Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 937–949

SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF RARE EARTH ELEMENTS WITH 1,1-CYCLOBUTANEDICARBOXYLIC ACID

Z. Rzączyńska and A. Bartyzel

Department of General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University,
20-031 Lublin, Poland

(Received January 9, 2002)

Abstract

The complexes of yttrium and lanthanide with 1,1-cyclobutanedicarboxylic acid of the formula: $Ln_2(C_6H_6O_4)_3 \cdot nH_2O$, where n=4 for Y, Pr–Tm, n=5 for Yb, Lu, n=7 for La, Ce have been studied. The solid complexes have colours typical of Ln^{3+} ions. During heating in air they lose water molecules and then decompose to the oxides, directly (Y, Ce, Tm, Yb) or with intermediate formation. The thermal decomposition is connected with released water (313–353 K), carbon dioxide, hydrocarbons (538–598 K) and carbon oxide for Ho and Lu. When heated in nitrogen they dehydrate to form anhydrous salt and next decompose to the mixture of carbon and oxides of respective metals. IR spectra of the prepared complexes suggest that the carboxylate groups are bidentate chelating.

Keywords: complexes, 1,1-cyclobutanedicarboxylates of rare earth elements, IR spectra, thermal analysis

Introduction

The 1,1-cyclobutanedicarboxylate ligand has been used much as a component of platinum complexes studied as potential antitumor drugs. The most useful famous compound is platinum(II) *cis*-diamine(1,1-cyclobutanedicarboxylate) known as carboplatin or paraplatin. Carboplatin is currently the therapeutically most important second-generation platinum complex. It produces an equally strong antitumor effect as cisplatin, but carboplatin is less nephrotoxic than cisplatin. The cytotoxic activity is also exhibited by carboplatin derivatives in which two amine ligands have been replaced by different ligands, e.g. 1,2-bis(fluorophenyl)ethylenediamine or crown ester-linked bipyridine homologs [1–5]. Another compound of 1,1-cyclobutane-dicarboxylic acid is palladium(II) *cis*-diamine(1,1-cyclobutanedicarboxylate). It was shown to be isostructural with carboplatin, i.e. forms a square-planar complex [5, 6]. 1,1-Cyclobutanedicarboxylic acid is a solid crystalline substance. Crystals of 1,1-cyclobutanedicarboxylic acid are monoclinic, space group $P2_1/c$, with four molecules per unit cell (Fig. 1). The crystal structure consists of infinite chains of mole-

1418–2874/2002/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

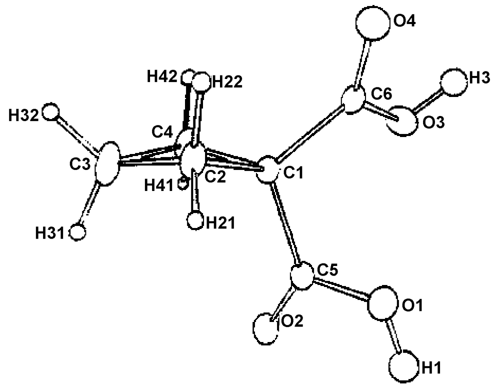

Fig. 1 Structure of 1,1-cyclobutanedicarboxylic acid [8]

cules, with each molecule hydrogen bonded to two others across centers of symmetry. Both carbonyl groups in 1,1-cyclobutanedicarboxylic acid do, in fact, assume nearly synplanar conformation. An unusual electron density distribution for one carbon atom (C3) in the cyclobutane ring suggests a dynamic inversion of the ring conformation [7]. The structure of 1,1-cyclobutanedicarboxylic acid has also been determined at 20 K. At room temperature the structure is disordered, with atom C3 (Cγ) of the cyclobutane ring occupying sites on each side of the plane of the other three ring atoms. At 20 K the structure is ordered, one site is fully populated. Similarly, as at room temperature the carboxyl groups adopt synplanar conformation, with $C_β$–$C_α$=O torsion angles of –1.7° (C4–C1–C5–O2) and –5.2°, at room temperature the respective values are 2 and 8° [8]. 1,1-Cyclobutanedicarboxylic acid melts at 154–157°C and in the range 210–220°C decomposes to cyclobutanecarboxylic acid. It is soluble in water, sparingly soluble in ether, benzene, and chloroform. Its primary dissociation constant at 25°C is equal to $7.7\cdot10^{-4}$. The compounds of 1,1-cyclobutanedicarboxylic acid with cobalt, nickel and copper have been studied. There exist compounds of general formula $ML\cdot nH_2O$, where n=1 for M=Co, Cu and n=3 for M=Ni, where the Co complex has an octahedral structure, the Cu complex has a tetragonal structure and Ni compound structure is octahedral [9]. Still another compound is beryllium(II) 1,1-cyclobutanedicarboxylate, which forms monoclinic, dihydrated complexes of formula $K_2[Be(C_4H_6(COO_2)_2]\cdot2H_2O$ [10].

The aim of our work was to prepare the complexes of Y(III) and lanthanides(III) with 1,1-cyclobutanedicarboxylic acid in the solid state and to examine some of their properties and thermal stability during heating to 1273 K.

Experimental

The complexes of Y(III) and lanthanide(III) from La, Nd–Lu (except for Pm) were prepared by adding a hot aqueous solution of 1,1-cyclobutanedicarboxylic acid to freshly-precipitated rare earth hydroxides. The complexes of Y, La–Er were precipitated, but compounds of Tm(III), Yb(III) and Lu(III) were obtained by crystallisation from an aqueous solution. The solids formed were filtered off, washed with hot water and dried at 303 K to a constant mass. Cerium(III) complex was prepared by the addition of the equivalent quantities of 0.1 M ammonium 1,1-cyclobutanedicarboxylate (pH≈5.5) to a hot solution of cerium(III) nitrate(V). The precipitate formed was filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass.

The contents of carbon and hydrogen were determined on the basis of elemental analysis by using a CHN 2400 Perkin Elmer analyser. Some of the results are presented in Table 1.

Table 1 The results of the elemental analysis some of 1,1-cyclobutanedicarboxylates complexes

Complex	M%		C%		H%	
	calc.	found	calc.	found	calc.	found
$Y_2L_3{\cdot}4H_2O$	26.31	26.30	31.96	31.78	3.85	3.73
$La_2L_3{\cdot}4H_2O$	33.48	33.89	26.03	25.96	3.86	3.74
$Pr_2L_3{\cdot}4H_2O$	36.14	35.94	27.70	27.63	3.33	3.30
$Gd_2L_3{\cdot}4H_2O$	38.71	39.08	26.58	25.97	3.94	3.25
$Tb_2L_3{\cdot}4H_2O$	38.96	38.92	26.47	26.32	3.19	2.88
$Ho_2L_3{\cdot}4H_2O$	39.84	39.68	26.09	25.89	3.14	2.86
$Tm_2L_3{\cdot}4H_2O$	40.42	40.48	25.84	25.56	3.11	2.99
$Lu_2L_3{\cdot}5H_2O$	40.41	40.52	24.94	24.95	3.23	2.89

L=$C_6H_6O_4$

IR spectra of the complexes were recorded over the range 4000–400 cm^{-1} by using a spectrometer FTIR 1725X Perkin Elmer. The samples were prepared as KBr discs (Table 2, Fig. 2). X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss Jena) diffractometer by using Ni filtered CuK_α radiation. The measurements were made within the range 2Θ=4–80° by means of the Debye–Scherrer–Hull method (Fig. 3). The thermal stability and decomposition of the prepared complexes in air were determined with the aid of a Paulik–Paulik–Erdey Q-1500D derivatograph with Derill converter, recording TG, DTA and DTG curves. Samples (100 mg) were heated in platinum crucibles at 293–1273 K in static air with a heating rate of 10 K min^{-1}. The products of decomposition were calculated from TG curves (Table 3). Thermogravimetric measurements of the selected complexes were also carried out in flowing nitrogen atmosphere by using a TGA 2950 high-resolution thermogravimetric analyzer. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. TG curves were recorded at a heating rate of β=5 K min^{-1} in the temperature range of 293–1273 K. The gas-phase products of decomposition were identified by using a Netzsch TG apparatus coupled with a Bruker FTIR IF566 spectrophotometer. The samples were heated in flowing argon atmosphere to 1223 K. DSC curves were obtained up to 873 K with a Netzsch

DSC 204, by using an aluminium closed crucible, in argon atmosphere, at a heating rate of 10 K min^{-1}.

Table 2 Spectroscopic data of COO^- groups 1,1-cyclobutanedicarboxylates of yttrium(III), lanthanides(III), Na and 1,1-cyclobutanedicarboxylic acid (cm^{-1})

Complex	ν_{asCOO^-}	ν_{sCOO^-}	$\Delta\nu_{COO^-}$
$Y_2L_3 \cdot 4H_2O$	1548	1376	172
$La_2L_3 \cdot 7H_2O$	1554	1385	169
$Ce_2L_3 \cdot 7H_2O$	1558	1366	192
$Pr_2L_3 \cdot 4H_2O$	1544	1366	178
$Nd_2L_3 \cdot 4H_2O$	1564	1360	204
$Sm_2L_3 \cdot 4H_2O$	1541	1367	174
$Eu_2L_3 \cdot 4H_2O$	1538	1369	169
$Gd_2L_3 \cdot 4H_2O$	1544	1370	174
$Tb_2L_3 \cdot 4H_2O$	1544	1371	173
$Dy_2L_3 \cdot 4H_2O$	1544	1372	172
$Ho_2L_3 \cdot 4H_2O$	1548	1373	175
$Er_2L_3 \cdot 4H_2O$	1544	1373	171
$Tm_2L_3 \cdot 4H_2O$	1548	1376	172
$Yb_2L_3 \cdot 5H_2O$	1559	1380^*	179
$Lu_2L_3 \cdot 5H_2O$	1558	1380^*	178
Na_2L	1581	1334	247

$L=C_6H_6O_4$; *probably

Results and discussion

1,1-Cyclobutanedicarboxylates of Y(III) and lanthanide(III) from La to Eu were obtained as crystalline hydrated products. The complexes of Tm(III), Yb(III) and Lu(III) were crystallised from aqueous solution, giving also hydrated compounds. The 1,1-cyclobutanedicarboxylic acid form complexes with rare elements ions where stoichiometric ratio metal:ligand is 2:3 and general formula is $Ln_2(C_6H_6O_4)_3 \cdot nH_2O$ (n=7 for La, Ce, n=4 for Y, Pr–Tm and n=5 for Yb, Lu). The colours of the complexes are typical of the appropriate trivalent ions lanthanide, i.e. Pr – green, Nd – violet, Sm – cream, Eu – pink, Ho – peach, and the remaining complexes are white.

Almost all the prepared complexes exhibit nearly similar solid state IR spectra (Fig. 2), only in case of Yb(III) and Lu(III) complexes differences were observed in IR spectra compared with other compounds. When the acid converted to salt, the stretching vibration of C=O group, ν(C=O) in COOH at 1698 cm^{-1} disappeared, whereas the bands of asymmetric vibration ν_{as}(OCO) at 1541–1564 cm^{-1} and the bands of symmetric vibration ν_s(OCO) at 1360–1385 cm^{-1} appeared (Y, La–Tm) (Ta-

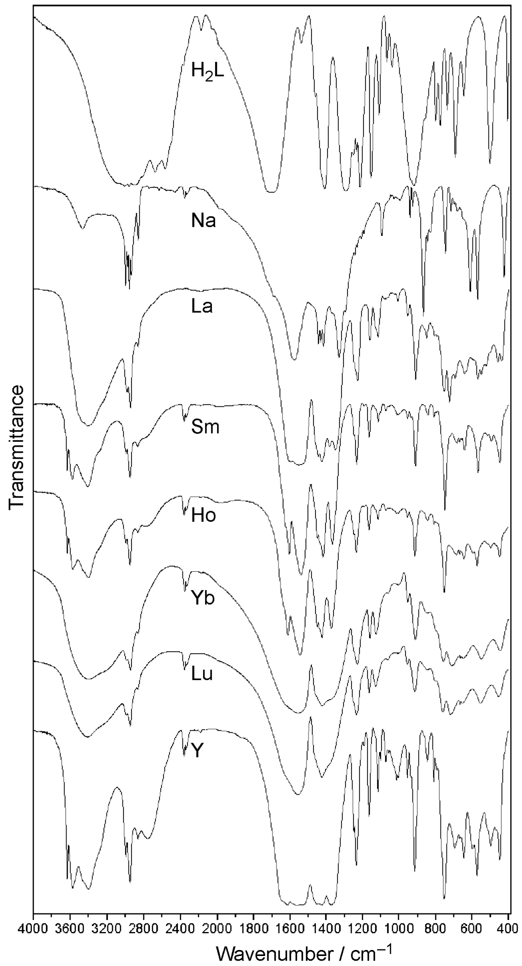

Fig. 2 Infrared spectra of 1,1-cyclobutanedicarboxylic acid, sodium salt and some lanthanide complexes

ble 1). In case of Yb(III) and Lu(III) complexes the bands of symmetric vibration ν_s(OCO) and deformation vibration δ_s(CH_2) are not separated. They may occur near 1380–1370 cm^{-1} [11–14]. In the infrared spectrum of $Ln_2(C_6H_6O_4)_3{\cdot}nH_2O$ one, two or three narrow bands of crystallisation water appear in the range of 3630–3328 cm^{-1} characteristic of the symmetric and asymmetric vibrations ν(OH) as a result of hydrogen bonding. For different complexes at 1617–1583 cm^{-1} the deformation vibration of water molecules is observed. In the obtained complexes water was coordinated in the inner and outer coordination spheres. The bands characteristic of coordinated water appear as rocking vibration at 855–844 cm^{-1} and wagging vibration at 774–751 cm^{-1} [12, 13]. The bands C–H appear at 2995–2974 cm^{-1} (3012 cm^{-1} for

Table 3 Temperature of dehydration and decomposition of 1,1-cyclobutanedicarboxylates of lanthanides and yttrium

Complex	ΔT_1/K	Mass loss/%		nH$_2$O	ΔT_2/K	Mass loss/%		ΔT_3/K	Mass loss/%	
		calc.	found			calc.	found		calc.	found
$Y_2L_3{\cdot}4H_2O$	360–437 464–511	7.99 10.65	8.2 10.74	3 1				564–1050	66.59	66.6
$La_2L_3{\cdot}7H_2O$	333–403	15.18	15.29	7	543–744	49.87	49.59	981–1094	60.74	60.25
$Ce_2L_3{\cdot}7H_2O$	310–410	15.14	15.28	7				505–751	41.32	41.36
$Pr_2L_3{\cdot}4H_2O$	316–410 414–446 451–479	4.62 6.93 9.23	4.66 7.23 9.5	2 1 1	537–701	46.42	46.06	746–904	56.34	56.58
$Nd_2L_3{\cdot}4H_2O$	341–445	9.15	9.47	4	526–697 862–951	46.03 51.62	45.65 51.95*	996–1095	57.22	57.47
$Sm_2L_3{\cdot}4H_2O$	320–436 440–495	6.76 9.02	6.61 9.1	3 1	529–704 877–947	45.32 50.83	44.82 50.21*	984–1102	56.34	56.21
$Eu_2L_3{\cdot}4H_2O$	352–438	8.98	9.09	4	529–684 771–850	45.12 50.63	44.05 50.41*	861–930	56.11	55.82
$Gd_2L_3{\cdot}4H_2O$	315–441	8.86	9.08	4	553–721	44.55	44.63	1017–1083	55.38	54.95
$Tb_2L_3{\cdot}4H_2O$	351–428	8.82	8.3	4	528–702	44.37	44.21	749–910	54.18	54.22
$Dy_2L_3{\cdot}4H_2O$	318–439 452–493	6.56 8.75	6.93 8.93	3 1	527–706	49.33	49.17*	960–1035	54.67	54.52
$Ho_2L_3{\cdot}4H_2O$	311–435	8.7	8.6	4	521–729	43.73	43.8	954–1051	54.36	54.54
$Er_2L_3{\cdot}4H_2O$	331–436	8.65	8.51	4	526–771	48.77	49.17*	974–1045	54.05	54.13
$Tm_2L_3{\cdot}4H_2O$	341–429 450–503	6.46 8.61	6.61 8.68	3 1				514–851	53.84	53.83
$Yb_2L_3{\cdot}5H_2O$	316–406 409–447 459–515	4.17 8.35 10.44	4.13 8.26 10.74	2 2 1				524–853	54.29	54.13
$Lu_2L_3{\cdot}5H_2O$	311–464	10.39	10.74	5				550–868	54.64	54.13

L=$C_6H_6O_4$, ΔT_1–temperature of dehydration process, ΔT_2 – temperature of decomposition of anhydrous complex to $Ln_2O(CO_3)_2$ or to $^*Ln_2O_2CO_3$, ΔT_3 – temperature of decomposition of anhydrous complex or oxocarbonates to oxides Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7

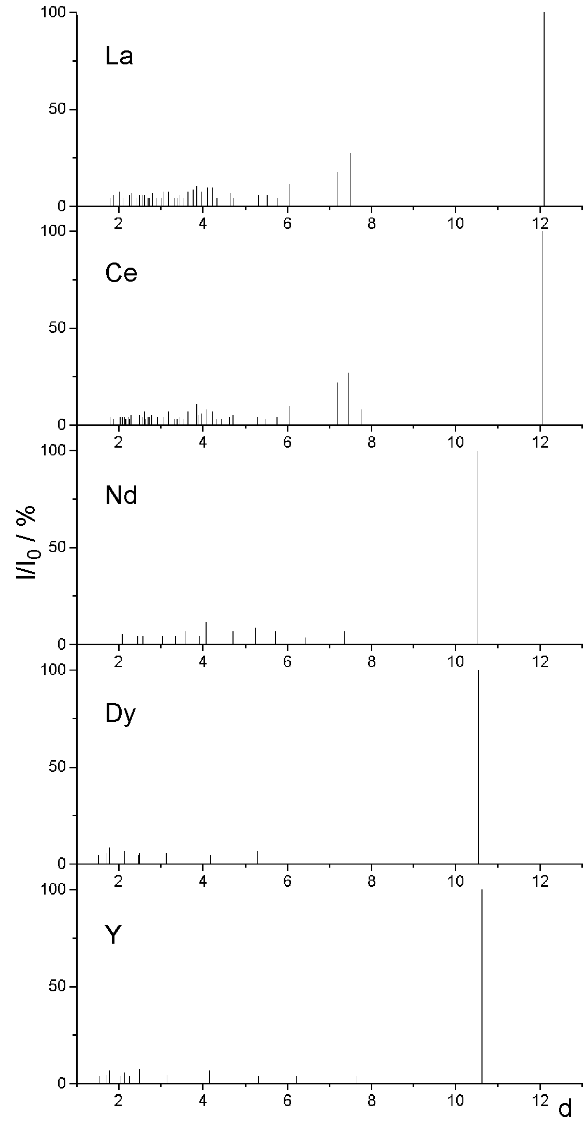

Fig. 3 Radiograms of some 1,1-cyclobutanedicarboxylates complexes

acid) as asymmetric and 2962–2948 cm^{-1} as symmetric stretching vibration. In the spectra region 1430–1419 cm^{-1} (1409 cm^{-1} for acid) deformation vibration δ_sCH_2 of cyclobutane derivatives can be seen. Wagging vibration of CH_2 appears also at 1229–1236 cm^{-1}; for Y, Tb, Dy, Er it splits into two bands: 1248 and 1235 cm^{-1} and for Pr complex into for three bands: 1256, 1238 and 1229 cm^{-1}. At 808–812 cm^{-1} rocking vibrations of CH_2 groups are observed. The skeletal cyclobutane ring modes C–C are observed at 1169–1161 (stretching), 1130–1116 (twisting), 1025–1001, 921–912 (stretching), 654–640 (deformation) and 575–554 cm^{-1} (bending) [11–14]. The bands corresponding to the metal–oxygen stretching appear at 440–456 cm^{-1} for the whole series of complexes. It is therefore reasonable to assume that 1,1-cyclobutanedicarboxylic acid forms with lanthanide and yttrium complexes of similar stability [13, 15]. The separation value, the ν_{asCOO^-} and ν_{sCOO^-} modes ($\Delta\nu_{COO^-}$), of the complexes is smaller ($\Delta\nu_{COO^-}$=169–204 cm^{-1}, Table 2) than that of the sodium salt ($\Delta\nu_{COO^-}$=247 cm^{-1}). For 1,1-cyclobutanedicarboxylates of yttrium and lanthanide the bands of ν_{asCOO^-} are shifted to lower frequencies whereas of ν_{sCOO^-} to higher ones compared with sodium 1,1-cyclobutanedicarboxylates. Probably the carboxylate ions appear to be bidentate chelating ligands [11, 12, 15–17].

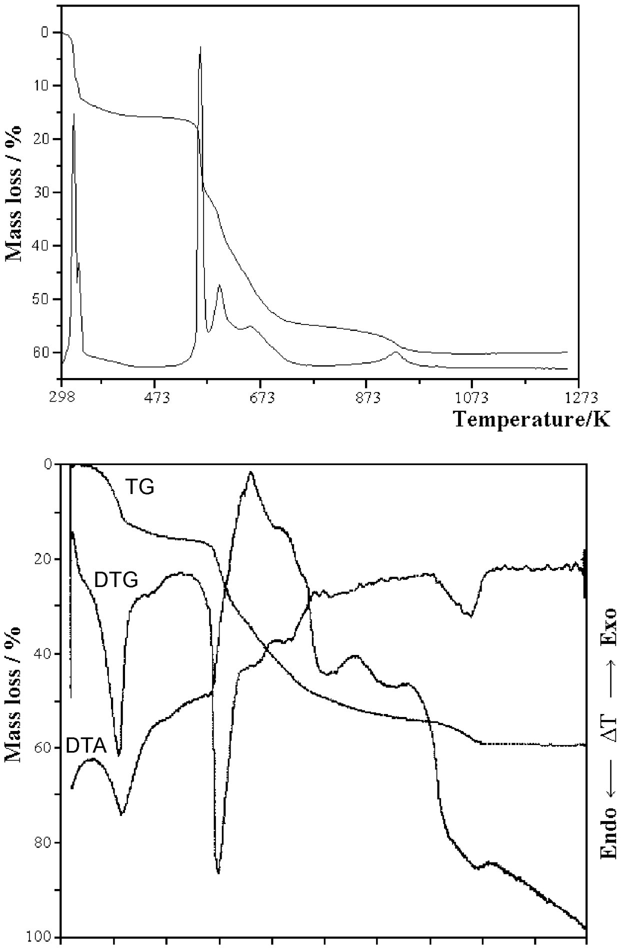

Fig. 4 Bottom: TG, DTG and DTA curves of $La_2(C_6H_6O_4)_3 \cdot 7H_2O$ in static air atmosphere. Top: TG and DTG curves of $La_2(C_6H_6O_4)_3 \cdot 7H_2O$ in dynamic N_2 atmosphere

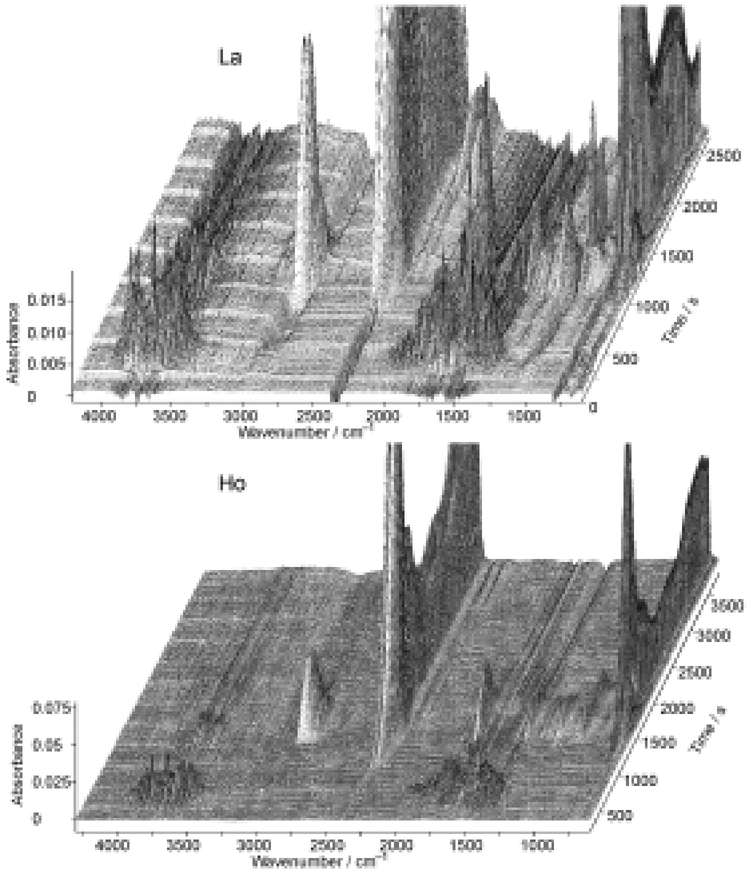

Fig. 5 FTIR spectra of gaseous products of thermal decomposition of lanthanum and holmium 1,1-cyclobutanedicarboxylates

X-ray spectra of 1,1-cyclobutanedicarboxylates of rare earth elements were recorded (Fig. 3). They form three groups of isostructural compounds. The first group contains two compounds which have seven molecules of water i.e. lanthanum(III) and cerium(III) complexes. The second isostructural group contains tetrahydrated complexes, i.e. Y(III), Pr(III)–Tm(III). The last isostructural group consists of two complexes – lutetium(III) and ytterbium(III), which are obtained as pentahydrated, amorphous complexes.

The hydrated 1,1-cyclobutanedicarboxylates are stable up to 310–360 K. On further heating they are dehydrated in different ways thus forming anhydrous complexes stable up to 505–564 K. The heptahydrated complexes, i.e. La, Ce, dehydrated in one step losing all water molecules:

$$Ln_2L_3\cdot 7H_2O \xrightarrow{-7H_2O} Ln_2L_3$$

The terahydrated complexes – Y(III), Pr(III)–Tm(III) dehydrated in different ways. They can dehydrate in one stage losing four water molecules:

$$Ln_2L_3\cdot 4H_2O \xrightarrow{-4H_2O} Ln_2L_3\text{, where } Ln\text{=Nd, Eu, Gd, Tb, Ho, Er}$$

Dehydration of complexes Y(III), Sm(III), Dy(III), Tm(III) proceeds in two stages; in the first stage three water molecules are lost, then one water molecule is lost and the compounds become anhydrous in the following way:

$$Ln_2L_3\cdot 4H_2O \xrightarrow{-3H_2O} Ln_2L_3\cdot H_2O \xrightarrow{-H_2O} Ln_2L_3$$

The compound of Pr(III) is dehydrated in three steps:

$$Pr_2L_3\cdot 4H_2O \xrightarrow{-2H_2O} Ln_2L_3\cdot 2H_2O \xrightarrow{-H_2O} Pr_2L_3\cdot H_2O \xrightarrow{-H_2O} Pr_2L_3$$

In the case of pentahydrated complexes of 1,1-cyclobutanedicarboxylic acid with Yb(III) and Lu(III) dehydration process proceeds in one stage for Lu or in three stages for Yb:

$$Yb_2L_3\cdot 5H_2O \xrightarrow{-2H_2O} Yb_2L_3\cdot 3H_2O \xrightarrow{-2H_2O} Yb_2L_3\cdot H_2O \xrightarrow{-H_2O} Yb_2L_3$$

The anhydrous compounds decomposed on heating into oxide (Ln_2O_3, CeO_2, Tb_4O_7 and Pr_7O_{11}) directly or with intermediate formation. The anhydrous complexes of Y(III), Ce(III), Tm(III), Yb(III) and Lu(III) decomposed over the range 505–564 K directly to oxides. The temperatures of oxide formation are 751–1050 K. The remaining

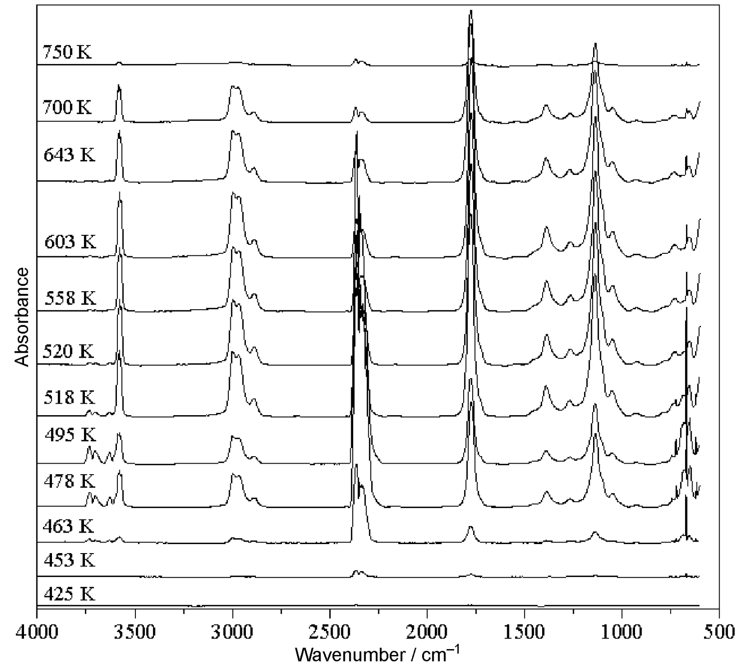

Fig. 6 FTIR spectra of gaseous products of thermal decomposition of 1,1-cyclobutanedicarboxylic acid

complexes decomposed with one or two intermediate stages. 1,1-cyclobutanedicarboxylates of La(III), Pr(III), Gd(III), Tb(III), Dy*(III), Ho(III) and Er*(III) decomposed to oxides Ln_2O_3 and Pr_7O_{11} with intermediate oxocarbonates either $Ln_2O(CO_3)_2$ or $Ln_2^*O_2CO_3$. The anhydrous compounds of Nd(III)–Eu(III) are stable up to about 520 K. When heated over 520 K the complexes decomposed in two stages: first $Ln_2O(CO_3)_2$ (526–529 K) and then $Ln_2O_2CO_3$ (771–877 K), forming Ln_2O_3.

The results indicate that thermal decomposition of anhydrous 1,1-cyclobutanedicarboxylates of rare earth elements in air may proceed in the following way:

1. $Ln_2L_3 \rightarrow Ln_2O_3$; *Ln*=Y, Ce, Tm, Yb, Lu
2. $Ln_2L_3 \rightarrow Ln_2O(CO_3)_2$ or $Ln_2^*O_2CO_3 \rightarrow Ln_2O$; *Ln*=La, Pr, Ho, Gd; *Ln**=Dy, Er
3. $Ln_2L_3 \rightarrow Ln_2O(CO_3)_2 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$; *Ln*=Nd, Sm, Eu

Temperatures of oxide formation change from 751 K (CeO_2) to 1102 K (Sm_2O_3). The dehydrating processes are connected with endothermic effects observed in DTA curves whereas the combustion of the organic ligand with exothermic one.

Thermal stability and decomposition of La(III), Nd(III), Ho(III), Tm(III) and Yb(III) complexes in nitrogen atmosphere were monitored. At first, they lose water molecules in one or more stages to form anhydrous salts. The dehydration process of lanthanum complex in nitrogen atmosphere was controlled by using the high-resolution technique and took place in two stages. In the first stage it lost four and next three water molecules. The anhydrous compound is stable up to 500 K and next decomposes to a mixture of oxide and carbon with intermediate formation. Temperatures of anhydrous complexes formation in nitrogen atmosphere are lower than in air i.e. 330–400 K. The anhydrous complexes decompose in the range of 485–510 K with intermediate formations. The values of initial decomposition temperature of anhydrous complexes are also lower (below 510 K) than those in air (above 510 K), which indicates they are more stable in air than in nitrogen. The final decomposition products are mixtures of the respective metal oxides and carbon.

Decomposition with the gas product analysis (Figs 5 and 6) and DSC curves of some complexes: La(III), Ho(III), Lu(III), as representatives of isostructural groups as well as free acid are recorded. The DSC curves of La complexes show a sharp endothermic peak at 346 K with ΔH equal to 352.51 kJ mol^{-1}. This peak is connected with the dehydration process. For holmium and lutetium complexes the peaks are observed at 405 and 404.5 K, respectively. The values ΔH are lower than for the compound of lanthanum and equal to 197.03 kJ mol^{-1} for Ho and to 284 kJ mol^{-1} for Lu. The loss of water molecules is reflected by FTIR spectra of gaseous decomposition products (Fig. 5). The characteristic valence and deformation vibration bands of water molecules appear in the wavenumber ranges of 3950–3500 and 1900–1300 cm^{-1}, respectively. In FTIR spectra of the gas-phase products of heating the compounds, the H_2O bands were observed at 323 K for La, 353 K for Ho and 313 K for Lu. Anhydrous complexes are stable at 513–533 K. When the complexes are heated above this temperature they decompose. The exothermic peak as the overall effect of compounds heating in argon atmosphere is observed on DSC curves. In IR spectra of gaseous products of decomposing 1,1-cyclobutanedicarboxylates of holmium and lutetium the bands of CO_2 appear. Carbon dioxide molecules absorb in the wavenumber ranges: 2350–2250 and 750–600 cm^{-1} due to valence and deformation vibrations, respectively. At 538 K for Ho and 598 K for Lu compounds in the range of 3750–3550 cm^{-1} there appear stretching vibration bands which may be connected with valence vibrations of either water or carbon dioxide molecules. At this temperature bands in the wavenumber ranges 3150–2850 and 1050–850 cm^{-1} are also observed. This region is characteristic of stretching (ν(CH)) and skeleton (γ(C–C)) vibration. These bands are connected with occurrence of gaseous hydrocarbons, probably with cyclobutane, alkanes and alkenes. Upon further heating, these bands disappear at 748 K for Ho and 888 K for Lu. Additionally, at 680 K for lutetium very weak bands can be seen at 2176 and 2098 cm^{-1}. These peaks are characteristic of valence vibration of CO. At a higher temperature intensity of CO bands increases rapidly. In the case of holmium compound vibrations characteristic of CO are also observed, but intensities of these bands are very small. The scheme of lanthanum complex decomposition is slightly different. The first step of organic ligand degradation is connected with the release of CO_2, H_2O and hydrocarbons at 523 K. Similarly to lutetium complex at 673 K very weak bands of CO appear, their intensities increase rapidly at 990 K [18, 19].

In the case of 1,1-cyclobutanedicarboxylic acid decomposition two endothermic peaks are observed on the DSC curves. The first at 439 K with ΔH equal to 27.60 kJ mol^{-1} which is connected with melting process. The second peak at 485.5 K is connected with acid decomposition and ΔH is equal to 53.54 kJ mol^{-1}. The decomposition products are reflected by FTIR spectra (Fig. 6). The bands characteristic of CO_2, H_2O and hydrocarbons are observed at 450 K distinctly, and are hardly observable at 463 K.

Conclusions

Complexes of Y(III) and lanthanide(III) with 1,1-cyclobutanedicarboxylic acid were prepared as crystalline solid with colours characteristic of lanthanide(III) ions. The carboxylate groups in the complexes are bidentate chelating. The diffractogram analysis suggests that they are polycrystalline compounds and form three groups of isostructural compounds. The 1,1-cyclobutanodicarboxylates of rare elements are hydrated, the water molecules are located probably in inner and outer coordination spheres. During heating in air and in nitrogen the hydrated complexes lose all water molecules in one or more steps. Next, the complexes heated in air decomposed to oxide directly or with intermediate formation. In the case of decomposition in nitrogen the complexes decomposed to metal oxides and carbon. FTIR spectra of the gas-phase products indicate that decomposition of complexes is connected with the release of CO_2, H_2O, hydrocarbons and CO.

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