

THERMAL AND SPECTRAL STUDIES OF Y(III) AND LANTHANIDE(III) COMPLEXES WITH MESACONIC ACID

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(Received in revised form October 11, 2001)

Abstract

Y(III) and lanthanide(III) mesaconates were prepared as crystalline solids with general formula $\text{Ln}_2(\text{C}_5\text{H}_4\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, where $n=7$ for La–Pr, $n=4$ for Y, Nd–Ho, $n=8$ for Er–Lu. IR spectra of the prepared mesaconates suggest that carboxylate groups are bidentate bridging and chelating. During heating the hydrated complexes are dehydrated in one (Y, Nd–Lu) or two steps (La–Pr) and then decompose directly to oxides (Y, Ce, Pr, Sm, Gd–Lu) or with intermediate formation $\text{Ln}_2\text{O}_2\text{CO}_3$ (La, Nd, Eu).

Keywords: DTA, IR spectra, mesaconate, rare earth elements, synthesis, TG

Introduction

Mesaconic acid ($\text{C}_5\text{H}_6\text{O}_4$) is a crystalline solid soluble in water, ethanol, ether, CHCl_3 and CS_2 [1]. Its compounds of NH_4 , Na, K, Ca and Ba [1] were prepared as solids soluble in water, whereas the complexes of Ag(I), Hg(II), Cu(II) and Pb(II) as sparingly soluble in water. The complexes of Y(III) and lanthanides(III) have not been prepared.

The aim of our work was to study some physicochemical properties and thermal decomposition of Y(III) and all series of lanthanide(III) mesaconates under the same conditions and determine the changes of the data in the lanthanide family.

Experimental

The complexes of mesaconic acid with Y(III) and lanthanide(III) from La to Lu (without Pm) were prepared by adding equivalent amount of 0.2 M solution of ammonium mesaconate (pH 5–5.5) to a hot 0.2 M solution of Y(III) and lanthanide(III) chloride (cerium(III) was used as nitrate) (pH 4.5). The precipitate formed was heated in mother liquor for 0.5 h at 343–353 K, filtered off, washed with hot water to remove NH_4^+ ions and dried at 303 K to a constant mass. The carbon and hydrogen contents in the prepared mesaconates were determined by elemental analysis (Perkin Elmer

CHN 2400). Contents of yttrium and lanthanide were determined from TG curve and by heating the prepared complexes to oxides at 1273 K. The content of crystallization water molecules were calculated from TG curve and by heating the complexes at suitable temperature (Table 1).

Table 1 Analytical data

Complex	C/%		H/%		M/%	
	calc.	found	calc.	found	calc.	found
Y ₂ L ₃ ·4H ₂ O	28.39	28.34	3.18	3.04	28.03	28.2
La ₂ L ₃ ·7H ₂ O	22.83	22.90	3.32	3.16	35.24	35.5
Ce ₂ L ₃ ·7H ₂ O	22.84	22.84	3.32	3.19	35.75	36.4
Pr ₂ L ₃ ·7H ₂ O	22.72	23.32	3.31	3.27	35.57	35.4
Nd ₂ L ₃ ·4H ₂ O	24.10	23.91	2.71	2.66	38.73	38.3
Sm ₂ L ₃ ·4H ₂ O	23.78	23.72	2.66	2.56	39.72	39.6
Eu ₂ L ₃ ·4H ₂ O	23.40	23.65	2.63	2.54	39.46	39.6
Gd ₂ L ₃ ·4H ₂ O	23.35	23.45	2.62	2.51	40.80	40.6
Tb ₂ L ₃ ·4H ₂ O	23.25	22.69	2.60	2.86	41.05	40.8
Dy ₂ L ₃ ·4H ₂ O	23.04	23.45	2.58	2.51	41.59	41.9
Ho ₂ L ₃ ·4H ₂ O	22.89	22.93	2.54	2.40	41.96	42.0
Er ₂ L ₃ ·8H ₂ O	20.86	20.96	3.19	3.07	38.74	38.7
Tm ₂ L ₃ ·8H ₂ O	20.77	20.89	3.25	3.08	39.00	39.0
Yb ₂ L ₃ ·8H ₂ O	20.58	20.75	3.28	3.15	39.57	39.5
Lu ₂ L ₃ ·8H ₂ O	20.49	20.59	3.20	3.01	39.84	40.1



IR spectra of the prepared complexes and spectra of mesaconic acid and its sodium salt were recorded as KBr discs on a Specord M 80 Spectrophotometer (4000–400 cm⁻¹). The powder diffractograms in the complexes were recorded using X-ray diffractometer HZG 4 AZ. The thermal stability of the prepared mesaconates were investigated by TG, DTG and DTA curves. Measurements were made with a Q 1500 D derivatograph by method described in [2]. The products of decomposition were calculated from TG curve and verified by diffractograms registration.

Results and discussion

Mesaconates of Y(III) and lanthanide(III) from La to Lu (without Pm) were prepared as crystalline solids with colour characteristic for hydrated lanthanide ions and with molar ratio of metal to organic ligand of 2.0:3.0 and general formula Ln₂(C₃H₄O₄)₃·nH₂O, where n=7 for La–Pr, n=4 for Y, Nd–Ho and n=8 for Er–Lu. The prepared complexes are char-

acteristic due to their low symmetry and are isostructural in the 3 groups: La–Pr; Y, Nd–Ho and Er–Lu.

Table 2 Frequencies of characteristic bands in IR spectra of Na(I), Y(III) and lanthanide(III) mesaconates (cm^{-1})

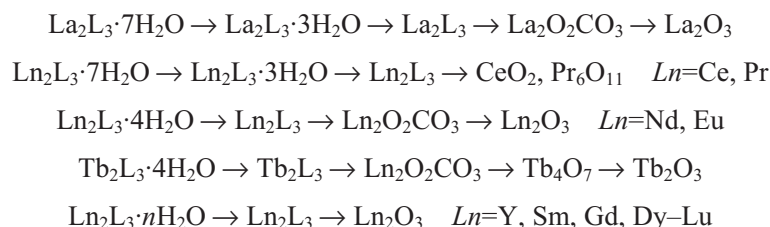
Complex	$\nu(\text{OH})$	$\delta(\text{H}_2\text{O})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu_{\text{as}}-\nu_{\text{s}}$	$\nu(\text{M}-\text{O})$
$\text{Y}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3408	1620	1568/1544	1420	148/124	552
$\text{La}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	3424	1610	1560/1536	1408	152/128	548
$\text{Ce}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	3416	1610	1564/1544	1408	156/136	548
$\text{Pr}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	3424	1620	1560/1544	1408	152/136	552
$\text{Nd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3424	1620	1568/1534	1412	156/122	552
$\text{Sm}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3424	1620	1560/1534	1412	148/122	549
$\text{Eu}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3424	1620	1566/1544	1412	154/132	544
$\text{Gd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3400	1620	1568/1544	1416	152/128	544
$\text{Tb}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3424	1620	1568/1544	1416	152/128	540
$\text{Dy}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3408	1620	1568/1548	1416	152/128	540
$\text{Ho}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	3424	1610	1568/1544	1416	152/128	540
$\text{Er}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	3408	1620	1576/1536	1416	160/120	540
$\text{Tm}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	3408	1620	1582/1540	1416	166/124	540
$\text{Yb}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	3424	1610	1588/1536	1420	166/116	540
$\text{Lu}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	3424	1610	1588/1544	1420	168/124	540
$\text{Na}_2\text{L} \cdot n\text{H}_2\text{O}$	3424		1568	1388	180	

All the prepared mesaconates exhibit similar solid state IR spectra (Table 2). When the acid is converted to the complex, the bands of stretching vibration of C=O group, $\nu(\text{C}=\text{O})$ in COOH at 1688 cm^{-1} disappears, whereas the bands of asymmetric vibrations $\nu_{\text{as}}(\text{OCO})$ at $1588\text{--}1560$ and $1548\text{--}1534 \text{ cm}^{-1}$ and the bands of symmetric vibrations $\nu_{\text{s}}(\text{OCO})$ at $1420\text{--}1408 \text{ cm}^{-1}$ appear. In IR spectra of the prepared complexes there are broad absorption bands of (OH) with max. at $3420\text{--}3408 \text{ cm}^{-1}$ and narrow bands of $\delta(\text{H}_2\text{O})$ at $1620\text{--}1610 \text{ cm}^{-1}$ confirming the presence of crystallization water molecules linked by hydrogen bonds, the bands of C–H vibrations at $1100, 900\text{--}700 \text{ cm}^{-1}$. The bands of $\nu_{\text{as}}(\text{OCO})$ are split, which is shown on the diversity of the coordination mode. The values of $\Delta\nu = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})$ have values $168\text{--}152$ and $132\text{--}120 \text{ cm}^{-1}$ and are smaller than those of the sodium salt ($\Delta\nu = 180 \text{ cm}^{-1}$) suggesting a smaller degree of ionic bond characteristic for the mesaconates compared to the sodium salt. Some of the $\nu_{\text{as}}(\text{OCO})$ are shifted to higher frequencies (1588 cm^{-1}) or have the same values compared to the sodium salt (1568 cm^{-1}), and the others are shifted to lower frequencies ($1548\text{--}1534 \text{ cm}^{-1}$), and the $\nu_{\text{s}}(\text{OCO})$ are to higher frequencies. On the basis of spectroscopic criteria [3, 4] and our previous work [5, 6] it is possible to suggest that the carboxylate groups are bidentate chelating and bridging, and the mesaconates exist as

polymeric complexes. Taking into account the high value of the coordination number characteristic for lanthanide (CN=9 for light element and CN=8 for heavy ones), it can suggest that the water molecules are probably in the inner and outer sphere of the complexes but coordinated and uncoordinated water molecules are not distinguished (except of La–Pr complexes) by 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 of the complexes, but they have not been obtained so far.

The prepared complexes are stable at room temperature and can be stored for several months without change. During heating they are decomposed in two, three or four steps (Table 3, Figs 1–3). The hydrated mesaconates are stable up to 300–350 K and on further heating they are dehydrated in one (Y, Nd–Lu) or two steps (La–Pr) forming anhydrous complexes, which are stable up to 493–616 K. The complexes of La, Ce and Pr during heating lose first four and next three water molecules. The dehydration process is connected with strong endothermic effect (Table 3). The anhydrous complexes heated decompose to oxides Ln_2O_3 , Pr_6O_{11} , Tb_4O_7 (next at 1273 K Tb_2O_3), whereas the complexes of La, Nd and Eu decompose to oxides Ln_2O_3 with intermediate formation $\text{Ln}_2\text{O}_2\text{CO}_3$. The combustion of the organic ligand and products of decomposition are connected with a very strong exothermic effect at 573 C (Ce)–715 K (Y). The exothermic effect connected with combustion of organic ligand is so strong that in many causes it masks the endothermic effect attached with the decomposition of the complexes. The decomposition of the oxocarbonates is accompanied with an endothermic effect.

The results indicated that the prepared mesaconates decompose in the following way:



The temperatures of dehydration (T_0) of different lanthanide complexes are similar to each other and change in the lanthanide series (Table 3, Fig. 4) from 300–350 K. The temperatures of decomposition (T_D) changes from 493 K for Ce(III) to 619 K for Ho(III). The temperatures over which the oxides exist change periodically in the lanthanide series. Cerium(IV) oxide is formed at the lowest temperature (845 K) whereas La_2O_3 at the lowest one (1107 K). The lanthanide oxides from Ho to Lu exist over 1073 K. The temperature of CeO_2 formation almost always has the lowest value in the lanthanide family [2, 6, 7].

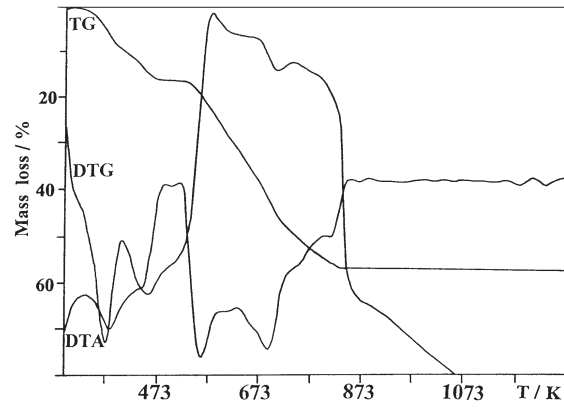


Fig. 1 TG, DTG and DTA curve of $\text{Ce}_2(\text{C}_5\text{H}_4\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$

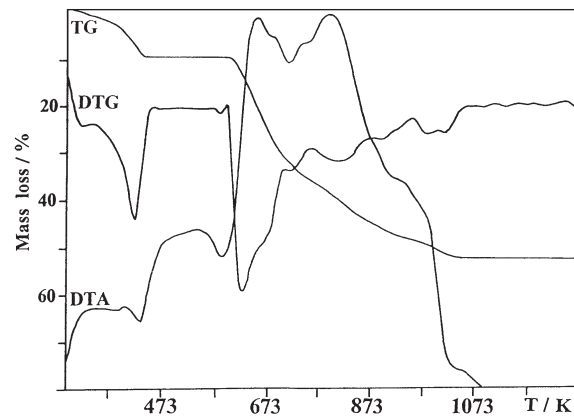


Fig. 2 TG, DTG and DTA curve of $\text{Gd}_2(\text{C}_5\text{H}_4\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$

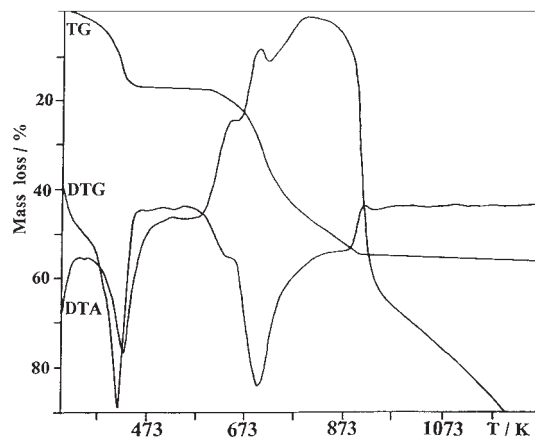


Fig. 3 TG, DTG and DTA curve $\text{Tm}_2(\text{C}_5\text{H}_4\text{O}_4)_3 \cdot 8\text{H}_2\text{O}$

Table 3 Data of thermal decomposition of Y(III) and lanthanide(III) complexes with mesaconic acid

Complex	$\Delta T_1/K$	Mass loss/%		n H ₂ O	$\Delta T_2/K$	Mass loss/%		$\Delta T_3/K$	Mass loss/%		DTA/ K endo	DTA/ K exo	DTG/ K	T_K/K
		calc.	found			calc.	found		calc.	found				
Y ₂ L ₃ ·4H ₂ O	330–440	11.36	11.2	4	–	–	–	608–1005	64.40	64.0	423, 573	633	715	1005
La ₂ L ₃ ·7H ₂ O	300–400	9.14	8.8	4	–	–	–	–	–	–	–	–	–	–
	400–493	16.00	15.9	3	552–873	53.08	52.8	1018–1107	58.73	58.4	390, 480, 973	573	693	1107
Ce ₂ L ₃ ·7H ₂ O	328–390	9.14	9.0	4	–	–	–	–	–	–	–	–	–	–
	390–490	16.00	15.8	3	–	–	–	520–841	56.63	56.5	373, 449	593	573	845
Pr ₂ L ₃ ·7H ₂ O	328–398	9.10	9.1	4	–	–	–	–	–	–	–	–	–	–
	398–470	15.92	15.6	3	–	–	–	572–973	57.05	57.2	371, 434	623	623	973
Nd ₂ L ₃ ·4H ₂ O	323–467	9.66	9.6	4	570–965	48.92	49.0	965–1086	54.83	55.0	453, 573, 1053	643	633	1086
Sm ₂ L ₃ ·4H ₂ O	350–463	9.50	9.3	4	–	–	–	592–1071	53.94	54.1	453, 588	665	643	1071
Eu ₂ L ₃ ·4H ₂ O	330–458	9.40	9.3	4	578–937	47.92	47.8	937–1029	53.69	54.1	380, 903	623	603	1029
Gd ₂ L ₃ ·4H ₂ O	328–455	9.34	9.3	4	–	–	–	588–1051	52.98	53.2	428, 573	639	623	1051
Tb ₂ L ₃ ·4H ₂ O	328–446	9.31	9.0	4	–	–	–	612–1043	51.72	52.0	433, 593	653	673	1043
Dy ₂ L ₃ ·4H ₂ O	338–444	9.22	9.0	4	–	–	–	605–1063	52.26	52.0	423, 573	613	673	1063
Ho ₂ L ₃ ·4H ₂ O	328–435	9.15	9.0	4	–	–	–	616–1073	51.94	52.0	406, 603	678	663	1073
Er ₂ L ₃ ·8H ₂ O	329–450	16.70	16.5	8	–	–	–	585–1073	55.68	55.7	433, 573	703	683	1073
Tm ₂ L ₃ ·8H ₂ O	328–456	16.63	16.5	8	–	–	–	568–1073	55.47	55.4	415, 583	718	698	1073
Yb ₂ L ₃ ·8H ₂ O	323–454	16.48	16.5	8	–	–	–	575–1073	54.94	55.0	415, 573	715	690	1073
Lu ₂ L ₃ ·8H ₂ O	328–450	16.30	16.1	8	–	–	–	569–1073	54.70	54.3	423	708	698	1073

ΔT_1 – temperature range of dehydration, ΔT_2 – temperature range of decomposition to Ln₂O₂CO₃, ΔT_3 – temperature range of decomposition to oxides
 Ln₂O₂CO₃, CeO₂, Pr₆O₁₁, Tb₄O₇, T_K – temperature over which the oxides exist

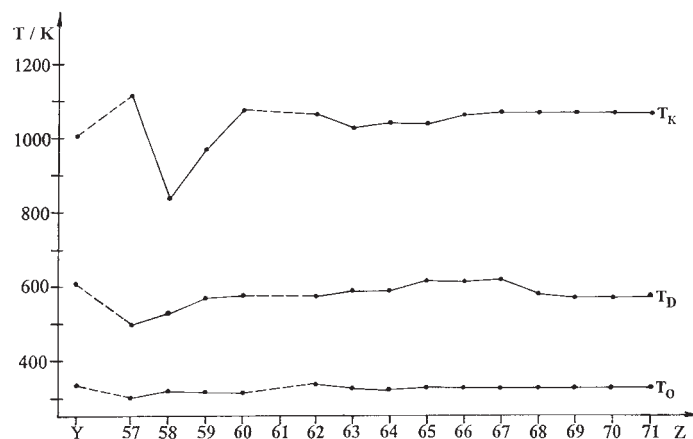


Fig. 4 The relationship between T_0 , T_D , T_K and Z of Ln(III)

Conclusions

Complexes of Y(III) and lanthanide(III) with mesaconic acid were prepared as crystalline solids with molar ratio of metal to organic ligand of 2.0 : 3.0 and general formula $\text{Ln}_2\text{L}_3 \cdot n\text{H}_2\text{O}$, where $n=4, 7, 8$. The carboxylate groups in the complexes are bidentate bridging and chelating. The oxygen atoms of the carboxylate groups are not only coordinated to metal ions, but they are linked with hydrogen bonds to the water molecules of crystallization. The water molecules are probably in inner and outer sphere of the complexes. The complexes are isostructural in the groups: La–Pr, Nd–Ho and Y, and Ho–Lu. During heating the hydrated complexes of Y, Nd–Lu lose crystallization water molecules in one step, whereas these of La–Pr in two steps. Next the anhydrous complexes heated decompose to oxides (Y, Ce, Sm, Gd – Lu) without forming stable indirect compounds or with intermediate formation of $\text{Ln}_2\text{O}_2\text{CO}_3$ (La, Nd, Eu). The temperatures of dehydration of the prepared complexes are similar to each other. The temperatures over which the oxides are formed change periodically in the lanthanide series from 845 K for cerium(III) complex to 1107 K for lanthanum(III) one.

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