Polish J. Chem., **75**, 43–47 (2001)

Spectral and Thermal Investigations of Y(III) and Lanthanide(III) Complexes with 3,3-Dimethylglutaric Acid

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(Received August 3rd, 2000; revised manuscript September 8th, 2000)

Conditions for the preparation of Y(III) and lanthanide(III) (La–Lu) 3,3-dimethylglutarates were investigated and their quantitative composition and solubility in water at 293 K were determined (10^{-2}–10^{-5} mole dm^{-3}). The IR spectra of the complexes prepared with the general formula $Ln_2\{C_5H_{10}(COO)_2\}_3 \cdot nH_2O$ (n = 2–15) were recorded and their thermal decomposition in air were investigated. During heating the hydrated 3,3-dimethylglutarates are dehydrated in one (La, Ce, Pr, Sm, Gd, Lu), two (Y, Nd, Eu, Dy, Ho, Tm) or three (Tb, Er) steps and next the anhydrous complexes and dihydrated Yb(III) complex decompose to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 with intermediate formation $Ln_2O_2CO_3$ except of Ce(III) complex, which decomposes directly to CeO_2. The carboxylate groups in the complexes studied are bidentate.

Key words: DTA, IR spectra, 3,3-dimethylglutarate, syntheses, TG

3,3-Dimethylglutaric acid, $C_5H_{10}(COOH)_2$, is a crystalline solid soluble in water and ethanol [1]. It is used in the synthesis of (+)-bicyclohumelone, an important perfume component [2]. Compounds of 3,3-dimethylglutaric acid with metal ions are little known. The complex of La was prepared as a solid with formula $La_2(C_7H_{10}O_4)_3 \cdot 11H_2O$, sparingly soluble in water [3]. The complexes of residue lanthanides have not been studied so far.

The aim of our work was to study some physicochemical properties and thermal decomposition of Y(III) and all series of lanthanide 3,3-dimethylglutarates under the same conditions and to determine the changes of the data in the lanthanide family.

EXPERIMENTAL

The complexes of 3,3-dimethylglutaric acid with Y(III) and lanthanide(III) from La to Lu (without Pm) were prepared by adding equivalent amount of 0.25 M solution of ammonium 3,3-dimethylglutarate to a hot 0.25 M solution of Y(III) or lanthanide(III) chloride. The precipitates formed were heated in mother liquor for 0.5 h at 343–353 K, filtered off, washed with hot water and dried at 303 K to a constant mass.

The carbon and hydrogen contents in the complexes prepared were determined by elemental analysis using Perkin Elmer CHN 2400. Contents of yttrium and lanthanide were determined from TG curve and by ignition of the prepared 3,3-dimethylglutarates to oxides at 1273 K. The content of crystallization water molecules were calculated from TG curve and by heating the complexes at a suitable temperature. The experimental results confirm the calculated data.

IR spectra of the complexes, and spectra of 3,3-dimethylglutaric acid and its sodium salt were recorded as KBr discs of FT–IR 1725 X Perkin Elmer spectrophotometer (range 4000–400 cm^{-1}). The solubility in water was determined at 293 K, preparing the saturated solution isothermally. The concentration of Y(III) and lanthanide(III) ions were determined by spectroscopic method using arsenazo III.

The thermal stability of the complexes prepared was studied by TG, DTG and DTA techniques. Measurements were made with Q 1500 D derivatograph with Derill converter at a heating rate of 10 K for full scale. Samples of 100 mg mass were heated in platinum crucibles in air atmosphere to 1273 K at sensitivity TG = 100 mg. The sensitivity of DTA and DTG curves were regulated by Derill computer program. The products of decomposition were calculated from TG curves and were confirmed by IR spectra and X-ray patterns. Al_2O_3 was used as a standard material.

RESULTS AND DISCUSSION

Y(III) and lanthanide(III) (from La–Lu) 3,3-dimethylglutarates were prepared as solids with molar ratio of metal to organic ligand of 2:3 and a general formula $Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$, where n = 2–15 with colour characteristic for hydrated Ln(III) ions. The complexes prepared are crystalline solids with different structure [4] and a low symmetry. They are soluble in water. Their solubility are of the order 10^{-2}–10^{-3} mole dm^{-3} (Table 1). Only the complexes of La(III) and Ce(III) are sparingly soluble in water. Their solubility is of the order 10^{-5} mole dm^{-3}. The analysis confirm the compositions.

All prepared 3,3-dimethylglutarates exhibit similar solid state IR spectra, though a little difference is observed between the spectra of light and heavy lanthanide complexes (Table 1). When the acid is converted to salt, the stretching vibration of C=O group (ν(C=O) characteristic for free acid, at 1715 and 1690 cm^{-1}) disappears, whereas the bands of asymmetrical vibrations ν_{as}(OCO) at 1550–1580 cm^{-1} and the bands of symmetrical vibrations ν_s(OCO) at 1400 cm^{-1} for light lanthanide complexes and at 1400–1450 cm^{-1} for heavy lanthanide compounds, appear. The IR spectra of Y(III) and lanthanide(III) 3,3-dimethylglutarates exhibit strong broad absorption bands with max. at 3400–3450 cm^{-1} and narrow band at 1630–1610 cm^{-1} confirming the presence of crystallization water molecules linked by hydrogen bonds, the bands of C–H vibrations at 1295–1260, 900–700 cm^{-1} and the bands of metal–oxygen bond at 510–500 cm^{-1}. The bands of metal–oxygen bond for heavy lanthanide complexes are insignificantly shifted to higher frequencies, compared to those for the light lanthanide complexes, what shows that the energy of M–O bonding increases with increasing of the atomic number Z and decreasing of the ionic radius of the metal ions. The splitting for the absorption bands of valence vibrations ν_{as}(OCO) and ν_s(OCO) ($\Delta\nu = \nu_{as} - \nu_s$) in the IR spectra of the complexes have values 145–177 cm^{-1} and are bigger than those for the sodium salt (126 cm^{-1}), suggesting a larger degree of ionic bond character in the complexes prepared, compared to the sodium salt. $\Delta\nu$ changes irregularly in the lanthanide series. The bands of ν_{as}(OCO) in the IR spectra do not change their position for the complexes of heavy lanthanide and are shifted to lower frequencies for the complexes of light lanthanide, compared to those bands for the sodium salt and the bands of ν_s(OCO) are shifted to lower frequencies (20–50 cm^{-1}) (Table 1). On the basis of spectroscopic criteria [5–7] it is possible to suggest that the carboxylate groups are bidentate, but the mode of coordination in the complexes of light lanthanide differs from that in heavy lanthanide complexes. Water molecules are probably in inner and outer spheres (except of ytterbium(III) compound, which has only inner sphere water molecules), but the coordinated and uncoordinated water molecules are not distinguished by the thermogravimetric curve. Probably, the mode of water molecules coordination and the hydrogen bonds influence on the mode of metal–carboxylate group coordination. Full interpretation of the mode of coordination of metal–organic ligand bond would be possible after determination of crystallographic and molecular structure of monocrystals, but they were not obtained so far.

Table 1. Frequencies of characteristic absorption bands in IR spectra of Na(I) and rare earth 3,3-dimethylglutarates (cm^{-1}) and the solubilities.

Complex	ν(OH)	ν_{as}(OCO)	ν_s(OCO)	$\nu_{as} - \nu_s$	ν(M–O)	Solubilities $mol\cdot dm^{-3}$
Y_2L_3* × $10H_2O$	3416	1550	1405	145	504	1.46×10^{-3}
La_2L_3 ×$10H_2O$	3400	1555	1400	155	502	7.19×10^{-5}
Ce_2L_3 × $7H_2O$	3400	1565	1400	164	502	6.42×10^{-5}
Pr_2L_3 × $3H_2O$	3400	1565	1400	165	502	2.76×10^{-2}
Nd_2L_3 × $8H_2O$	3400	1568	1400	168	502	1.76×10^{-2}
Sm_2L_3 × $6H_2O$	3400	1565	1400	165	502	1.10×10^{-3}
Eu_2L_3 × $8H_2O$	3400	1576	1400	176	502	1.54×10^{-3}
Gd_2L_3 × $6H_2O$	3400	1565	1400	165	500	9.89×10^{-3}
Tb_2L_3 ×$15H_2O$	3450	1580	1430	150	510	1.38×10^{-3}
Dy_2L_3 × $9H_2O$	3420	1580	1425	155	510	1.32×10^{-3}
Ho_2L_3 × $10H_2O$	3410	1580	1425	155	510	1.42×10^{-3}
Er_2L_3 × $7H_2O$	3420	1570	1400	170	510	1.58×10^{-3}
Tm_2L_3 × $8H_2O$	3410	1580	1420	160	510	1.77×10^{-3}
Yb_2L_3 × $2H_2O$	3420	1580	1410	170	510	1.18×10^{-3}
Lu_2L_3 × $8H_2O$	3420	1580	1420	160	510	1.94×10^{-3}
Na_2L × nH_2O	3420	1576	1450	126	500	–

*L = $C_5H_{10}(COO)_2^{2-}$

3,3-Dimethylglutarates of yttrium(III) and lanthanide(III) are stable at room temperature and can be stored for several months without change. During heating in air (Table 2) they decompose in different ways in two, three or four steps. The hydrated complexes are stable up to 337–394 K and on further heating they are dehydrated in one (La, Ce, Pr, Sm, Gd, Lu), two (Y, Nd, Eu, Dy, Ho, Tm) or three (Tb, Er) steps, and transformed to the anhydrous compounds stable up to 543 K (Ce) – 659 K (Ho), except of Yb(III) complex, which is stable up to 478 K and then the dehydrated compound decomposes simultaneously with dehydration. The degree of hydration does not influence the stability of the prepared 3,3-dimethylglutarates. The dehydration process is connected with a strong endothermic effect. The anhydrous yttrium(III) and lanthanide(III) 3,3-dimethylglutarates are stable up to 543 K (Ce) to 659 K (Ho). On heating they are decomposed in the range 543–659 K to 733–1070 K to oxides Ln_2O_3, Pr_6O_{11} and Tb_4O_7 with intermediate formation of oxocarbonates $Ln_2O_2CO_3$, whereas the anhydrous complex of Ce(III) decomposes directly to CeO_2 between 543–733 K. Dihydrated ytterbium(III) complex heated decomposes to Yb_2O_3 with intermediate formation of $Yb_2O_2CO_3$. The combustion of organic ligand and products of decomposition are connected with strong exothermic effect.

Table 2. Thermoanalytical data of Y(III) and lanthanide(III) 3,3-dimethylglutarates.

Complex	ΔT_1 (K)	Mass loss (%)		n H_2O (mol)	ΔT_2 (K)	Mass loss (%)		T_k (K)
		calcd.	found.			calcd.	found.	
Y_2L_3*×$10H_2O$	387–483	4.3	4.4	2				
	503–333	21.6	21.6	10	633–900	72.8	73.0	900
La_2L_3×$10H_2O$	345–575	19.3	19.0	10	593–1070	65.0	65.0	1070
Ce_2L_3×$7H_2O$	337–428	14.3	14.2	7	543–733	60.9	61.0	733
Pr_2L_3×$3H_2O$	350–411	6.6	7.0	3	627–880	57.9	58.0	880
Nd_2L_3×$8H_2O$	350–380	3.9	4.0	2				
	525–582	15.9	16.0	8	633–953	62.8	63.0	953
Sm_2L_3×$6H_2O$	345–417	12.2	12.0	6	617–920	60.5	60.5	920
Eu_2L_3×$8H_2O$	350–413	5.9	6.0	3				
	493–603	15.6	15.8	8	608–893	61.8	62.0	893
Gd_2L_3×$6H_2O$	350–410	12.0	12.0	6	642–895	59.8	60.0	895
Tb_2L_3×$15H_2O$	360–403	3.39	3.40	2				
	433–473	10.10	10.10	6				
	475–535	25.40	25.00	15	631–893	64.79	64.60	893
Dy_2L_3×$9H_2O$	360–413	3.75	3.70	2				
	472–533	16.85	16.90	9	625–958	61.18	61.20	958
Ho_2L_3×$10H_2O$	394–427	3.61	3.60	2				
	490–541	18.29	18.00	10	659–925	61.59	62.00	925
Er_2L_3×$7H_2O$	343–368	3.80	3.80	2				
	393–413	5.78	6.00	3				
	495-613	13.48	13.50	7	636–923	59.00	59.00	923
Tm_2L_3×$8H_2O$	393–463	1.88	2.00	1				
	468–545	15.05	15.00	8	623–984	59.58	59.60	984
Yb_2L_3×$2H_2O$					478–1018	53.90	53.70	1018
Lu_2L_3×$8H_2O$	393–513	9.25	9.00	5	633–960	58.88	58.80	960

*L = $C_5H_{10}(COO)_2^{2-}$
ΔT_1 – temperature range of dehydration
ΔT_2 – temperature range of decomposition to oxides
T_k – temperature of oxide formation

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

$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3, CeO_2, Pr_6O_{11}$, Ln = La, Sm, Gd, Lu

$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \cdot mH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3$ Ln = Y, Nd, Eu, Dy, Ho, Tm

$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3{\cdot}mH_2O \rightarrow Ln_2L_3{\cdot}zH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3, Tb_4O7,$
Ln = Er

$Ce_2L_3{\cdot}7H_2O \rightarrow Ce_2L_3 \rightarrow CeO_2$

$Yb_2L_3{\cdot}2H_2O \rightarrow Yb_2O_2CO_3 \rightarrow Yb_2O_3$

The temperatures of dehydration (T_1) and decomposition (T_2) (except of Ce and Yb) are similar to each other and change insignificantly in the lanthanide series. Temperatures of the oxide formation (T_k) change periodically with increasing the atomic number Z of the metal, according the double–double effect (Fig. 1). Lanthanum(III) oxide is formed at the highest temperature (1070 K), whereas CeO_2 at the lowest one (733 K). The temperature of Y_2O_3 formation (900 K) is similar to those of heavy lanthanide oxide formation, what is connected with the contraction effect and similarity of the ionic radii. Almost always the temperature of CeO_2 formation has the lowest value in the lanthanide series [8,9].

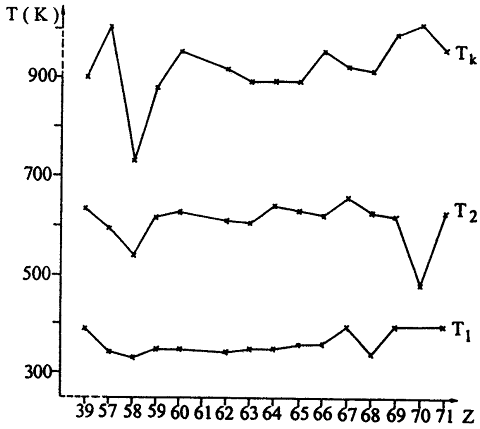

Figure 1. Relationship between T_1, T_2, T_k and Z of Ln(III).

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