

SPECTRAL AND THERMAL INVESTIGATION OF RARE EARTH ELEMENT 4-METHOXY-2-METHYLBENZOATES

W. Brzyska and W. Ożga*

Department of General Chemistry, Faculty of Chemistry, Marie Curie Skłodowska University,
Pl-20031 Lublin, Poland

(Received January 9, 2002; in revised form March 22, 2002)

Abstract

4-Methoxy-2-methylbenzoates of Y(III) and lanthanides(III) (La–Lu) were prepared as crystalline anhydrous complexes with general formula $\text{Ln}(\text{C}_9\text{H}_9\text{O}_3)_3$ (complexes of La and Pr as monohydrates). Monohydrates heated in air lose crystallization water molecule and then anhydrous complexes decompose directly to oxides. Only La(III) complex decomposes to oxide with intermediate formation $\text{La}_2\text{O}_2\text{CO}_3$. The carboxylate group in the studied complexes is a tridentate chelating – bridging or bidentate chelating (Y).

Keywords: complexes, IR spectra, 4-methoxy-2-methylbenzoic acid, thermal analysis

Introduction

4-Methoxy-2-methylbenzoic acid $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)\text{COOH}$, known as 2-methylanisic acid, is a crystalline solid, sparingly soluble in water [1, 2]. The complexes of 4-methoxy-2-methylbenzoic acid with rare earth elements were previously unknown. A survey of literature shows that the complexes of rare earth with 2,4-dimethoxybenzoic acid [3–5] were prepared as solids, sparingly soluble in water, with molar ratio of metal to organic ligand of 1:3 and various degree of hydration or anhydrous ones (Ce, Pr, Nd, Yb, Lu). During heating they are dehydrated in one step and next anhydrous complexes decompose directly to oxides.

As a continuation of our work on the rare earth element carboxylates [6–10], we now report on the preparation, and spectral and thermal studies of Y(III) and lanthanide(III) (La–Lu) complexes with 4-methoxy-2-methylbenzoic acid in solid state.

Experimental

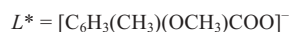
4-Methoxy-2-methylbenzoates of Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by reaction of stoichiometric quantities of hot 0.2 M solution of

* Author for correspondence: E-mail: BRZYSKA@hermes.umcs.lublin.pl

ammonium 4-methoxy-2-methylbenzoate (pH 5.5) and solution of lanthanide chlorides (Ce was used as its nitrate). The precipitate was formed during heating the mixture for 0.5 h at 343–353 K; it was then filtered off, washed with hot water to remove NH_4^+ and Cl^- ions, and dried at 303 K to a constant mass. The sodium salt was prepared by adding stoichiometric quantities of 4-methoxy-2-methylbenzoic acid to a solution of NaOH and crystallizing at room temperature.

Table 1 Analytical data and solubilities in water at 293 K of Y(III) and lanthanide(III) 4-methoxy-2-methylbenzoates

Complex	Ln/%		C/%		H/%		Solubilities/ 10^{-4} mol dm $^{-3}$
	calcd.	found	calcd.	found	calcd.	found	
Yl $_3$ *	15.24	15.2	55.48	55.50	4.62	4.60	5.50
	21.30	21.3	49.70	49.80	4.45	4.40	8.10
	22.06	22.1	51.02	51.00	4.25	4.28	8.49
	21.55	21.6	49.55	49.60	4.43	4.40	38.20
	22.56	22.6	50.68	50.70	4.22	4.20	98.60
	23.29	23.3	50.20	50.00	4.18	4.20	9.37
	23.48	23.5	50.08	50.00	4.17	4.20	7.88
	24.10	21.0	49.67	49.90	4.14	4.15	12.00
	24.30	24.3	49.55	49.60	4.13	4.12	2.76
	24.71	24.8	49.27	49.30	4.10	4.10	2.76
	24.99	25.0	49.09	49.10	4.09	4.10	3.15
	25.25	25.2	48.92	49.00	4.07	4.10	2.65
	25.49	25.5	48.77	48.80	4.06	4.10	1.52
	25.90	26.0	48.50	48.50	4.04	4.00	1.60
	26.11	26.2	48.36	48.40	4.03	4.00	1.00



The carbon and hydrogen in the prepared complexes were determined by elemental analysis on a Perkin Elmer CHN 2400 analyser. The metal content was determined from TG curve and by ignition of the complexes in air to the oxides at 1273 K. The content of crystallization water was determined from the TG curve and by heating the samples isothermally at 453 K to a constant mass.

The IR spectra of 4-methoxy-2-methylbenzoic acid, its sodium salt and of the separated Y(III) and lanthanide(III) complexes were recorded over the range 4000 – 400 cm^{-1} on a Specord M80 spectrophotometer. The samples were prepared as KBr discs. The X-ray patterns were recorded with a HZG 4 (Zeiss Jena) diffractometer by Debye–Scherrer powder method using Ni filtered CuK_α radiation. The measurements were made over the range $2\theta=5\text{--}80^\circ$ (Fig. 1).

The solubility of the prepared complexes in water was determined at 293 K. The saturated solutions were prepared under isothermal conditions. The content of Ln(III) ions was determined by spectrophotometric analysis using UV-VIS Specord M 40 spectrophotometer. The solubility of the complexes was calculated on the basis of metal(III) concentration in the saturated solution (Table 1).

The thermal stability of the prepared 4-methoxy-2-methylbenzoates was determined using a Paulik–Paulik–Erdey Q 1500 D derivatograph with Derill converter. Measurements were made with a sensitivity of 100 mg (TG). The sensibility of DTG and DTA curves were regulated by Derill computer program. Samples of 100 mg were heated in air atmosphere in platinum crucibles to 1273 K at a heating rate 10 K min^{-1} with a full scale. The hydrated complexes were heated isothermally at a set temperatures to a constant mass. The products of dehydration and decomposition were confirmed by the IR spectra and X-ray diffractograms.

Results and discussion

Complexes of Y(III) and lanthanides from La(III) to Lu(III) with 4-methoxy-2-methylbenzoic acid were prepared as crystalline solids with the colour characteristic for lanthanide(III) ions and with molar ratio of metal to organic ligand of 1.0 to 3.0 and general formula $\text{Ln}(\text{C}_9\text{H}_9\text{O}_3)_3$. Only the complexes of La(III) and Pr(III) were prepared as monohydrates (Table 1).

The IR absorption spectra of the prepared 4-methoxy-2-methylbenzoates are similar to each other (except of La and Pr) and have many bands. When the acid is converted to complexes the absorption band of C=O of COOH group at 1680 cm^{-1} disappears and the bands of asymmetrical (ν_{as}) and symmetrical (ν_{s}) vibrations of OCO group appear at $1516\text{--}1508$ and $1392\text{--}1385 \text{ cm}^{-1}$, respectively (for Y complex at 1512 and 1400 cm^{-1}) the bands of OCH_3 with a maximum at $1388\text{--}1384$, $1288\text{--}1284$ and 1248 cm^{-1} , the bands of CH_3 at 2980 and 2850 , 1453 , 1411 , 1322 , 1270 cm^{-1} and the bands of the M–O bond at $426\text{--}425 \text{ cm}^{-1}$. In the IR spectra of the prepared complexes there are numerous bands of aromatic ring at $1172\text{--}1168$, $1104\text{--}1096$, $1048\text{--}1044$ and 920 cm^{-1} , and the CH bond at $848\text{--}836$ and $792\text{--}780 \text{ cm}^{-1}$ [6–12]. These bands are shifted insignificantly ($10\text{--}5 \text{ cm}^{-1}$) compared to the respective bands of 4-methoxy-2-methylbenzoic acid; this indicates that Ln(III) ions have only a weak influence on the benzene ring. The frequencies of M–O bond for all the complexes studied have similar values (Table 2). Accordingly, it may be suggested that 4-methoxy-2-methylbenzoic acid forms complexes with Y(III) and lanthanides(III) that have similar stability [6]. The separation value ($\Delta\nu$) of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ in the IR spectra of the prepared complexes ($\Delta\nu=124\text{--}120 \text{ cm}^{-1}$) are almost the same as for the sodium salt, what shows on the similar degree of ionic bond in the complexes studied and in the sodium salt. Only for yttrium(III) complex the separation value ($\Delta\nu$) is smaller ($\Delta\nu=112 \text{ cm}^{-1}$) than for the sodium salt. The bands of asymmetric and symmetric vibrations of OCO group are shifted insignificantly to the smaller values or do not change their position (Yb, Lu). Only in the spectrum of Y(III) complex the band $\nu_{\text{as}}(\text{OCO})$ is shifted to lower frequencies and the bands $\nu_{\text{s}}(\text{OCO})$ to higher ones. From the

shifts of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ in the IR spectra of the complexes, compared to the bands of sodium, it can be suggested that the OCO group is bonded probably as chelating – bridging, whereas in Y(III) one – as bidentate chelating [7–9]. In the complexes of La(III) and Pr(III) there are broad absorption bands of $\nu(\text{OH})$ with a max. at 3400 cm^{-1} and the narrow bands $\delta(\text{H}_2\text{O})$ at 1680 cm^{-1} that are characteristic for hydrates.

The Y(III) and lanthanide(III) 4-methoxy-2-methylbenzoates are crystalline solids of low symmetry and different structure. They are sparingly soluble in water (Table 1). Their solubilities are of the order 10^{-4} – $10^{-3}\text{ mol dm}^{-3}$ and change periodically in the lanthanide series. The complexes of heavy lanthanides are more sparingly soluble in water than those of light lanthanides, what is connected with contraction effect.

4-Methoxy-2-methylbenzoates of Y(III) and lanthanides(III) are stable in air and can be stored without change. When heated in air, the complexes decompose in various ways (Table 2, Figs 1–3). The monohydrated complexes of La and Pr are stable up to 333–348 K and next lose crystallization water molecule over the range 333–396 K. The water molecule in the hydrated complexes is probably in outer coordination sphere. According to Nikolaev *at al.* [13] and Singh *at al.* [14] water released below 423 K can be considered as crystallization water, whereas that eliminated above 423 K, as chemically bounded to the central ion through coordination bond, but generally it is possible to say, that the temperature of dehydration is not connected directly with the compound structure and weak and strong bonding of water molecules [15].

Table 2 Frequencies of characteristic absorption bands in IR spectra of Na(I) and rare earth 4-methoxy-2-methylbenzoates (cm^{-1})

Complex	$\nu(\text{OH})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu_{\text{as}}-\nu_{\text{s}}$	$\nu(\text{M}-\text{O})$
YL_3^*	–	1512	1400	112	426
$\text{LaL}_3\cdot\text{H}_2\text{O}$	3400	1508	1385	123	425
CeL_3	–	1505	1385	120	425
$\text{PrL}_3\cdot\text{H}_2\text{O}$	3400	1509	1385	124	425
NdL_3	–	1508	1385	123	425
SmL_3	–	1512	1385	127	426
EuL_3	–	1512	1385	127	425
GdL_3	–	1512	1385	127	426
TbL_3	–	1512	1389	123	425
DyL_3	–	1512	1389	123	425
HoL_3	–	1512	1389	123	425
ErL_3	–	1512	1393	119	426
TmL_3	–	1512	1392	120	426
YbL_3	–	1516	1392	120	426
LuL_3	–	1516	1392	124	426
$\text{NaL}\cdot n\text{H}_2\text{O}$	3400	1516	1392	124	

* $L = [\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)\text{COO}]^-$

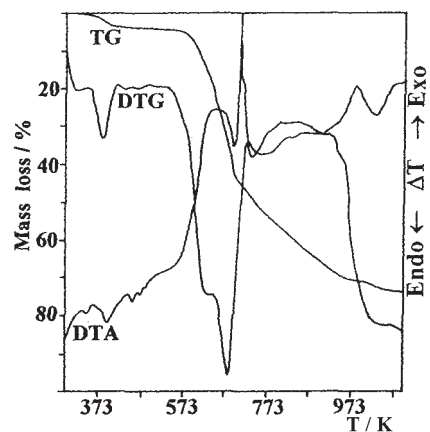


Fig. 1 TG, DTG and DTA curves of $\text{La}\{\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)\}_3 \cdot \text{H}_2\text{O}$

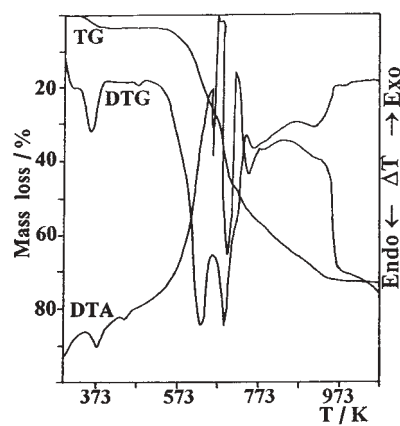


Fig. 2 TG, DTG and DTA curves of $\text{Pr}\{\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)\}_3 \cdot \text{H}_2\text{O}$

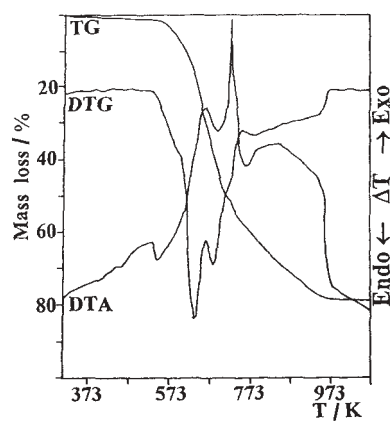
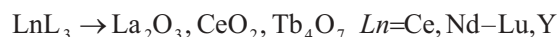
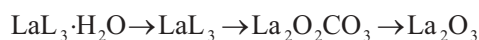


Fig. 3 TG, DTG and DTA curves of $\text{Y}\{\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)\}_3$

Table 3 Thermoanalytical data of Y(III) and lanthanide(III) 4-methoxy-2-methylbenzoates

Complex	ΔT_1 /K	Mass loss /%		$n\text{H}_2\text{O}/$ mol	ΔT_2 /K	Mass loss /%		T/K
		calcd.	found			calcd.	found	
YL ₃ *	–	–	–	–	533–933	80.80	80.5	973
LaL ₃ ·H ₂ O	348–413	2.76	2.7	1	523–1083	75.01	75.0	1083
CeL ₃	–	–	–	–	483–983	72.91	73.0	983
PrL ₃ ·H ₂ O	333–396	2.75	2.7	1	523–903	74.00	74.0	903
NdL ₃	–	–	–	–	473–973	73.68	74.0	973
SmL ₃	–	–	–	–	513–993	72.98	73.0	993
EuL ₃	–	–	–	–	531–998	72.70	72.0	998
GdL ₃	–	–	–	–	513–983	72.22	72.0	983
TbL ₃	–	–	–	–	523–968	71.42	71.5	968
DyL ₃	–	–	–	–	523–953	71.64	71.6	953
HoL ₃	–	–	–	–	533–978	71.17	71.0	978
ErL ₃	–	–	–	–	533–988	71.12	71.0	998
TmL ₃	–	–	–	–	538–993	70.89	70.5	993
YbL ₃	–	–	–	–	538–973	70.51	70.5	973
LuL ₃	–	–	–	–	533–998	70.30	70.5	998

The anhydrous complexes of Y(III) and all lanthanides are stable up to 513–538 K (Ce complex up to 483, Nd one – up to 473 K) and next decompose directly to oxides, Ln₂O₃, CeO₂, Pr₆O₁₁ and Tb₄O₇ except of La complex which decompose to oxide with intermediate formation Ln₂O₂CO₃ (953 K). The results indicate that the thermal decomposition of Y(III) and lanthanide(III) 4-methoxy-2-methylbenzoates can be presented in the following manner:



The dehydration and decomposition of the complexes are connected with a strong endothermic effects, whereas the combustion of the organic ligand and products of its decomposition shows exothermic effects. The temperatures of the beginning of decomposition (T_1) and the temperatures of the beginning of decomposition (T_2) change insignificantly with increasing atomic number Z of the metal (Fig. 4) except of neodymium complex, which begins to decompose over 473 K. The temperatures over which oxides exist (T_k) change irregularly in the lanthanide series: Pr₆O₁₁ forms at the lowest temperature (903 K) and La₂O₃ at the highest (1083 K).

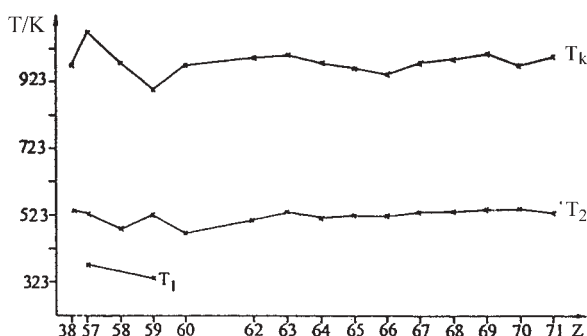


Fig. 4 Relationship between T_1 , T_2 , T_K and Z

Comparing the obtained results with the properties of rare earth element 2,4-dimethoxybenzoates [3–6] it is possible to say that substitution of one OCH_3 group by the CH_3 group in benzene ring influences on the number of crystallization water molecules in the complexes, the position of the asymmetric and symmetric vibration bands of carboxylate group in their IR spectra and the temperature over which the oxides exist.

Conclusions

4-Methoxy-2-methylbenzoates of Y(III) and lanthanides(III) from La to Lu were prepared as crystalline solids with a molar ratio of metal to organic ligand of 1.0:3.0. Complexes of La(III) and Pr(III) were prepared as monohydrates, whereas the complexes of Y(III), Ce(III) and Nd(III)–Lu(III) as anhydrous complexes. The prepared complexes are sparingly soluble in water (10^{-4} – 10^{-3} mol dm^{-3}). Upon heating in air the hydrated complexes of La and Pr lose water molecule and then all anhydrous complexes decompose directly to oxides (Ln_2O_3 , CeO_2 , Pr_6O_{11} , Tb_4O_7), except of anhydrous La complex which decomposes to oxide with intermediate formation $\text{La}_2\text{O}_2\text{CO}_3$. Temperatures over which exist oxides change irregularly in the lanthanide series. The oxide of lanthanum have the highest formation temperature while praseodymium oxide has the lowest one.

References

- 1 Beilsteins Handbuch der organischen Chemie, Springer Verlag, Berlin 1927, Vol. 19, p. 214.
- 2 Beilsteins Handbuch der organischen Chemie, Springer Verlag, Berlin 1971, Vol. E II, p.128 19, p. 214.
- 3 W. Ferenc and A. Walków-Dziewulska, J. Serb. Chem. Soc., 65 (2000) 789.
- 4 W. Ferenc and A. Walków-Dziewulska, J. Serb. Chem. Soc., 65 (2000) 27.
- 5 W. Ferenc and A. Walków-Dziewulska, J. Thermal Anal. Cal., 63 (2001) 865.
- 6 W. Brzyska, J. Therm. Anal. Cal., 59 (2000) 799.
- 7 W. Brzyska and W. Oźga, J. Therm. Anal. Cal., 60 (2000) 123.
- 8 W. Brzyska, A. Bartyzel, K. Zieniewicz and A. Zielińska, J. Therm. Anal. Cal., 63 (2001) 493.

- 9 R. Kurpiel-Gorgol and W. Brzyska, *J. Therm. Anal. Cal.*, 66 (2001) 851.
- 10 W. Brzyska, A. Tarnawska, A. Twardowska and E. Wiśniewska, *J. Therm. Anal. Cal.*, 68 (2002) 123.
- 11 K. Burger, *Coordination Chemistry., Experimental Methods*, Academic Press, Budapest 1973.
- 12 L. J. Bellamy, *The Infrared Spectra of Complex Molecules.*, Chapman and Hill, London 1975.
- 13 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, N. Y. 1997.
- 14 B. S. Manhas and A. K. Trikha, *J. Indian Chem. Soc.*, 59 (1982) 315.
- 15 R. C. Mehotra and R. Bohra, *Metal Complexes*, Academic Press, London 1983.
- 16 A. K. Bridson, *Inorganic Spectroscopic Methods*, Oxford University Press, Oxford 1998.
- 17 L. H. Harwood and T. D. Claridge, *Introduction to Organic Spectroscopy*, Oxford University Press, Oxford 1999.
- 18 A. V. Nikolaev, V. A. Lodvienko and L. J. Myachina, *Thermal Analysis, Vol. 2*, Academic Press, New York 1969.
- 19 B. Singh, B. A. Agarwala, P. L. Mourya and A. K. Dey, *J. Indian Chem. Soc.*, 59 (1992) 1130.
- 20 V. A. Longvinenko and A. V. Nikolaev, *J. Thermal Anal.*, 13 (1978) 253.