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Spectrochemical and thermal behaviours of the 2,4- and 3,4-dimethoxybenzoates of rare earth elements

WIESLAWA FERENC* and AGNIESZKA WALKÓW-DZIEWULSKA

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

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The physicochemical properties and thermal stability in air of the 2,4- and 3,4-dimethoxybenzoates of rare earth elements were compared in order to observe the influence of the position of the $–OCH_3$ substituent on their thermal stability. The complexes of these two series are crystalline, hydrated or anhydrous salts with colours typical of trivalent rare earth ions. The carboxylate group is a bidentate, chelating ligand. The thermal stability of the 2,4- and 3,4-dimethoxybenzoates of the lanthanide elements was studied in the temperature range 273–1173 K. The positions of methoxy- groups in the benzene ring influence the number of crystallization water molecules in the complexes and their thermal stability, which is connected with the varying influence of inductive and mesomeric effects of the $–OCH_3$ substituent on the electron density in the benzene ring.

Keywords: 2,4- and 3,4-dimethoxybenzoates of rare earth elements, thermal stability of complexes, influence of methoxy- groups on the properties of dimethoxybenzoates, influence of substituents.

INTRODUCTION

According to a literature survey, the compounds of 2,4- and 3,4-dimethoxybenzoic acids with various metal ions have been studied scarcely. Papers exist on their complexes with the following cations only: Cu(II), Ag(I), Na(I), Ba(II), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er (III), Tm(III), Yb(III), Lu(III) and Y(III).[1–7] These compounds were obtained as solids or were investigated in solution and some of their physicochemical properties were studied. In the past years there has been no information in the literature about these acid complexes with the rare earth elements. Therefore, lately we decided to prepare them as solids and to examine some of their physicochemical properties.[4–7] In our previous papers,[4–7] these complexes were characterized by elemental analysis, IR spectroscopy, thermogravimetric studies, X-ray diffraction or magnetic measurements. In this paper, the influence of the presence and positions of two methoxy-groups in the benzene ring were investigated by comparing the properties of dimethoxybenzoates of rare earth elements.

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* Corresponding author.

EXPERIMENTAL

The 2,4- and 3,4-dimethoxybenzoates of the lanthanides were prepared by the addition of the equivalent quantities of 0.1 M ammonium 2,4- and 3,4-dimethoxybenzoates (pH≈5) to hot solutions containing the lanthanide chlorides and 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 a constant mass. The carbon, and hydrogen contents were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The contents of the rare earth element were established spectrophotometrically.

The IR spectra of the complexes, as well as the spectra of 2,4- and 3,4-dimethoxybenzoic acid and their sodium salts were recorded in the 4000–400 cm^{-1} range, using KBr discs on an M-80 spectrophotometer. Some of the results are presented in Fig. 1 and in Table I.

TABLE I. Frequencies of the maxima of the absorption bands of the COO^{-} and M– O vibrations for 2,4- and 3,4-dimethoxybenzoates of rare earth elements and sodium (cm^{-1}) and their solubility products in water (at 293 K)

	Complex L = $C_9H_9O_4$	ν_{asCOO^-}	ν_{sCOO^-}	$\Delta\nu_{COO^-}$	$\nu_{M\text{-}O}$	Solubility products (mol dm^{-3})^4
I	$LaL_3\cdot3H_2O$	1520	1400	120	580	$2.0\cdot10^{-10}$
	CeL_3	1520	1400	120	570	$7.9\cdot10^{-9}$
	PrL_3	1520	1400	120	570	$6.7\cdot10^{-9}$
	NdL_3	1530	1400	130	570	$5.5\cdot10^{-8}$
	$SmL_3\cdot2H_2O$	1530	1400	130	575	$3.2\cdot10^{-10}$
	$EuL_3\cdot2H_2O$	1520	1400	120	570	$8.7\cdot10^{-9}$
	$GdL_3\cdot3H_2O$	1520	1410	110	570	$2.8\cdot10^{-9}$
	$TbL_3\cdot2H_2O$	1530	1425	105	566	$6.3\cdot10^{-10}$
	$DyL_3\cdot2H_2O$	1530	1425	105	560	$9.8\cdot10^{-10}$
	$HoL_3\cdot2H_2O$	1530	1430	100	560	$6.0\cdot10^{-10}$
	$ErL_3\cdot2H_2O$	1540	1430	110	566	$7.2\cdot10^{-10}$
	$TmL_3\cdot2H_2O$	1540	1430	110	566	$6.2\cdot10^{-10}$
	YbL_3	1530	1430	100	566	$9.5\cdot10^{-9}$
	LuL_3	1530	1430	100	566	$1.6\cdot10^{-9}$
	$YL_3\cdot2H_2O$	1540	1430	110	566	$1.6\cdot10^{-9}$
	NaL	1560	1400	160	580	-
II	$LaL_3\cdot4H_2O$	1520	1400	120	545	$2.7\cdot10^{-12}$
	$CeL_3\cdot4H_2O$	1520	1400	120	550	$1.4\cdot10^{-10}$
	$PrL_3\cdot4H_2O$	1520	1400	120	540	$7.0\cdot10^{-13}$
	$NdL_3\cdot4H_2O$	1530	1400	130	540	$1.0\cdot10^{-11}$
	$SmL_3\cdot4H_2O$	1530	1400	130	550	$2.5\cdot10^{-11}$
	$EuL_3\cdot4H_2O$	1520	1400	120	540	$9.0\cdot10^{-13}$
	$GdL_3\cdot4H_2O$	1520	1410	110	540	$1.0\cdot10^{-13}$
	$TbL_3\cdot4H_2O$	1520	1410	110	550	$5.0\cdot10^{-12}$
	$DyL_3\cdot4H_2O$	1520	1410	110	550	$4.2\cdot10^{-11}$
	$HoL_3\cdot3H_2O$	1520	1410	110	550	$1.4\cdot10^{-10}$
	ErL_3	1520	1415	105	550	$1.6\cdot10^{-10}$
	TmL_3	1550	1415	135	545	$6.2\cdot10^{-11}$
	YbL_3	1550	1415	135	545	$8.6\cdot10^{-12}$
	LuL_3	1530	1415	135	545	$4.3\cdot10^{-12}$
	YL_3	1525	1415	105	545	$2.0\cdot10^{-10}$
	NaL	1560	1400	160	560	-

I - complexes with 2,4-dimethoxybenzoic acid, **II** - complexes with 3,4-dimethoxybenzoic acid

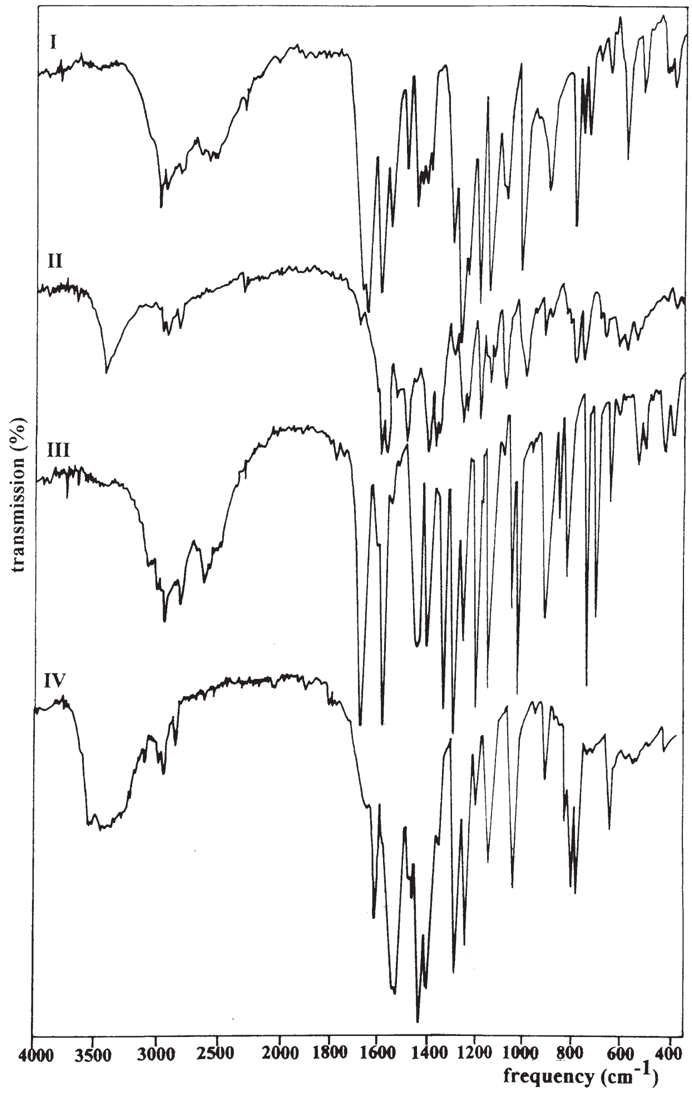

Fig. 1. Infrared spectra of (**I**)-2,4- and (**III**)-3,4-dimethoxybenzoic acids and (**II**)-2,4- and (**IV**)-3,4-dimethoxybenzoates of Sm.

X-Ray powder patterns were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range 2θ = 4–80° by means of the Debye-Scherrer-Hull method. The thermal stabilities of these complexes in air were studied in the range 273–1173 K using a Paulik-Paulik-Erday Q-1500 D derivatograph with a Derill converter recording TG, DTG and DTA curves. The measurements were recorded at a heating rate of 10 K min^{-1} using the full scale of the balance. The 100 mg samples were heated in platinum crucibles in static air to 1173 K with a TG sensitivity, of 100 mg (*i.e.*, the whole scale of the balance was equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer programme. Tha paper speed was 2.5 mm min^{-1} and Al_2O_3 was used as the standard.

The solubilities of the 2,4- and 3,4-dimethoxybenzoates of lanthanides in water (at 298 K) were determined by measuring the concentration of the metal ions in a saturated solution by a spectrophotometrical method using a Specord M-40 spectrophotometer. The absorbance of the complexes was measured using Arsenazo III in formic buffer (HCOOH and HCOONa; $c = 0.1$M; pH 3.5) at the wavelength $\lambda = 650$ nm using the blank as references.[4-7]

RESULTS AND DISCUSSION

The 2,4- and 3,4-dimethoxybenzoates of rare earth elements are crystalline compounds with a metal : ligand ratio of 1 : 3. The 2,4-dimethoxybenzoates of La and Gd form trihydrates, those of Sm, Eu, Tb, Dy, Ho, Er, Tm dihydrates, while the remainder are anhydrous compounds. The 3,4-dimethoxybenzoates of rare earth elements are tetrahydrates (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy), trihydrate (Ho) or anhydrous salts (Er, Tm, Yb, Lu, Y). In these two series of dimethoxybenzoates the number of crystallization water molecules changes with the change of position of the $-OCH_3$ group in benzene ring. The number is greater for the 3,4-dimethoxybenzoates than for the 2,4-dimethoxybenzoates. The 2,4- and 3,4-dimethoxybenzoates of the rare earth metals are similar types of compounds having one carboxylic group and two methoxy- groups in benzene ring. In these compounds one of the two methoxy- groups occupies the position *para-* to the carboxylic group in benzene ring while the second one is in the *ortho-* or *meta-* position. The methoxy- group in the *ortho-* position in benzene ring of the 2,4-dimethoxybenzoates increases the steric effects which may cause the decrease of the degree of hydration degree in the 2,4-dimethoxybenzoates compared to the 3,4-dimethoxybenzoates, in which the methoxy- group in the *meta-* position is probably conducive for the coordination of a greater number of water molecules.

The colours of the 2,4- and 3,4-dimethoxybenzoates of the rare earth elements are typical of the particular Ln(III) ion, *i.e.,* white for La, Ce, Eu, Gd, Tb, Dy, Tm, Yb, Lu and Y, cream for Sm, Ho, greenish for Pr, violet for Nd and pink for Er, having their origin in the lowest-energy f-f electronic transitions of the central ions.[8–11] The compositions of the complexes were established on the basis of elemental analysis and IR spectra data and their external crystalline forms were also estimated.[4–7] From the analysis of the IR spectra of the 2,4- and 3,4-dimethoxybenzoates of the rare earth element, it appears that the carboxylate ion is a bidentate, chelating ligand.[4–7,12–14] The magnitudes of the separation, $\Delta\nu_{OCO^-}$, where $\Delta\nu_{OCO^-} = \Delta\nu_{asOCO^-} - \Delta\nu_{sOCO^-}$, which characterizes the metal-oxygen bond, change in the range from 135–110 cm^{-1} for the 3,4-dimethoxybenzoates to 130–100 cm^{-1} for the 2,4-dimethoxybenzoates. The position of the bands of the metal-oxygen group change depending on the position of the $-OCH_3$ substituents in the aromatic ring. Accordingly, in the case of the 2,4-dimethoxybenzoates of rare earth elements, these bands appear in the range 580 – 566 cm^{-1} while for the 3,4-dimethoxybenzoates they are shifted to lower frequencies, being found in the 550–540 cm^{-1} range. The larger values of the frequencies of the M–O vibration bands for the 2,4-dimethoxybenzoates may suggest stronger M–O bonding in these complexes compared to the 3,4-dimethoxybenzoates. The values of $\Delta\nu_{OCO^-}$ are greater for the 3,4-dimethoxybenzoates of the heavy lanthanides than those for the 2,4-dimetho-

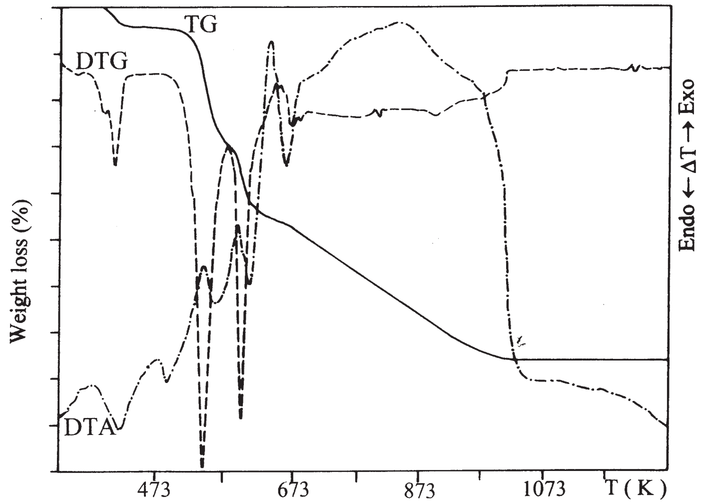

Fig. 2. TG, DTG and DTA curves of 2,4-dimethoxybenzoate of Eu.

xybenzoates. In the 3,4-dimethoxybenzoates the inductive and mesomeric effects of the $-OCH_3$ group in the *meta-* position influence the electron density of the system causing a greater increase of the polarity of the carboxylate group compared to the 2,4-dimethoxybenzoates, in which the steric effects of the $-OCH_3$ group in the *ortho-* position are predominat.[9,11,15] The values of the frequencies of the bands due to ν_{asOCO^-} vibrations are the same for the 2,4- and 3,4-dimethoxybenzoates of the light lanthanides while those due to the ν_{sOCO^-} vibrations are greater for the 2,4-dimethoxybenzoates of the heavy lanthanides compared to the 3,4-dimethoxybenzoates (Table I). The changes in these

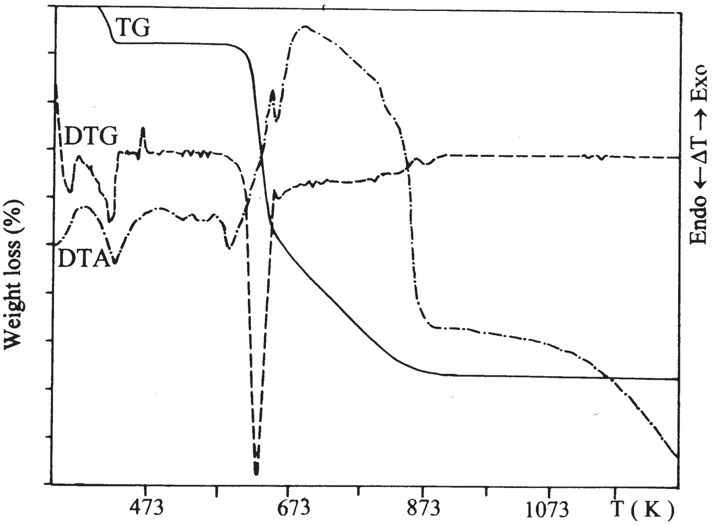

Fig. 3. TG, DTG and DTA curves of 3,4-dimethoxybenzoate of Eu.

values probably result from the size of the central ions of the complexes and their ionic potential, which is greater for the heavy lanthanides than for the light ones because of the contraction phenomena in the lanthanide series.

The X-ray spectra of the 2,4- and 3,4-dimethoxybenzoates of the rare earth elements were recorded and their interpretations are presented in our previous papers.[4–7] The analysis of the diffractograms suggests that the complexes are polycrystalline compounds with different structures.[16]

The thermal stability of these complexes was studied in air in the range 273–1173 K by the TG, DTG and DTA techniques. The obtained results are presented in Figs. 2–4 and Table II. The complexes decompose in various ways on heating. The anhydrous complexes of cerium, praseodymium, neodymium, ytterbium and lutetium 2,4-dimethoxybenzoates are stable up to 483–563 K and then (except that of Nd) decompose to the oxides of the respective metals. Only the 2,4-dimethoxybenzoate of Nd(III) decomposes with the intermediate formation of the oxycarbonate, $Nd_2O_2CO_3$. The hydrated 2,4-dimethoxybenzoates of Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III) decompose in two steps: first crystallization water molecules are released (358–413 K) followed by the formation of the anhydrous complexes (478–548 K) which in turn decompose to the oxides of the particular metal. The trihydrate of lanthanum 2,4-dimethoxybenzoate decomposes in three steps: first water molecules are expelled with the formation of the anhydrous complex, which then next decomposes to La_2O_3 with the intermediate formation of the oxycarbonate, $La_2O_2CO_3$. The oxides of rare earth elements, which are the final products of the 2,4-dimethoxybenzoate decompositions, are formed at 978 K (Gd_2O_3) – 1098 K (La_2O_3, Ho_2O_3) (Fig. 4, Table II). In the series of hydrated 2,4-dimethoxybenzoates, the most thermally stable is the complex of dysprosium (388 K), while the least thermally stable is gadolinium 2,4-dimethoxybenzoate, which starts to release the crystallization water at 358 K. In the series of anhydrous 2,4-dimethoxybenzoates, the complex of ytterbium is the most thermally stable (563 K), while the least thermally stable is that of samarium (478 K). In the series of 3,4-dimethoxybenzoates, the anhydrous complexes of Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are stable up to 563–618 K when they decompose to the oxides of the respective metals. The tetrahydrates of Ce(III), Pr(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and the trihydrate of Ho(III) decompose in two steps. They are stable up to 313–383 K, thereafter losing four water molecules in one step (313–413 K) forming the anhydrous compounds which then decompose to the oxides of the particular metal. The tetrahydrates of La(III) and Nd(III) decompose in three steps: first the molecules of water are lost (333–413 K) with the formation of the anhydrous complexes which then decompose to La_2O_3 and Nd_2O_3 with the intermediate formation of the oxycarbonates. The oxides of the rare earth elements are formed at 863 K (Yb_2O_3) – 1083 K (La_2O_3) (Fig. 4, Table II). In the series of hydrated 3,4-dimethoxybenzoates, the most thermally stable is the complex of dysprosium (383 K), while the least thermally stable is cerium 3,4-dimethoxybenzoate which starts to release water molecules at 313 K. In the case of the anhydrous 3,4-dimethoxybenzoates, the complex of erbium is the most thermally stable (613 K), while the least thermally stable is the complex of cerium (533 K). In the complexes being compared, the dehydration process is connected with an endothermic effect in the DTA curves, whereas the combustion of the organic ligand involves an exothermic one. Considering the relatively low temperatures at which the dehydration process starts and the fact that the water molecules are lost in a single step, it is reasonable to assume that in the rare earth 2,4- and 3,4-dimethoxybenzoates the crystallization water molecules bind in the outer coordination sphere.[17–19] From the obtained results, it appears that in the series of these two isomers of the dimethoxybenzoates of the rare earth elements, the complexes of the 2,4-dimethoxybenzoates are more stable compared to the 3,4-dimethoxybenzoates. Also the temperatures of oxide formation obtained by the ignition of 2,4- and 3,4-dimethoxybenzoates are also greater for those obtained from the 2,4-dimethoxybenazoates.

TABLE II. Temperature ranges of the dehydration and decomposition processes of the 2,4- and 3,4-dimethoxybenzoates of the rare earth elements in an air atomosphere

	Complex $L = C_9H_9O_4$	ΔT_1/K	Weight loss/ % calcd.	found	n	ΔT_2/K	Weight loss/ % calcd.	found	T_K/K
I	$LaL_3 \cdot 3H_2O$	363–383	7.16	7.30	3	513–1053	78.39	77.90	1098
	CeL_3	-	-	-	-	508–1003	74.80	74.90	1063
	PrL_3	-	-	-	-	483–1003	75.10	75.60	1048
	NdL_3	-	-	-	-	498–1043	75.52	76.20	1098
	$SmL_3 \cdot 2H_2O$	368–398	4.93	4.60	2	478–1023	76.09	76.20	1073
	$EuL_3 \cdot 2H_2O$	363–403	4.92	4.90	2	488–1013	75.93	76.20	1073
	$GdL_3 \cdot 3H_2O$	358–398	720	7.00	3	498–923	77.57	77.60	978
	$TbL_3 \cdot 2H_2O$	383–413	4.87	4.62	2	533–983	74.66	74.92	998
	$DyL_3 \cdot 2H_2O$	388–408	4.85	4.62	2	538–998	74.85	74.92	1048
	$HoL_3 \cdot 2H_2O$	383–403	4.84	4.62	2	548–973	74.60	74.92	1098
	$ErL_3 \cdot 2H_2O$	378–398	4.82	4.62	2	543–983	74.37	74.26	1073
	$TmL_3 \cdot 2H_2O$	373–393	4.81	4.62	2	548–963	74.20	74.16	1053
	YbL_3	-	-	-	-	563–973	72.48	72.94	1023
	LuL_3	-	-	-	-	543–988	72.28	72.94	998
	$YL_3 \cdot 2H_2O$	383–403	5.38	5.28	2	548–988	82.97	82.84	1073
II	$LaL_3 \cdot 4H_2O$	333–413	10.50	10.40	4	573–933	75.76	75.56	1083
	$CeL_3 \cdot 4H_2O$	313–393	10.50	10.45	4	533–933	78.00	77.99	943
	$PrL_3 \cdot 4H_2O$	368–408	9.50	9.24	4	553–893	75.10	75.20	923
	$NdL_3 \cdot 4H_2O$	353–413	10.40	10.30	4	573–953	75.76	75.76	1073
	$SmL_3 \cdot 4H_2O$	343–413	10.40	10.35	4	573–953	78.00	78.00	973
	$EuL_3 \cdot 4H_2O$	358–393	9.30	9.40	4	553–898	74.98	75.00	993
	$GdL_3 \cdot 4H_2O$	363–393	9.30	9.20	4	563–943	74.10	74.00	1003
	$TbL_3 \cdot 4H_2O$	373–573	9.30	9.30	4	573–883	72.89	72.90	1033
	$DyL_3 \cdot 4H_2O$	383–598	9.25	9.15	4	598–918	73.58	74.00	973
	$HoL_3 \cdot 3H_2O$	373–603	7.08	7.10	3	603–918	73.33	73.50	993
	ErL_3	-	-	-	-	618–868	73.09	72.99	983
	TmL_3	-	-	-	-	563–933	72.90	72.80	953
	YbL_3	-	-	-	-	613–843	72.50	72.60	863
	LuL_3	-	-	-	-	563–853	72.31	72.36	873
	YL_3	-	-	-	-	608–948	82.02	80.00	968

I - complexes with 2,4-dimethoxybenzoic acid, **II** - complexes with 3,4-dimethoxybenzoic acid, ΔT_1 – temperature range of the dehydration process, n – number of molecules of crystallization water being lost in one endothermic process, ΔT_2 – temperature range of the decomposition of the anhydrous complexes, T_K – temperature of oxide formation

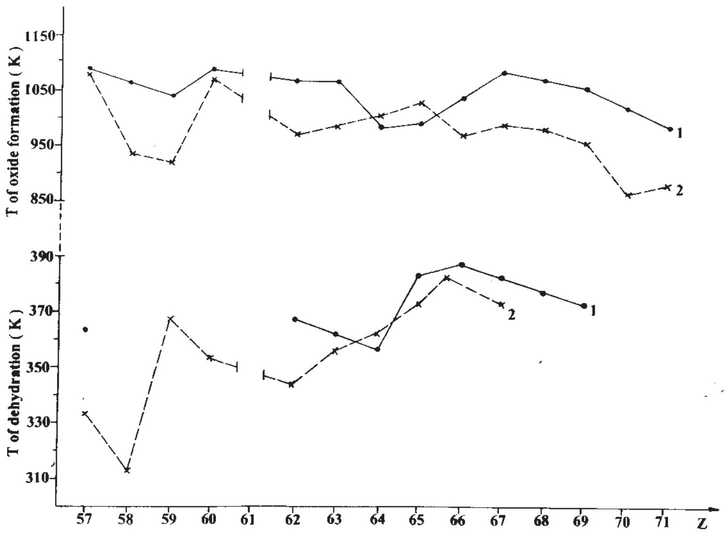

Fig. 4. Dependence of the initial dehydration and oxide formation temperature of 2,4- and 3,4-dimethoxybenzoates of lanthanides and Z.

The solubilities of the 2,4- and 3,4-dimethoxybenzoates of the rare earth elements at 293 K in water were measured and their solubility products were determined (Table I). They are in the order of $10^{-3} - 10^{-4}$ mol dm^{-3} and $10^{-8} - 10^{-13}$ (mol dm^{-3})^4, for the 2,4- and 3,4- isomers, respectively. The 2,4-dimethoxybenzoates are more soluble than the 3,4-dimethoxybenzoates (Fig. 5). In the series of the 2,4-dimethoxybenzoates, the complex of Nd is the most soluble salt while that of lanthanum is the least soluble. In the case of the 3,4-dimethoxybenzoates, the complex of erbium is the most soluble whereas that of samarium is the least. The greater solubility of the 2,4-dimethoxybenzoates is connected with the steric effect caused by the $-OCH_3$ group in the *ortho-* position. The magnitudes of the solubities of these complexes are greater than the electrolytic dissociation constants of the parent acids, which are $K = 5.10\times10^{-10}$ and $K = 3.6\times10^{-5}$ for 2,4- and 3,4-dimethoxybenzoic acids, respectively.[2,3] The lower value of the dissociation constant of 2,4-dimethoxybenzoic acid is probably caused by the formation of a hydrogen bond between the hydrogen atom of the $-COOH$ group and the oxygen atom of the $-OCH_3$ group, which stabilizes the acid molecule and thus decreases its strength.

In the view of the low values of the solubilities of the complexes, 2,4- and 3,4-dimethoxybenzoic acids appear unsuitable for the separation of rare earth elements by ion-exchange chromatography or by extraction methods.

In conclusion, the obtained results show that the position of the $-OCH_3$ substituents in the benzene ring influences the thermal stability of complexes, their solubility in water (at 293 K) and the temperature of oxide formation that change in the order: 3,4-dimethoxy- < 2,4-dimethoxy-. The position of the methoxy- groups also influence the number of crystallization water molecules in the complexes and the positions of the asymmetrical vibration bands of the carboxylate groups in their IR spectra.

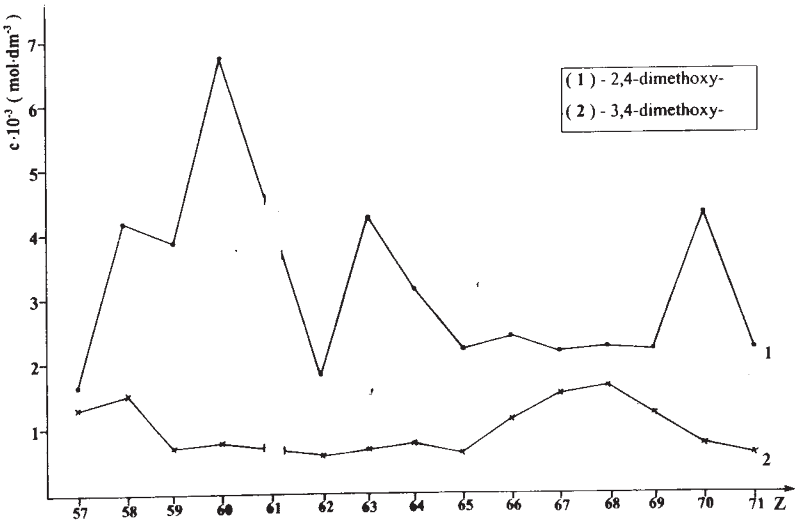

Fig. 5. Relationship between the solubilities of 2,4- and 3,4-dimethoxybenzoates of the rare earth elements and Z.

Moreover, the results reveal that the colours of the complexes and the dentate of the carboxylate group remain the same for both series of rare earth element dimethoxybenzoates, irrespective of the positions of the methoxy- group in the benzene ring.

ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО И ТЕРМИЧКО ПОНАШАЊЕ 2,4- И 3,4-ДИМЕТОКСИБЕНЗОАТА ЕЛЕМЕНАТА РЕТКИХ ЗЕМАЉА

WIESLAWA FERENC and AGNIESZKA WALKÓW-DZIEWULSKA

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

Упоређене су физичкохемијске особине и термичка стабилност у ваздуху 2,4- и 3,4-диметоксибензоата елемената ретких земаља у циљу проучавања утицаја положаја $-OCH_3$ супституента на њихову термичку стабилност. Комплекси ове две серије су кристалиничне, хидратисане или анхидроване соли боја типичних за јоне елемената ретких земаља. Карбоксилатна група је бидентатни хелатни лиганд. Термичка стабилност 2,4- и 3,4-диматоксибензоата лантанидних елемената проучавана је у температурном опсегу 273 – 1173 K. Положај метокси група у бензеновом прстену утиче на број молекула кристалне воде у комплексу и њихову термичку стабилност, а што је повезано са различитим утицајима индуктивних и мезомерних ефеката $-OCH_3$ супституента на електронске густине у бензеновом прстену.

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