y, La–Lu, n=3, 4, 5, 6, 8 (Table 1) with colour characteristic for Ln(III) ions. They are soluble in water. Their solubilities are of the order 10^{-4} mol dm^{-3} (Table 1) and change periodically in the lanthanide series according to double-double effect.

All prepared complexes exhibit similar solid state IR spectra (Table 2). When the acid is converted to salt, the streching vibration of C=O group, ν(C=O) at 1696 cm^{-1} disappears, whereas the bands of asymmetric vibrations ν_{as}(OCO) at 1555–1565 cm^{-1} and the bands of symmetric vibrations (OCO) at 1450–1460 cm^{-1} appear. The IR spectra of rare earth 3-methylglutarates exhibit broad absorption bands with max. at 3380–3450 cm^{-1}, confirming the presence of water molecules linked by hydrogen bonds, the bands of C–H vibrations at 1295–1260, 920–700 cm^{-1} and the bands of metal–oxygen bond at 510–520 cm^{-1}. The splitting for the absorption bands of valency vibrations ν_{as}(OCO) and ν_s (OCO) ($\Delta\nu=\nu_{as}-\nu_s$) in the IR spectra of the complexes have values 95–105 cm^{-1} and are sligtly smaller than for the sodium salt (120 cm^{-1}) suggesting a smaller degree of ionic bond character in these complexes compared to the sodium salt. The bands of ν_{as}(OCO) in the IR spectra of the prepared complexes are shifted to lower frequencies and the bands ν_s(OCO) do not change practically their positions (Table 2). On the basis of spectroscopic criteria [2–4] and our previous study [5, 6] it is possible to suggest that the carboxylate group is bidentate chelating, and complexes exist as polymers. The water molecules are probably in the inner sphere of the complexes, except of the lanthanum complex in which there are inner and outer sphere water molecules, but the coordinated and uncoordinated water molecules are not distinguished by the thermogravimetric curve. Full interpretation of the mode of coordination of metal-ligand would be possible after the determination of the crystallographic and molecular structure of the monocrystals, but they were not obtained so far.

Table 1 Analytical data and solubilities in water at 293 K of Y(III) and lanthanide(III) 3-methylglutarates

Complex	*Ln*/%		C/%		H/%		Solubilities/ 10^{-4} mol dm^{-3}
	calcd.	found	calcd.	found	calcd.	found	
$Y_2L_3\cdot 3H_2O$	26.81	26.8	32.53	32.5	4.52	4.4	1.97
$La_2L_3\cdot 8H_2O$	32.52	32.5	25.31	25.3	4.68	4.6	1.83
$Ce_2L_3\cdot 6H_2O$	34.15	34.2	26.34	26.4	4.39	4.3	2.67
$Pr_2L_3\cdot 3H_2O$	36.69	36.7	28.12	27.1	3.90	3.9	2.66
$Nd_2L_3\cdot 4H_2O$	36.42	36.4	27.27	27.1	4.04	4.1	3.61
$Sm_2L_3\cdot 4H_2O$	37.36	37.4	26.84	26.7	3.97	3.9	3.82
$Eu_2L_3\cdot 5H_2O$	36.26	36.3	25.77	25.9	4.05	4.0	2.94
$Gd_2L_3\cdot 4H_2O$	38.42	38.4	26.38	26.3	3.91	4.0	2.52
$Tb_2L_3\cdot 4H_2O$	38.66	38.6	26.27	26.1	3.89	3.8	2.40
$Dy_2L_3\cdot 3H_2O$	40.07	40.0	26.63	26.6	3.69	3.6	2.07
$Ho_2L_3\cdot 5H_2O$	38.71	38.7	25.35	25.3	4.69	4.6	1.90
$Er_2L_3\cdot 5H_2O$	39.05	39.0	25.20	25.2	3.96	3.9	2.10
$Tm_2L_3\cdot 5H_2O$	39.35	39.3	25.08	24.9	3.95	3.9	2.22
$Yb_2L_3\cdot 4H_2O$	40.71	40.7	25.41	25.4	3.76	3.8	2.41
$Lu_2L_3\cdot 4H_2O$	40.97	41.0	25.29	25.1	3.74	3.6	2.94

$L - C_4H_8(COO)_2^{2-}$

Table 2 Frequencies of characteristic absorption bands in IR spectra of Na(I) and rare earth 3-methylglutarates (cm^{-1})

Complex	ν(OH)	ν_{as}(OCO)	ν_s(OCO)	ν_{as}–ν_s	ν(M–O)
$Y_2L_3\cdot 3H_2O$	3400	1565	1460	105	520
$La_2L_3\cdot 8H_2O$	3400	1560	1460	100	510
$Ce_2L_3\cdot 6H_2O$	3450	1560	1450	100	510
$Pr_2L_3\cdot 3H_2O$	3400	1560	1450	100	510
$Nd_2L_3\cdot 4H_2O$	3400	1560	1460	100	510
$Sm_2L_3\cdot 4H_2O$	3390	1560	1450	105	510
$Eu_2L_3\cdot 5H_2O$	3380	1560	1460	100	520
$Gd_2L_3\cdot 4H_2O$	3400	1555	1460	100	520
$Tb_2L_3\cdot 4H_2O$	3380	1560	1455	110	510
$Dy_2L_3\cdot 3H_2O$	3390	1560	1460	100	510
$Er_2L_3\cdot 5H_2O$	3400	1560	1450	100	520
$Tm_2L_3\cdot 5H_2O$	3400	1560	1460	105	520
$Ho_2L_3\cdot 5H_2O$	3390	1560	1455	105	520
$Yb_2L_3\cdot 4H_2O$	3380	1560	1455	95	520
$Lu_2L_3\cdot 4H_2O$	3400	1560	1460	100	520
$Na_2L_3\cdot nH_2O$	3450	1580	1460	120	540

The 3-methylglutarates of rare earth elements are stable at room temperature and can be stored for several months without change. During heating in air atmosphere they decompose in two or three steps (Figs 1–5). The hydrated complexes are stable

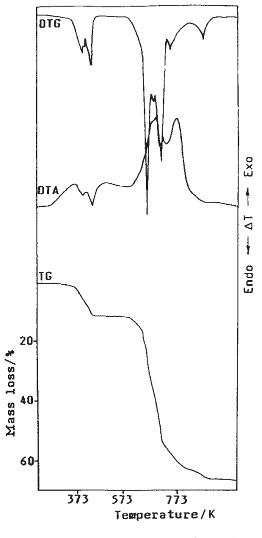

Fig. 1 TG, DTG, DTA curves of $Y_2(C_6H_8O_4)_3\cdot 3H_2O$

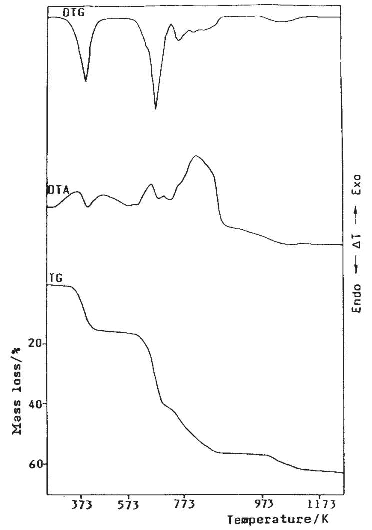

Fig. 2 TG, DTG, DTA curves of $La_2(C_6H_8O_4)_3 \cdot 8H_2O$

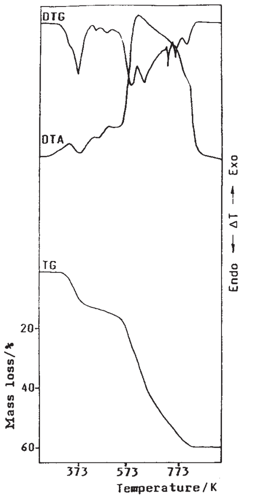

Fig. 3 TG, DTG, DTA curves of $Ce_2(C_6H_8O_4)_3 \cdot 6H_2O$

up to 323–353 K and on further heating they are dehydrated in one step over the range 323–493 K, and transformed to the anhydrous compounds stable to 573–623 K, except of the Ce(III) complex, which is stable up to 493 K. The degree of hydration does not influence the stability of the hydrated 3-methylglutarates. The dehydration process is connected with strong endothermic effect at 413–453 K, only for the Ce(III) complex at 373 K. The anhydrous rare earth 3-methylglutarates heated decompose in different ways over the range 493–1073 K. On heating the anhydrous complexes of

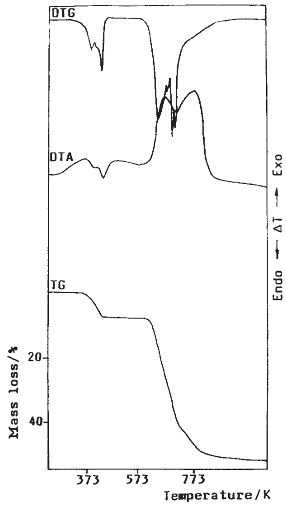

Fig. 4 TG, DTG, DTA curves of $Gd_2(C_6H_8O_4)_3 4H_2O$

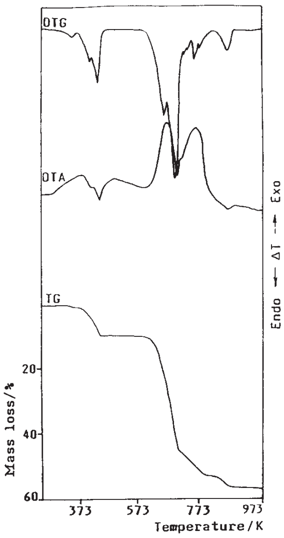

Fig. 5 TG, DTG, DTA curves of $Lu_2(C_6H_8O_4)_3 4H_2O$

Y(III), Nd(III)–Gd(III) decompose over the range 573–623 to 873–1073 K to oxides Ln_2O_3 with intermediate formation oxocarbonates $Ln_2O_2CO_3$ (Figs 1, 2, 4), whereas the anhydrous complexes of Ce(III), Pr(III) and Tb(III)–Lu(III) decompose directly to Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 over the range 493–623 to 803–903 K (Figs 3, 5). The combustion of the organic ligand and products of its decomposition are connected with strong exothermic effect.

Table 3 Thermoanalytical data of Y(III) and lanthanide(III) 3-methylglutarates

Complex	ΔT_1/K	Mass loss/%		n H_2O	ΔT_2/K	Mass loss%/		ΔT_3/K	Mass loss/%		T_k/K
		calcd.	found			calcd.	found		calcd.	found	
$Y_2L_3 \cdot 3H_2O$	323–433	8.13	8.2	3	593–793	61.99	62.0	793–873	65.99	66.0	873
$La_2L_3 \cdot 8H_2O$	323–453	16.80	16.7	8	573–983	56.84	57.0	983–1073	61.24	62.0	1073
$Ce_2L_3 \cdot 6H_2O$	323–473	13.17	13.0	6	–	–		493–803	58.00	58.0	803
$Pr_2L_3 \cdot 3H_2O$	363–463	7.03	7.0	3	–			603–893	54.80	55.0	893
$Nd_2L_3 \cdot 4H_2O$	333–443	9.09	9.0	4	593–833	52.01	52.0	833–973	57.51	57.5	973
$Sm_2L_3 \cdot 4H_2O$	353–453	8.95	9.0	4	603–813	51.96	52.0	813–913	56.66	56.7	913
$Eu_2L_3 \cdot 5H_2O$	323–443	10.74	10.5	5	583–793	54.0	54.0	793–903	58.00	58.0	903
$Gd_2L_3 \cdot 4H_2O$	333–433	8.80	9.0	4	583–713	51.71	52.0	713–993	55.71	56.0	993
$Tb_2L_3 \cdot 4H_2O$	373–443	8.75	8.7	4	–	–		613–853	54.52	54.5	853
$Dy_2L_3 \cdot 3H_2O$	353–443	6.67	7.0	3	–	–		593–893	54.00	54.0	893
$Ho_2L_3 \cdot 5H_2O$	323–423	10.56	10.5	5	–	–		613–903	55.65	56.0	903
$Er_2L_3 \cdot 5H_2O$	333–443	10.50	10.5	5	–	–		623–843	55.34	55.3	843
$Tm_2L_3 \cdot 5H_2O$	333–493	10.45	10.5	5	–	–		593–863	55.07	55.0	863
$Yb_2L_3 \cdot 4H_2O$	343–443	8.47	8.5	4	–	–		623–843	53.64	53.5	843
$Lu_2L_3 \cdot 4H_2O$	353–423	8.43	8.5	4	–	–		593–903	53.40	53.5	903

L – $C_4H_8(COO)_2^{2-}$
ΔT_1 – temperature range of dehydration
ΔT_2 – temperature range of decomposition of $Ln_2O_2CO_3$
ΔT_3 – temperature range of decomposition of oxides
T_k– temperature of oxide formation

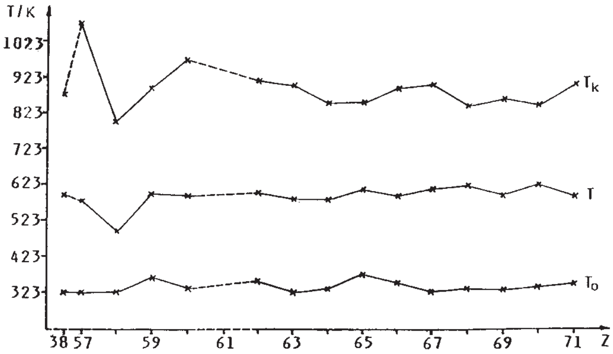

Fig. 6 Relationship between T_o, T, T_k and Z of Ln(III)

The results suggest the following schemes of the thermal decomposition of rare earth 3-methylglutarates:

$$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$$

Ln=Y, La, Nd–Gd, n=3, 4, 5, 8

$$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7$$

Ln=Ce, Pr, Tb–Lu, n=3, 4, 5, 6

The temperatures of dehydration (T_o) and decomposition (T) of different rare earth complexes are similar to each other and change insignificantly in the lanthanide series. Temperatures of oxide formation (T_k) change periodically with increasing the atomic number Z of the metal according the double-double effect. Lanthanum oxide is formed at the highest temperature (1073 K), whereas CeO_2 at the lowest one (803 K). The temperature of Y_2O_3 formation (873 K) is similar to those of heavy lanthanide oxide formation, what is connected with the contraction effect. Almost always the temperature of CeO_2 formation has the lowest value and the temperature of La_2O_3 formation the highest value in the lanthanide series [7–9].

References

1 F. Beilstein, Handbuch der organischen Chemie, Bd 2, Springer Verlag, Berlin 1939.
2 K. Itoh and H. J. Bernstein, Canad. J. Chem., 34 (1956) 170.
3 B. S. Manhas and A. K. Trikha, J. Indian Chem., 59 (1982) 315.
4 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York 1978.
5 W. Brzyska and W. Wołodkiewicz, Polish J. Chem., 71 (1997) 285.
6 W. Brzyska, W. Wołodkiewicz, Z. Rzączyńska and T. Głowiak, Monatsh. Chem., 126 (1995) 285.
7 W. Brzyska and W. Oźga, Thermochim. Acta, 273 (1996) 205.
8 W. Brzyska and W. Oźga, Thermochim. Acta, 288 (1996) 113.
9 W. Brzyska and E. Świta, Thermochim. Acta, 255 (1995) 191.