

Complexes of light lanthanides with 2,4-dimethoxybenzoic acid

WIESŁAWA FERENC* and AGNIESZKA WALKÓW-DZIEWULSKA

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

(Received 19 July, revised 21 October 1999)

The complexes of light lanthanides with 2,4-dimethoxybenzoic acid of the formula: $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ where $\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}$, and $n = 3$ for $\text{La(III)}, \text{Gd(III)}$, $n = 2$ for $\text{Sm(III)}, \text{Eu(III)}$, and $n = 0$ for $\text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}$ have been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric studies and X-ray diffraction measurements. The complexes have colours typical for Ln^{3+} ions (La, Ce, Eu, Gd-white, Sm-cream, Pr-green, Nd-violet). The carboxylate group in these complexes is a symmetrical, bidentate, chelating ligand. They are crystalline compounds characterized by various symmetry. On heating in air to 1273 K the 2,4-dimethoxybenzoates of the light lanthanides decompose in various ways. The hydrated complexes decompose in two or three steps while those of anhydrous ones only in one or two. The trihydrate of lanthanum 2,4-dimethoxybenzoate first dehydrates to form the anhydrous salt, which then decomposes to La_2O_3 via the intermediate formation of $\text{La}_2\text{O}_2\text{CO}_3$. The hydrates of Sm(III) , Eu(III) , Gd(III) decompose in two stages. First, they dehydrate forming the anhydrous salts, which then decompose directly to the oxides of the respective metals. The anhydrous complexes of Ce(III) , Pr(III) decompose in one step, while that of Nd(III) in two. The solubilities of the 2,4-dimethoxybenzoates of the light lanthanides in water and ethanol at 293 K are in the order of: $10^{-3} \text{ mol dm}^{-3}$ and 10^{-4} – $10^{-3} \text{ mol dm}^{-3}$, respectively.

Keywords: 2,4-dimethoxybenzoates of the light lanthanides, thermal stability of the complexes, spectrochemical investigations, solubility of the complexes

A literature survey indicated that the compounds of 2,4-dimethoxybenzoic acid with various cations have been relatively seldom studied. Papers exist on its complexes with the following cations only: Cu(II) , La(III) , Pr(III) , Nd(III) , Sm(III) , Gd(III) , Dy(III) , and Yb(III) . The compounds were obtained as solids or were investigated in solution.^{1,2} The 2,4-dimethoxybenzoate of Cu(II) was obtained in the solid state and its magnetic properties were determined,¹ while those of La(III) , Pr(III) , Nd(III) , Sm(III) , Gd(III) , Dy(III) , Yb(III) were only investigated in solution and their dissociation constants were established potentiometrically.² 2,4-Dimethoxybenzoic acid is a white crystalline solid, which easily sublimates under high vacuum³ and is sparingly soluble in water.⁴ On heating in air and argon it decomposes in one step.³ The $\text{p}K_{\text{a}}$ value of its dissociation constant is equal to 9.29 (25 °C)

and its melting point is 109 °C.^{2,4} There is no information about the solid-state properties of the complexes of 2,4-dimethoxybenzoic acid with light lanthanides. Therefore, we decided to synthesize them in the solid state and to examine some of their physico-chemical properties, that is their thermal stability in air, solubility in water and ethanol at room temperature, IR spectral characteristics and crystalline form in order to know if they are crystalline or amorphous compounds.

The thermal stability investigations enabled the evaluation of the assumed position of crystallization water molecules, *i.e.*, in outer or inner spheres of coordination, to know the mechanism of complex decomposition, to determine the endo- or exo-effects connected with such processes as: dehydration, melting, crystallization, oxidation, reduction, and to estimate the strength of the bonding between atoms or groups of atoms and ions. The determination of the solubility is valuable because it gives information about the practical use of the acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

EXPERIMENTAL

The 2,4-dimethoxybenzoates of the light lanthanides were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,4-dimethoxybenzoate (pH ≈ 5) to a hot solution containing the chloride of the light lanthanides followed by crystallization at 293 K. The formed solids were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant weight.

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser.

The contents of the metal(III) ions and crystallization water molecules were determined spectrophotometrically and from the TG curves (Table I).

The IR spectra of complexes were recorded over the range 4000–400 cm⁻¹ using a M-80 spectrophotometer. Samples were prepared as KBr discs. Some of the results are presented in Table II.

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK α radiation. The measurements were made within the range $2\theta = 4-80^\circ$ by means of the Debay-Scherrer-Hull method. The radiograms of the complexes are presented in Fig. 1.

The thermal stability and decomposition of the prepared complexes were determined using a Paulik-Paulik-Erdy Q-1500D derivatograph with a Derill converter recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min⁻¹ with a full scale. The 100 mg samples were heated in platinum crucibles in static air to 1173 K with a sensitivity of the TG, 100 mg (it means that the whole scale in the balance is equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm min⁻¹ and Al₂O₃ was used as the standard. The products of decomposition were calculated from the TG curves and verified by the registration of the diffraction pattern (Table III).

The solubilities of the 2,4-dimethoxybenzoates of the light lanthanides in water and ethanol at 298 K were determined by measuring the concentration of Ln³⁺ ions in a saturated solution by a spectrophotometrical method using the spectrophotometer Specord M-40 (Table I). The absorbance of the complexes was measured by using the Arsenazo III in the formic buffer (pH ≈ 3.5) and the wavelength $\lambda = 650$ nm, and with the use of the blank as reference.^{5,6}

RESULTS AND DISCUSSION

The 2,4-dimethoxybenzoates of the light lanthanides were obtained as crystalline hydrated or anhydrous products with a metal to ligand ratio of 1:3, and general

formula: $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, where $\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}$. For $\text{La(III)}, \text{Gd(III)}$ $n = 3$, for $\text{Sm(III)}, \text{Eu(III)}$ $n = 2$, and for $\text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}$ $n = 0$.

TABLE I. Analytical data of the light lanthanide 2,4-dimethoxybenzoates and the values of their solubilities in water and ethanol at 293 K

Complex $\text{L} = \text{C}_9\text{H}_9\text{O}_4$	C/%		H/%		Ln/%		Solubilities/mol dm ⁻³	
	calcd.	found	calcd.	found	calcd.	found	water	ethanol
$\text{LaL}_3 \cdot 3\text{H}_2\text{O}$	44.03	44.50	4.48	4.37	18.87	18.84	$1.65 \cdot 10^{-3}$	$5.76 \cdot 10^{-4}$
CeL_3	47.43	47.50	3.95	3.75	20.51	20.43	$4.14 \cdot 10^{-3}$	$6.42 \cdot 10^{-4}$
PrL_3	47.37	47.54	3.95	3.76	20.60	20.19	$3.97 \cdot 10^{-3}$	$3.55 \cdot 10^{-4}$
NdL_3	47.14	47.28	3.93	3.75	20.98	20.40	$6.72 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	44.42	44.55	4.25	4.13	20.61	20.52	$1.86 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	44.32	44.29	4.24	4.10	20.79	20.55	$4.24 \cdot 10^{-3}$	$4.08 \cdot 10^{-3}$
$\text{GdL}_3 \cdot 3\text{H}_2\text{O}$	42.95	43.51	4.37	4.11	20.84	20.04	$3.21 \cdot 10^{-3}$	$4.58 \cdot 10^{-3}$

The colours of the complexes are those typical for the appropriate trivalent Ln^{3+} ion, *i.e.*, white for La, Ce, Eu, and Gd, cream for Sm, greenish for Pr, and violet for Nd.⁷

The complexes were characterized by elemental analysis (Table I) and IR spectroscopy (Table II). All the 2,4-dimethoxybenzoates of the light lanthanides show similar solid state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from the acid to the salts. The band of the COOH group at 1668 cm^{-1} , present in the spectrum of the acid, disappears in the spectra of the complexes and two bands arising from the asymmetric and symmetric vibrations of the COO^- group occur at $1530\text{--}1510 \text{ cm}^{-1}$ and $1440\text{--}1425 \text{ cm}^{-1}$, respectively.⁸⁻¹¹ The bands with maxima at $3550\text{--}3456 \text{ cm}^{-1}$, characteristic for $\nu(\text{OH})$ vibrations, and the narrow band $\delta(\text{H}_2\text{O})$ at 1584 cm^{-1} confirm the presence of crystallization water molecules in the complexes of La(III), Sm(III), Eu(III) and Gd(III). The bands of C–H antisymmetric stretching of the CH_3 groups are observed at $2968\text{--}2952 \text{ cm}^{-1}$, whereas their symmetric stretching occur at $2850\text{--}2832 \text{ cm}^{-1}$. The symmetric deformation vibration bands of the CH_3 group occur at $1392\text{--}1376 \text{ cm}^{-1}$. The presence of $-\text{OCH}_3$ groups in the benzene ring is confirmed by the bands at $1288\text{--}1276 \text{ cm}^{-1}$. The skeletal ring mode region is observed at $1608\text{--}1450 \text{ cm}^{-1}$. The $=\text{C}\text{--}\text{H}$ bond stretches appear at $3440\text{--}3424 \text{ cm}^{-1}$ and the out-of-plane C–H bonding in the $944\text{--}696 \text{ cm}^{-1}$ range. The bands typical for the aromatic ring vibrations are shifted insignificantly in the complexes compared to the respective bands in 2,4-dimethoxybenzoic acid, which indicates that the Ln(III) ions only weakly influence the benzene ring. The bands due to metal-oxygen bond appear at $580\text{--}570 \text{ cm}^{-1}$ and they are not regularly shifted in the spectra of the complexes. Therefore, it is possible to suppose that 2,4-dimethoxybenzoic acid forms complexes of similar stability with the light lanthanides.¹²

TABLE II. Frequencies of the maxima of the absorption bands of COO^- and M-O group vibrations for the 2,4-dimethoxybenzoates of the light lanthanides and Na and for 2,4-dimethoxybenzoic acid (cm^{-1})

Complex $\text{L}=\text{C}_9\text{H}_9\text{O}_4$	$\nu_{\text{C=O}}$	$\nu_{\text{as COO}^-}$	$\nu_{\text{s COO}^-}$	$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{M-O}}$
$\text{LaL}_3 \cdot 3\text{H}_2\text{O}$	—	1530	1440	90	580
CeL_3	—	1520	1430	90	570
PrL_3	—	1520	1440	80	570
NdL_3	—	1520	1440	80	570
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	—	1510	1430	80	575
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	—	1510	1430	80	570
$\text{GdL}_3 \cdot 3\text{H}_2\text{O}$	—	1530	1430	100	570
NaL	—	1550	1425	125	555
HL	1668	—	—	—	—

Tables II presents the frequency maxima of the absorption bands of the asymmetric and symmetric vibrations of the COO^- group for the 2,4-dimethoxybenzoates of the light lanthanides and of the sodium, as well as of the CO group for 2,4-dimethoxybenzoic acid.^{8,10,13} The magnitudes of the separation, $\Delta\nu$, between the frequencies $\nu_{\text{as COO}^-}$ and $\nu_{\text{s COO}^-}$ in the complexes are lower ($\Delta\nu = 100\text{--}80\text{ cm}^{-1}$) than in the sodium salt ($\Delta\nu = 125\text{ cm}^{-1}$), which indicates a lower degree of ionic bonding in the light lanthanide 2,4-dimethoxybenzoates. The shifts of the frequencies $\nu_{\text{as COO}^-}$ and $\nu_{\text{s COO}^-}$ are lower and higher, respectively, in the light lanthanide complexes than those for sodium 2,4-dimethoxybenzoate. Accordingly, the carboxylate ion appears to be a symmetrical, bidentate, chelating ligand.^{8,10,13}

In order to examine if the light lanthanide 2,4-dimethoxybenzoates are crystalline or amorphous compounds their X-ray powder diffractograms were recorded. Analysis of the diffractograms suggests that they are polycrystalline compounds probably with various symmetry¹⁴ (Fig. 1). The complexes seem not to be isostructural compounds. The structures of the complexes have not been determined because single crystals have not been obtained. On heating to 1273 K, the 2,4-dimethoxybenzoates of the light lanthanides form oxides of the respective metal having the same structures as the oxides obtained from the ignition of rare earth element oxalates.¹⁵

The thermal stabilities of the light lanthanide 2,4-dimethoxybenzoates were studied in air in the temperature range 273–1273 K (Table III). The results obtained from their thermal decomposition showed them to be trihydrates (La, Gd), dihydrates (Sm, Eu) or anhydrous salts (Ce, Pr, Nd), as was established on the basis of elemental analysis (Table I). All the complexes are stable in air at room temperature and do not change their mass after storage. When heated in air they decompose in various ways. The anhydrous complexes of Ce(III), Pr(III) and Nd(III) are stable up to 483–508 K and then they decompose (with the exception of the 2,4-dimethoxy-

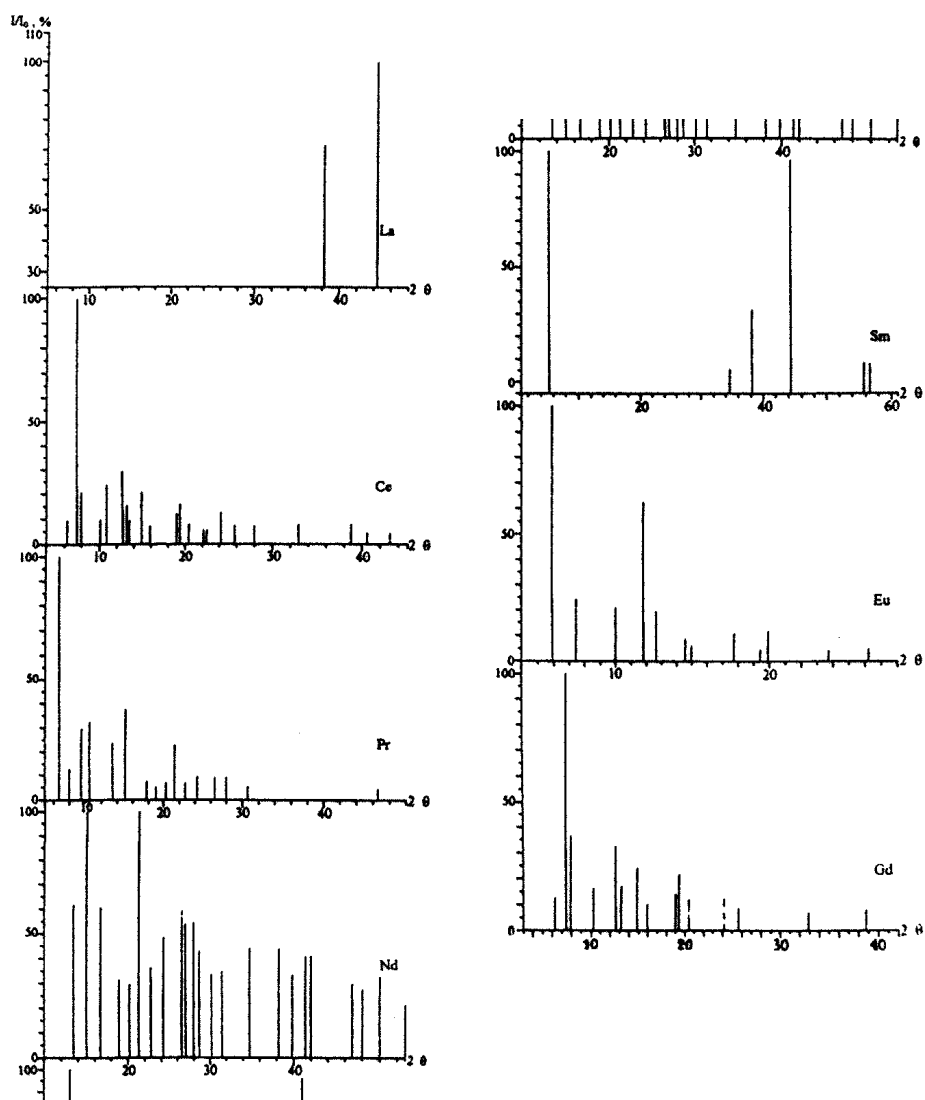


Fig. 1. Diffractograms of the light lanthanide 2,4-dimethoxybenzoates.

benzoate of Nd) to the oxides of the respective metal, which are formed at 1048–1098 K. The weight loss calculated from the TG curves are equal to 74.90–76.20 % (the theoretical: 74.80–75.52 %).

The 2,4-dimethoxybenzoate of Nd(III) decomposes to Nd_2O_3 *via* the intermediate formation of oxycarbonate of neodymium, $\text{Nd}_2\text{O}_2\text{CO}_3$ (993–1043 K).

The combustion of the organic ligands is accompanied by the strong exo-effects seen in the DTA curves. The large peaks recorded in the curves of the DTG correspond to the gradual loss of the weights of complexes during heating.

The trihydrates of 2,4-dimethoxybenzoates of La(III) and Gd(III) and the dihydrates of those of Sm(III) and Eu(III) are stable up to 358–363 K and then loose three (or two molecules) of crystallization water in one step (358–403 K) forming the anhydrous complexes, which decompose at 478–1053 K to the oxides of the respective metal. The found weight losses estimated from TG curves are equal to 4.60–7.30 % (the theoretical: 4.92–7.20 %) and 76.20–77.90 % (the calculated: 75.92–78.39 %) for the dehydration processes and the decomposition to oxides, respectively.

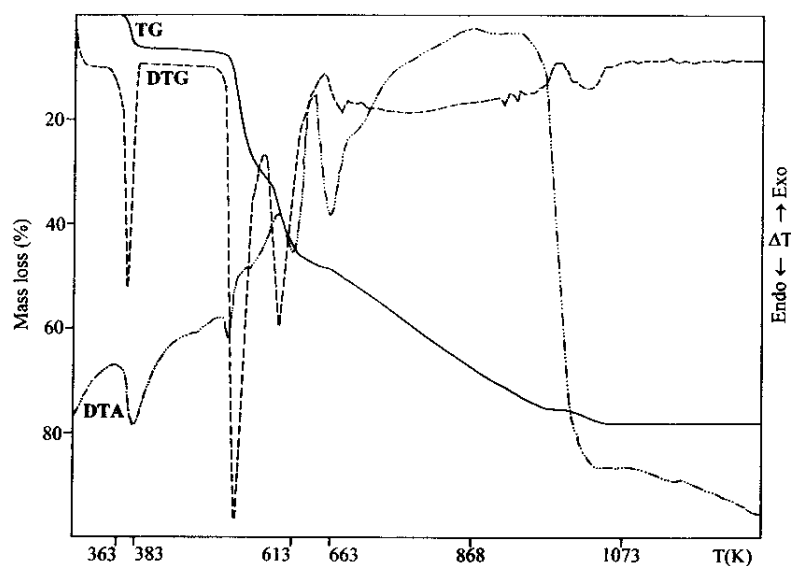


Fig. 2. TG, DTG and DTA curves of lanthanum 2,4-dimethoxybenzoate.

The derivatogram of lanthanum 2,4-dimethoxybenzoate is presented in Fig. 2. This complex decomposes in three steps. The weight loss of the complex starts at 363 K. The decrease in weight occurs in the range 363–383 K and therefore the TG curve deviates from horizontal. The loss in weight determined from the TG curve is equal to 7.30 % (the calculated value is 7.16 %), which corresponds to the loss of three molecules of water of crystallization.^{16,17} Accordingly, the peak ascribed to this loss of weight is also recorded in the curve of the DTG, which is the first derivative of the weight loss.

The dehydration process is connected with the endo-effect observed in the DTA curve. The anhydrous lanthanum 2,4-dimethoxybenzoate, in the second step at 513–1053 K, decomposes to the oxycarbonate of lanthanum, $\text{La}_2\text{O}_2\text{CO}_3$, and then to La_2O_3 (1098 K). La_2O_3 is the final product of the complex decomposition. The

farther loss of weight between 513–1053 K causes the TG curve to deviate from the horizontal. The loss in weight determined from the TG curve is equal to 77.90% (the calculated value is 78.39 %). This decrease in weight results from the oxidation of the organic ligand and the formation of $\text{La}_2\text{O}_2\text{CO}_3$ (983–1053 K), and La_2O_3 . The oxidation process is connected with the strong exo-effect seen in the DTA curve (868 K). Subsequently, above 1053 K the TG curve gains the plateau as the formed La_2O_3 is thermally stable.

TABLE III. Temperature of dehydration and decomposition of the 2,4-dimethoxybenzoates of the light lanthanides

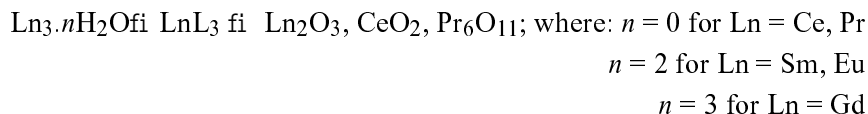
Complex $\text{L}=\text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$	DT_1/K	Weight loss/%		n	$T_{\text{endo DTA}}/\text{K}$	DT_2/K	Weight loss/%		T_{K}/K	Final product of decomp.
		calcd.	found				calcd.	found		
$\text{LaL}_3 \cdot 3\text{H}_2\text{O}$	363–383	7.16	7.30	3	383	513–1053	78.39	77.90	1098	La_2O_3
CeL_3	–	–	–	–	–	508–1003	74.80	74.90	1063	CeO_2
PrL_3	–	–	–	–	–	483–1003	75.10	75.60	1048	Pr_6O_{11}
NdL_3	–	–	–	–	–	498–1043	75.52	76.20	1098	Nd_2O_3
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	368–398	4.93	4.60	2	398	478–1023	76.09	76.20	1073	Sm_2O_3
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	363–403	4.92	4.90	2	398	488–1013	75.93	76.20	1073	Eu_2O_3
$\text{GdL}_3 \cdot 3\text{H}_2\text{O}$	358–398	7.20	7.00	3	388	498–923	77.57	77.60	978	Gd_2O_3

T_1 = temperature range of the dehydration process; n = number of crystallization water molecules lost in one endothermic step; DT_2 = temperature range of the decomposition of the anhydrous complex; T_{K} = temperature of oxide formation; T_{endo} = temperature of the maximum of the endo-effect of the dehydration process in the DTA curve.

In the series of hydrated complexes, the most thermally stable is complex of samarium, which starts to release water at 368 K, while the least thermally stable, is the 2,4-dimethoxybenzoate of Gd (358 K). In the case of the anhydrous complexes, the most thermally stable is lanthanum 2,4-dimethoxybenzoate (513 K), and the least thermally stable is the complex of samarium (478 K).

Considering the comparatively low temperature values at which the dehydration processes start to take place and the losses of water molecules only in one step, it is possible to assume that the molecules of water of crystallization are outer-sphere water. According to Nikolaev *et al.*¹⁸ and Singh *et al.*¹⁹ water eliminated below 423 K can be considered as water of crystallization, whereas water eliminated above 423 K may be that coordinated to the central ion. In our investigations the water is assumed to be crystallization water which was also confirmed by the IR studies.

The results obtained from the thermal decomposition of the complexes indicate that during heating in air to 1273 K they may decompose in the following ways:



$\text{Ln}_3 \cdot n\text{H}_2\text{O}$ fi LnL_3 fi $\text{Ln}_2\text{O}_2\text{CO}_3$ fi Ln_2O_3 ; where: $n = 3$ for $\text{Ln} = \text{La}$
 $n = 0$ for $\text{Ln} = \text{Nd}$

The oxides of the light lanthanide elements formed at 978–1098 K were identified by X-ray powder diffraction analysis.¹⁵ The measurements revealed them to be Ln_2O_3 for $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$, and CeO_2 for Ce and Pr_6O_{11} for Pr . From the obtained results it can be seen that the oxides of lanthanum and neodymium have the highest formation temperature while gadolinium oxide has the lowest one.

The solubilities of the 2,4-dimethoxybenzoates of the light lanthanides in water and ethanol (at 293 K) were measured and their solubility products determined (Table I). The solubilities are in the order of: $10^{-3} \text{ mol dm}^{-3}$ and 10^{-4} – $10^{-3} \text{ mol dm}^{-3}$ in water and ethanol, respectively. The values of the solubility products are of the order of: 10^{-10} – $10^{-8} \text{ mol}^4 \text{ dm}^{-12}$ (in water) and 10^{-12} – $10^{-8} \text{ mol}^4 \text{ dm}^{-12}$ (in ethanol). The 2,4-dimethoxybenzoates of La(III) , Ce(III) , Pr(III) are more soluble in water than in ethanol. The values of the solubilities of the light lanthanide 2,4-dimethoxybenzoates in water increase and decrease alternately, with increasing atomic number of the element, while in ethanol they practically increase steadily.

The 2,4-dimethoxybenzoate of Nd(III) is the most soluble complex in water and that of Gd(III) in ethanol, while the least soluble ones are the complexes of lanthanum and praseodymium in water and ethanol, respectively.

In view of the values of the complex solubilities, it would seem that 2,4-dimethoxybenzoic acid cannot be used for the separation of the light lanthanide elements by ion-exchange chromatography or by extraction methods because its complexes formed with them are not easily soluble.

ИЗВОД

КОМПЛЕКСИ ЛАКИХ ЛАНТАНИДА СА 2,4-ДИМЕТОКСИБЕНЗОЕВОМ КИСЕЛИНОМ

WIESŁAWA FERENC and AGNIESZKA WALKÓW-DZIEWULSKA

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

Синтетизовани су комплекси лаких лантанида са 2,4-диметоксибензоевом киселином формуле $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_n \cdot n\text{H}_2\text{O}$ где је $\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}$, и то су $n = 3$ за La(III) и Gd(III) , $n = 2$ за Sm(III) и Eu(III) и $n = 0$ за Ce(III) , Pr(III) и Nd(III) . Карактеризација је вршена елементалном анализом, IR спектроскопијом, термogrавиметријским мерењима и одређивањем рендгенске дифракције. Комплекси имају боје типичне за Ln^{3+} јоне (бела за La , Ce , Eu и Gd , крем за Sm , зелена за Pr и љубичаста за Nd). Карбоксилна група у овим комплексима је симетрични, бидентатни, хелатни лиганд. Стварају кристале различите симетрије. При грејању на 1273 K у ваздуху 2,4-диметоксисбензоати лаких лантанида разлажу се на различите начине. Хидратизовани комплекси разлажу се у два или три ступња, док се анхидровани облици разлажу у једном или два ступња. Трихидрат лантан-2,4-диметоксисбензоат се прво дехидратишује до анхидроване

соли која се затим разлаже до La_2O_3 пре интермедијарног $\text{La}_2\text{O}_2\text{CO}_3$. Хидрати $\text{Sm}(\text{III})$, $\text{Eu}(\text{III})$ и $\text{Gd}(\text{III})$ разлажу се у два ступња. Прво, дехидратацијом стварају анхидровану со, која се затим директно разлаже до оксида одговарајућих метала. Анхидровани комплекси $\text{Ce}(\text{III})$ и $\text{Pr}(\text{III})$ разлажу се у једном ступњу, док се комплекс $\text{Nd}(\text{III})$ разлаже у два ступња. Растворљивост 2,4-метоксибензоата лакних лантанида на 293 К су реда величине $10^{-3} \text{ mol dm}^{-3}$ у води и $10^{-4} - 10^{-3} \text{ mol dm}^{-3}$ у етанолу.

(Примљено 19. јула, ревидирано 21. октобра 1999)

REFERENCES

1. V. V. Zelentsov, *Zh. Neorg. Khim.* **13** (1968) 591
2. *Gmelin Handbook of Inorganic Chemistry*, Springer-Verlag, Berlin, 1984, p. 105
3. W. W. Wendlandt, J. A. Hoiberg, *Anal. Chim. Acta* **29** (1963) 539
4. *Beilsteins Handbuch der organischen Chemie*, Bd X, Springer-Verlag, Berlin, 1971, p. 1371
5. Z. Marczenko, *Spektrofotometryczne oznaczanie pierwiastków*, PWN, Warszawa, 1979
6. Z. Marczenko, M. Balcerzak, *Spektrofotometryczne metody w analizie nieorganicznej*, PWN, Warszawa, 1998
7. A. Bartecki, *Spektroskopia elektronowa związków nieorganicznych i kompleksowych*, PWN, Warszawa, 1971
8. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, Toronto, 1968
9. K. Nakamoto, P. J. Mc Carthy, *Spectroscopy and Structure of Metal Chelate Compounds*, Wiley, New York, 1968
10. R. C. Mehrotra, R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983
11. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975
12. K. Burger, *Coordination Chemistry: Experimental Methods*, Akademiai Kiado, Budapest, 1973
13. B. S. Manhas, A. K. Tripathi, *J. Indian Chem. Soc.* **59** (1982) 315
14. E. Lagiewka, Z. Bojarski, *Rentgenowska analiza strukturalna*, PWN, Warszawa, 1988
15. P. Pascal, *Nouveau Traité de Chimie Minerale*, VII, Masson et c^{ie} , Paris, 1959
16. D. N. Todor, *Thermal Analysis of Minerals*, Abacus Press, Tunbridge Wells, Great Britain, 1976
17. F. Paulik, *Special Trends in Thermal Analysis*, Wiley, Chichester, 1995
18. A. V. Nikolaev, V. A. Logvinenko, L. I. Myachina, *Thermal Analysis*, Academic Press, New York, 1989
19. B. Singh, B. V. Agarwala, P. L. Mourya, A. K. Dey, *J. Indian Chem. Soc.* **59** (1992) 1130.