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THERMAL PROPERTIES OF LIGHT LANTHANIDE 2,3,4-TRIMETHOXYBENZOATES

W. Ferenc, B. Bocian and M. Chudziak

Department of Inorganic and General Chemistry, Institute of Chemistry, Maria Curie-Skłodowska University, Pl 20-031, Lublin, Poland

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Abstract

The light lanthanide 2,3,4-trimethoxybenzoates were obtained by the addition of an equivalent quantity of 0.1 M ammonium 2,3,4-trimethoxybenzoate to a hot solution of the light lanthanide nitrate, followed by crystallization at 293 K. The contents of carbon and hydrogen were determined by elemental analysis, with V_2O_5 as oxidizing agent, and the lanthanide element contents were established by the oxalic acid method. The complexes are anhydrous compounds with a metal to ligand ratio of 1:3 and the general formula $Ln(C_{10}H_{11}O_5)_3$. They have the colour characteristic of Ln^{3+}. Their IR spectra were run in the range 4000–400 cm^{-1} on an M-80 spectrophotometer by using KBr discs. In these complexes, the carboxylate group appears to be a bidentate chelating ligand. The X-ray powder patterns were taken on a DRON-2 diffractometer, using Ni-filtered CuK_α radiation, within the range $2\Theta=5–80^o$, by the Debye-Scherrer-Hull method. The diffractograms indicated that the complexes are crystalline compounds. Their thermal stabilities in air were studied (273–1173 K) through the use of TG, DTG and DTA techniques, with an OD-102 derivatograph.

The 2,3,4-trimethoxybenzoates of La and Nd decompose in two steps, but those of Ce, Pr, Sm and Eu in only one stop. The anhydrous 2,3,4-trimethoxybenzoates of La and Nd decompose to oxides with the intermediate formation of oxycarbonates, while those of Ce, Pr, Sm and Eu decompose directly to the oxides. The solubilities of these complexes in water (293 K) are in the order of 10^{-3} mol dm^{-3}.

Keywords: complexes to light lanthanides, spectromechanical investigations, thermal stability of complexes, 2,3,4-trimethoxybenzoates,

Introduction

2,3,4-Trimethoxybenzoic acid is a white crystalline solid, sparingly soluble in cold water; its solubility in water increases with rise of temperature. Its melting point is 97^oC [1]. A literature survey reveals no information on the properties and practical use of 2,3,4-trimethoxybenzoic acid or on its compounds with various cations. It appears that 2,3,4-trimethoxybenzoates of light lanthanides have not been obtained as solids and investigated so far. The aim of this work was therefore to prepare them in the solid state, to examine some of their physico-chemical properties, to determine

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their external crystalline form, to acquire IR spectra and to study their thermal stability in air in the temperature range 273–1173 K.

Experimental

2,3,4-Trimethoxybenzoates of light lanthanides were prepared by the addition of an equivalent quantity of 0.1 M ammonium 2,3,4-trimethoxybenzoate (pH~5) to a hot solution containing the light lanthanide nitrate, followed by crystallization at 293 K. The solid that formed was filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant mass. The contents of carbon and hydrogen were determined by elemental analysis, with V_2O_5 as oxidizing agent. The lanthanide element content was established by the oxalic acid method. From the results obtained (Table 1), it follows that the 2,3,4-trimethoxybenzoates of the light lanthanides are anhydrous compounds with a metal to ligand ratio of 1:3. All the 2,3,4-trimethoxybenzoates have colours characteristic of the Ln^{3+}.

Table 1 Analytical data on light lanthanide 2,3,4-trimethoxybenzoates

Complex $L=C_{10}H_{11}O_5$	H/%		C/%		M/%	
	calcd.	found	calcd.	found	calcd.	found
LaL_3	1.02	1.12	11.19	11.21	12.95	13.01
CeL_3	1.02	1.22	11.18	11.17	13.05	13.20
PrL_3	1.02	1.18	11.17	11.25	13.12	13.33
NdL_3	1.02	1.12	11.13	11.23	13.38	13.40
SmL_3	1.01	1.20	11.07	11.10	13.87	13.90
EuL_3	1.01	1.00	11.06	11.09	14.00	14.20

Table 2 Spectroscopic data on 2,3,4-trimethoxybenzoates of sodium and light lanthanides and on 2,3,4-trimethoxybenzoic acid (cm^{-1}), and the solubilities of the salts in water at 293 K

Complex $L=C_{10}H_{11}O_5$	$\nu_{C=O}$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\Delta\nu_{COO^-}$	ν_{M-O}	Solubility/ mol dm^{-3}
LaL_3	–	1540	1400	140	525	$6.35\cdot10^{-3}$
CeL_3	–	1540	1400	140	525	$4.02\cdot10^{-3}$
PrL_3	–	1540	1400	140	525	$3.58\cdot10^{-3}$
NdL_3	–	1540	1400	140	525	$3.87\cdot10^{-3}$
SmL_3	–	1540	1400	140	525	$3.28\cdot10^{-3}$
EuL_3	–	1540	1400	140	525	$3.43\cdot10^{-3}$
NaL	–	1555	1400	155		
HL		–	–	–	–	–

In order to confirm the chemical compositions of the salts, the IR spectra of the complexes, and of 2,3,4-trimethoxybenzoic acid and its sodium salt were run in the range 4000–400 cm^{-1} by using KBr discs on an M-80 spectrophotometer (Table 2).

In order to determine the external crystalline form of the 2,3,4-trimethoxybenzoates and the structures of the corresponding oxides obtained upon thermal decomposition of the complexes and ignition of the oxalates, X-ray powder patterns were taken on a DRON-2 diffractometer, using Ni-filtered CuK_{α} radiation, within the range $2\Theta=5–80^{o}$, by means of the Debye-Scherrer-Hull method. The thermal stabilities of the complexes in air were also studied by use of TG, DTG and DTA techniques. The measurements were made with an OD-102 derivatograph (MOM, Budapest) at a heating rate of 10 deg min^{-1}. The test samples were heated at a sensitivity TG – 100 mg, DTG – 500μV and DTA – 500 μV (Table 3).

Results and discussion

The 2,3,4-trimethoxybenzoates of the light lanthanides were obtained as anhydrous, crystalline compounds with a metal to ligand ratio of 1:3 and the general formula $Ln(C_{10}H_{11}O_5)_3$. The colours of the complexes are those typical for the corresponding trivalent ions, which is connected with the structures of the molecules and the electron density in the benzene ring. The 2,3,4-trimethoxybenzoate molecules probably have a planar structure and the OCH_3 groups are conjugated with the π electrons of the benzene ring. In these molecules, the $f \rightarrow f$ electronic transitions of the central ions are those of the lowest energy, and absorption occurs at relatively high wavelengths, depending on the nature of the metal ion.

The compounds were characterized by elemental analysis (Table 1) and IR spectroscopy. All the light lanthanide 2,3,4-trimethoxybenzoates exhibit similar solid-state IR spectra. However, the characteristic frequencies relating to the carbonyl group change markedly on going from the acid to the salts. The COOH band at 1690 cm^{-1}, present in the acid spectrum, is absent from the spectra of the complexes, while two bands, arising from the asymmetric and symmetric vibrations of the COO^- group, appear at 1540 and 1400 cm^{-1}, respectively [2–8]. The bands of the C–H antisymmetric stretching of the CH_3 group are observed at 2950 cm^{-1} whereas their symmetric stretching occurs at 2850 cm^{-1}. The symmetric deformation vibration bands of the CH_3 group lie at 1470 cm^{-1}. The skeletal ring mode region is clearly observed at 1600, 1500 and 1250 cm^{-1}. The =C–H band stretches appear at 3450 cm^{-1} and the out-of-plane C–H bonding at 990, 915 and 820–705 cm^{-1} [2–8]. The bands due to the metal–oxygen bonding appear at 525 cm^{-1} and their shifts are not observed. Accordingly, it is possible to suggest that 2,3,4-trimethoxybenzoic acid forms light lanthanide complexes that have similar stability. Table 2 presents the frequency maxima of the absorption bands of the asymmetric and symmetric vibrations of the COO^- group for the 2,3,4-trimethoxybenzoates of light lanthanides and sodium. The magnitudes of separation, Δν, between the frequencies ν_{asCOO^-} and ν_{sCOO^-} for the complexes are lower ($\Delta\nu=140\ cm^{-1}$) than for the sodium salt ($\Delta\nu=155\ cm^{-1}$), which indicates a smaller degree of ionicity of the bonding in the

Table 3 Data of light lanthanide 2,3,4-trimethoxybenzoate decompositions

Complex	Temp. range of decomp./K	Mass loss/%		Intermediate product	Temp. range of decomp./K	Mass loss/%		Final compound	Final mass/%		Final temp. of decomp./K
		calcd.	found			calcd.	found		calcd.	found	
LaL_3	553–953	75.73	76.08	$La_2O_2CO_3$	993–1093	78.91	79.25	La_2O_3	21.09	20.75	1093
CeL_3	563–928	–	–	–	–	77.73	77.98	CeO_2	22.27	22.02	943
PrL_3	533–943	–	–	–	–	78.00	77.98	Pr_6O_{11}	22.00	22.02	993
NdL_3	533–853	75.50	75.73	$Nd_2O_2CO_3$	893–1033	78.36	78.30	Nd_2O_3	21.64	21.70	1040
SmL_3	523–943	–	–	–	–	77.73	77.28	Sm_2O_3	22.27	22.72	1043
EuL_3	523–963	–	–	–	–	77.58	77.86	Eu_2O_3	22.42	22.14	1043

$L = C_{10}H_{11}O_5$

light lanthanide 2,3,4-trimethoxybenzoates. For the 2,3,4-trimethoxybenzoates of the light lanthanides, the shifts in the frequencies ν_{asCOO^-} and ν_{sCOO^-} are lower and stay the same in comparison with those for sodium 2,3,4-trimethoxybenzoate. Accordingly, taking into account the Nakamoto criterion, the carboxylate ion here appears to be a bidentate, chelating ligand [2, 3, 9–11].

In order to determine the external crystalline forms of the complexes, X-ray powder diffraction measurements were made. Diffractogram analysis suggests that they are polycrystalline compounds with low symmetry. They probably crystallize in monoclinic or triclinic systems [12]. The 2,3,4-trimethoxybenzoates of the light lanthanides seem to be isostructural, but their structures have not been determined because single-crystals of these compounds were not obtained. The structures of the light lanthanide oxides obtained from ignition of the oxalates or the 2,3,4-trimethoxybenzoates remain the same irrespective of the mode of their formation.

The thermal stabilities of the 2,3,4-trimethoxybenzoates of the light lanthanides were also studied in air in the temperature range 273–1173 K (Table 3). All the complexes are stable in air at room temperature, and undergo practically no change in mass on storage. From the results obtained, it follows that the light lanthanide 2,3,4-trimethoxybenzoates are anhydrous compounds. When heated at 273–1173 K, they decompose in various ways. The 2,3,4-trimethoxybenzoates of La and Nd are stable up to 553 and 533 K, respectively, and then decompose to the oxides with the intermediate formation of the oxycarbonates. From the thermoanalytical curve for lanthanum 2,3,4-trimethoxybenzoate (Fig. 1), it follows that the complex starts to decompose at 553 K. Next, in the temperature range 553–953 K, a sudden decrease in mass occurs and the TG curve does not proceed horizontally. The loss in mass is about 76% (theoretical and found values of 75.73 and 76.08%, respectively). This

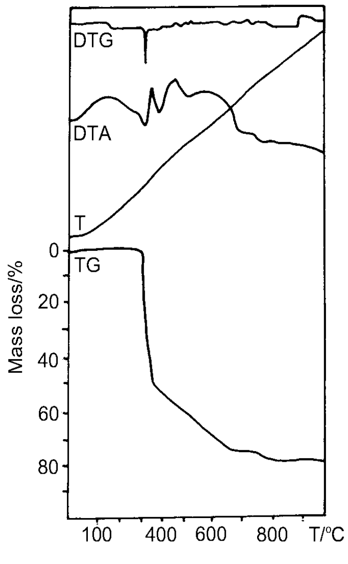

Fig. 1 TG, DTG and DTA curves of lanthanum 2,3,4-trimethoxybenzoate

decrease in mass is ascribed to oxidation of the organic ligand and the formation of $La_2O_2CO_3$. The oxidation process is connected with the strong exoeffect observed in the DTA curve, and the sharp DTG peak corresponds to the rapid loss in mass.

Above 953 K the TG curve is horizontal again, which is connected with $La_2O_2CO_3$ formation. In the temperature range 993–1093 K, the oxycarbonate of lanthanum decomposes to La_2O_3. The calculated and found mass losses are 78.91 and 79.25%, respectively. In this temperature range, the TG curve does not proceed horizontally, and a small DTG peak associated with mass loss is also observed. Next, above 1093 K, the TG curve attains a constant level which corresponds to the formation of La_2O_3, the final product of lanthanum 2,3,4-trimethoxybenzoate decomposition [13, 14], which was identified roentgenographically.

Neodymium 2,3,4-trimethoxybenzoate also decomposes in two steps. In the first stage, in the temperature range 533–853 K, it decomposes to $Nd_2O_2CO_3$ (theoretical and found mass losses of 75.50 and 75.73%, respectively), with further decomposition in the range 893–1033 K to form Nd_2O_3, the final product of neodymium 2,3,4-trimethoxybenzoate decomposition. Strong and small inflections are observed in the TG curve. The mass losses are confirmed by two DTG peaks, one of them sharp, while the second is smaller.

From the thermoanalytical curve of samarium 2,3,4-trimethoxybenzoate (Fig. 2), it follows that the anhydrous complex is stable up 523 K, above which it decomposes directly to the oxide. It starts to decompose above 523 K. Next, a rapid decrease in mass occurs in the temperature range 523–943 K. Accordingly, the TG curve does not proceed horizontally and the loss in mass is about 78% (theoretical and found mass losses of 77.73 and 78.28%, respectively). Such a decrease in mass is connected with oxidation of the organic ligand. A strong exoeffect is therefore observed in the DTA curve, and a sharp DTG peak is also seen. Above 943 K, the TG curve

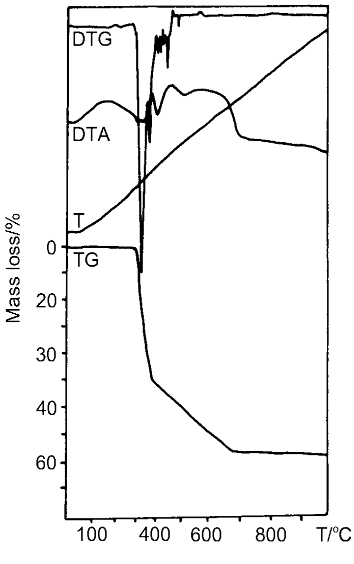

Fig. 2 TG, DTG and DTA curves of samarium 2,3,4-trimethoxybenzoate

attains a constant level corresponding to the formation of Sm_2O_3, the final product of samarium 2,3,4-trimethoxybenzoate, this product being identified roentgenographically.

Similarly, cerium, praseodymium and europium 2,3,4-trimethoxybenzoates also decompose in one step. The anhydrous salts decompose directly to the oxides (Table 3). The theoretical and found mass losses are 77.58–78.07% and 77.98–78.86%, respectively. The 2,3,4-trimethoxybenzoates of Ce, Pr, Sm and Eu decompose in the temperature range 523–963 K.

As the final products of the 2,3,4-trimethoxybenzoate decompositions, the lanthanide oxides are formed in the temperature range 943–1093 K. The temperature of their formation does not vary regularly in the series of light lanthanides. The lowest temperature of oxide formation is that of cerium oxide (943 K), while the highest is that of lanthanum oxide (1093 K).

Taking into account the initial temperature of decomposition, it may be assumed that samarium and europium 2,3,4-trimethoxybenzoates are the least thermally stable (523 K), while the most thermally stable is cerium 2,3,4-trimethoxybenzoate, which starts to decompose at 563 K.

The thermal stabilities of the light lanthanide 2,3,4-trimethoxybenzoates increase in the following sequence:

$$\mathrm{Eu = Sm < Nd = Pr < La < Ce}$$

The results obtained from the investigations of the thermal stabilities of the 2,3,4-trimethoxybenzoates suggest that the decompositions proceed in the following ways:

$$\mathrm{LnL_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3} \quad \text{for } Ln = \text{La and Nd} \tag{1}$$

$$\mathrm{LnL_3 \rightarrow Ln_2O_3} \quad \text{for } Ln = \text{Sm and Eu} \tag{2}$$

$$\mathrm{LnL_3 \rightarrow Pr_6O_{11}} \text{ and } \mathrm{CeO_2} \tag{3}$$

The solubilities of the light lanthanide 2,3,4-trimethoxybenzoates in water were measured at 293 K (Table 2). They are in the order of 10^{-3} mol dm^{-3}. The solubilities vary in the following sequence:

$$\mathrm{Sm < Eu < Pr < Nd < Ce < La}$$

The 2,3,4-trimethoxybenzoate of lanthanum is the best-soluble salt, while that of samarium is the least-soluble. The solubilities of the 2,3,4-trimethoxybenzoates of the light lanthanides are in good agreement with those determined for the rare earth element benzoates [15], 3-methoxy- and 4-methoxybenzoates [16–18] and 3,4,5-trimethoxybenzoates [19, 20], which are also of the order of 10^{-3} mol dm^{-3}. It appears that, irrespective of the number and the position of the methoxy groups on the benzene ring, the order of solubility remains the same. This is connected with the similar abilities of the benzoates, 3-methoxy-, 4-methoxy-, 3,4,5-trimethoxy- and 2,3,4-trimethoxybenzoates to dissociate in water, which results from the similar electron densities of the aromatic ring in the complexes, which leads to the similar stabilities of the M–O bond in water.

A comparison of the solubilities of the light lanthanide 3,4,5- and 2,3,4-trimethoxybenzoates shows that in both these series the lanthanum complexes are the best-soluble salts, while those of samarium are the least-soluble ones [19, 20].

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