

THERMAL AND SPECTRAL STUDIES OF 2,4,5-TRIMETHOXYBENZOATES OF HEAVY LANTHANIDES(III) AND YTTRIUM(III)

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2,4,5-Trimethoxybenzoates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are crystalline, hydrated salts with colours typical for M(III) ions. The carboxylate group is a bidentate, chelating ligand. The complexes of Tb(III), Dy(III) and Ho(III) are dihydrates while those of Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are trihydrates. These compounds are characterized by low symmetry. On heating in air to 1273 K, the 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) decompose in two steps. At first they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. The values of the enthalpy of dehydration process were determined. The solubility in water at 293 K for all heavy lanthanides(III) and yttrium(III) are in the orders of 10^{-3} – 10^{-4} mol dm⁻³. The magnetic moments of the complexes were determined in the temperature range 77–300 K.

Keywords: complexes of 2,4,5-trimethoxybenzoic acid, IR spectra, magnetic moments, thermal stability, 2,4,5-trimethoxybenzoates

Introduction

The carboxylates of lanthanides(III) have been studied in recent years according to their special physico-chemical properties, variety of structural types and potential uses as fluorescent sensors and in medicine [1]. We have been working for years on the isomers of mono-, di- and trimethoxybenzoates of rare earth elements(III) [2–11]. The –COOH group, as electron acceptor substituent decreases the electronic density of benzene ring and –OCH₃ group as electron donor decreases the acidity of benzoic acid derivatives. The opposite properties of these two kinds of substituents influence the properties of isomers of methoxybenzoic acids and their compounds.

We have obtained the complexes of 2,3,4-, 2,4,5-, and 3,4,5-trimethoxybenzoates of light lanthanides(III) and have investigated their physico-chemical properties. Some of them have been described in our published earlier articles [2–4]. This time as a continuation of our research on the compounds of trimethoxybenzoic acids we have decided to examine the complexes of 2,4,5-trimethoxybenzoic acid with Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III). Therefore the aim of our work was to prepare 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and Y(III) and to characterize their properties including thermal stability in air during heating to 1273 K, FTIR spectral characteristic, X-ray powder investigations, solubility in water at room temperature and magnetic properties. The decomposition of complexes was studied in air because a good deal of reactions of those type of compounds in the solid state are

often carried out in air atmosphere at room or at higher temperatures so we were interested in their behaviours under mentioned above conditions. Generally, the thermal stability investigations provide information about the scheme of complex decomposition and the endo- or exo-effects connected with such processes as: dehydration, melting, polymorphic changes, crystallization, oxidation or reduction. They also let determine the products of complex decompositions and establish the mechanism of its decomposition on the basis of a kinetic evaluation of the appropriate thermal break-down step. 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 chromatography methods. The magnetic measurements give information about the nature of metal–oxygen bond.

Experimental

The complexes of 2,4,5-trimethoxybenzoic acid with heavy lanthanides(III) and yttrium(III) were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,4,5-trimethoxybenzoate (pH≈5) to a hot solution containing the chlorides of these metal ions and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K.

The C, H analysis was performed using a CHN 2400 Perkin Elmer analyser. The contents of M³⁺ metals were established by oxalic acid method (Table 1) [12].

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The FTIR and FIR spectra of complexes were recorded over the ranges 4000–400 and 650–100 cm^{-1} , respectively using a FTIR 1725X Perkin Elmer and a DIGILAB FTS-14 spectrometers. The samples for FTIR spectroscopy were prepared as KBr discs while those for FIR spectroscopy were used in Apieson suspensions. Some of the results are presented in Table 2 and in Fig. 1.

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The measurements were made within the range $2\theta=4\text{--}80^\circ$ by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of the complexes were studied in air by Q-1500D derivatograph with Derill converter, simultaneously 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 1273 K with a sensitivity of the TG, 100 mg. The DTG and DTA sensitivities were regulated by the Derill computer programme. Some results are presented in Table 3.

The TG/DSC analysis was also performed at temperatures 303–1173 K using a Setaram differential thermoanalyser Setsys 16/18. The experiments were carried out under air flow rate of 1.1 $\text{dm}^3 \text{h}^{-1}$. The humidity of air flowing through apparatus was not controlled because for the experiments the dry air was used. The values of enthalpy of dehydration process were calculated and presented in Table 3.

The gaseous decomposition products were analysed over the range 4500–700 cm^{-1} using the Mettler Toledo Star System (Table 4). We used this kind of apparatus because only that one was accessible for our purpose to determine them.

Magnetic susceptibilities of polycrystalline samples of 2,4,5-trimethoxybenzoates of heavy lanthanides(III) were carried out at a magnetic field strength of $7.9 \cdot 10^{-5} \text{ A m}^{-1}$. The calibrant employed was $\text{Co}[\text{Hg}(\text{SCN})_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5} \text{ cm}^{-3} \text{ g}^{-1}$. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [13, 14]. The magnetism of the samples was found to be field

Table 1 Analytical data of heavy lanthanides(III) and yttrium 2,4,5-trimethoxybenzoates

Complex $L=\text{C}_{10}\text{H}_{11}\text{O}_5$	C%		H%		Ln(III)%	
	calcd.	found	calcd.	found	calcd.	found
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	43.48	43.45	4.50	4.73	19.18	19.10
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	43.30	43.16	4.48	4.72	19.53	19.13
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	43.18	43.06	4.47	4.50	19.76	19.18
$\text{ErL}_3 \cdot 3\text{H}_2\text{O}$	42.15	43.05	4.59	4.63	19.56	20.10
$\text{TmL}_3 \cdot 3\text{H}_2\text{O}$	42.06	42.91	4.55	4.63	19.74	20.16
$\text{YbL}_3 \cdot 3\text{H}_2\text{O}$	41.85	42.50	4.53	4.56	20.12	20.55
$\text{LuL}_3 \cdot 3\text{H}_2\text{O}$	41.76	42.73	4.52	4.58	20.30	20.65
$\text{YL}_3 \cdot 3\text{H}_2\text{O}$	46.40	47.10	5.03	4.99	11.46	12.13

Table 2 Spectroscopic data of 2,4,5-trimethoxybenzoates of heavy lanthanides(III), yttrium(III) and sodium, and of 2,4,5-trimethoxybenzoic acid (cm^{-1}) and the solubility of the salts (mol dm^{-3}) in water at 293 K

Complex $L=\text{C}_{10}\text{H}_{11}\text{O}_5$	$\nu_{\text{C=O}}$	ν_{asOCO}	ν_{sOCO}	$\Delta\nu$	$\nu_{(\text{M-O})}$	Solubility/ mol dm^{-3}
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	–	1524	1412	112	425	$1.5 \cdot 10^{-4}$
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	–	1528	1412	116	425	$2.2 \cdot 10^{-4}$
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	–	1524	1424	110	430	$1.2 \cdot 10^{-3}$
$\text{ErL}_3 \cdot 3\text{H}_2\text{O}$	–	1528	1424	104	425	$1.37 \cdot 10^{-3}$
$\text{TmL}_3 \cdot 3\text{H}_2\text{O}$	–	1525	1425	100	425	$2.07 \cdot 10^{-4}$
$\text{YbL}_3 \cdot 3\text{H}_2\text{O}$	–	1530	1430	100	445	$1.69 \cdot 10^{-4}$
$\text{LuL}_3 \cdot 3\text{H}_2\text{O}$	–	1530	1430	100	450	$1.18 \cdot 10^{-3}$
$\text{YL}_3 \cdot 3\text{H}_2\text{O}$	–	1530	1420	110	450	$3.64 \cdot 10^{-3}$
NaL	–	1560	1388	172	–	–
HL	1700	–	–	–	–	–

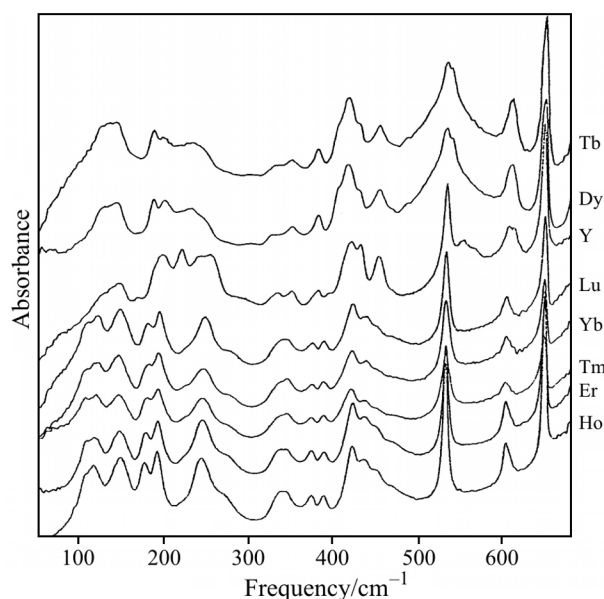


Fig. 1 FIR spectra for 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III)

independent. The temperature-independent paramagnetism of heavy lanthanides(III) was assumed to be zero. Magnetic moments were calculated according to Eqs (1) and (2).

$$\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2} \quad (1)$$

$$\mu_{\text{eff}} = 2.83[\chi_M(T-\theta)]^{1/2} \quad (2)$$

The results of magnetic moments for analysed complexes are presented in Table 5 and in Fig. 2.

Results and discussion

The complexes of 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) were obtained as polycrystalline solids with a metal to ligand ratio of 1:3 and a general formula $M(\text{C}_{10}\text{H}_{11}\text{O}_5)_3 \cdot n\text{H}_2\text{O}$, where $M(\text{III}) = \text{Tb, Dy, Ho, Er, Tm, Yb, Lu}$ and Y and $n=2$ for $\text{Tb(III), Dy(III), Ho(III)}$, and $n=3$ for $\text{Er(III), Tm(III), Yb(III), Lu(III)}$ and Y(III) . Their colours are typical for the appropriate trivalent ions.

Table 3 Data of the heavy lanthanides(III) and yttrium(III) 2,4,5-trimethoxybenzoate thermal decompositions in air atmosphere

Complex $L=\text{C}_{10}\text{H}_{11}\text{O}_5$	$\Delta T_1^a/\text{K}$	Mass loss/%		n	$\Delta T_2^b/\text{K}$	Mass loss/%		T_K^c/K	$\Delta H_d/\text{kJ mol}^{-1}$
		calcd.	found			calcd.	found		
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	303–425	4.35	4.32	2	530–900	77.44	78.34	989	94.85
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	340–410	4.33	4.68	2	515–910	77.49	78.35	990	99.70
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	330–390	4.32	4.36	2	520–920	77.43	77.52	980	113.50
$\text{ErL}_3 \cdot 3\text{H}_2\text{O}$	360–420	6.46	6.29	3	520–930	76.63	77.63	950	154.40
$\text{TmL}_3 \cdot 3\text{H}_2\text{O}$	362–425	6.30	6.04	3	510–954	71.16	71.90	960	170.50
$\text{YbL}_3 \cdot 3\text{H}_2\text{O}$	360–420	6.28	6.13	3	510–925	70.81	71.78	930	165.38
$\text{LuL}_3 \cdot 3\text{H}_2\text{O}$	380–430	6.15	6.09	3	530–930	68.75	69.46	954	167.13
$\text{YL}_3 \cdot 3\text{H}_2\text{O}$	360–420	6.95	6.69	3	510–970	78.55	79.11	980	160.14

ΔT_1^a – temperature range of dehydration process, n – numbers of molecules of crystallization water lost in one dehydration process, ΔT_2^b – temperature range of anhydrous complex decomposition, T_K^c – final temperature of decomposition, ΔH_d – value of enthalpy of dehydration process

Table 4 Frequencies of absorption bands of some gaseous product evolved during decomposition of 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) (cm^{-1})

Range of frequency	Identified gaseous products
4000–3500	H_2O
2000–1350	
1830–1330	
3800–3500	CO_2
2400–2280	
670	
2060–2220	CO
3100–1420	Hydrocarbons
1000	
905	

Table 5 Values of μ_{eff} for the heavy lanthanides(III) determined by Hund, van Vleck and at room temperature

Ln(III)	Ground term	Hund μ_{eff}	van Vleck μ_{eff}	$\mu_{\text{eff}}^*/\text{BM}$
Tb	$^7\text{F}_6$	9.7	9.7	9.62
Dy	$^6\text{H}_{15/2}$	10.6	10.6	10.58
Ho	$^5\text{I}_8$	10.6	10.6	10.64
Er	$^4\text{J}_{15/2}$	9.6	9.6	9.62
Tm	$^3\text{H}_6$	7.6	7.6	7.60
Yb	$^2\text{F}_{7/2}$	4.5	4.5	4.48
Lu	$^1\text{S}_0$	0.0	0.0	0.00

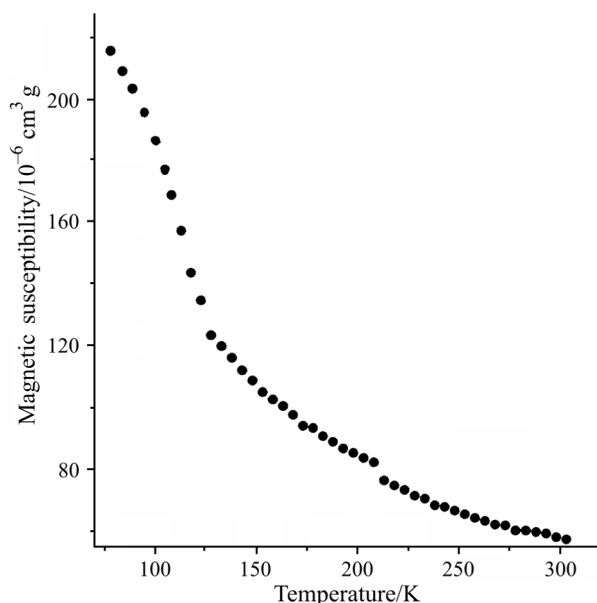


Fig. 2 Dependence between magnetic susceptibilities and temperatures for 2,4,5-trimethoxybenzoates of Ho(III)

The complexes were characterized by elemental analysis (Table 1), and FTIR and FIR spectroscopy (Table 2, Fig. 1). The infrared spectrum of 2,4,5-trimethoxybenzoic acid shows the following absorption bands: a strong band of COOH group at 1700 cm^{-1} , the bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups at 2960 and 2850 cm^{-1} , respectively. The bands of ring vibrations appear at 1620 , 1590 – 1475 , 1190 and 1090 cm^{-1} . The $-\text{C}-\text{O}-\text{C}-$ symmetric vibration bands, $\nu_s(\text{C}-\text{O}-\text{C})$ occur at 1050 – 1030 cm^{-1} . The bands observed at 980 – 930 cm^{-1} are associated to the out-of-plane deformation ring vibrations, $\phi(\text{C}-\text{C})$, and the C–H wagging vibrations, $\gamma(\text{C}-\text{H})$. The bands at 890 cm^{-1} have been assigned to the $\gamma(\text{C}-\text{H})$ vibrations (in 1,2,4,5 substituted ring) [2–4, 15–25].

In the FTIR spectra of 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) the band at 1700 cm^{-1} disappears which indicates that COOH group is not present in the analysed complexes. In their spectra there are two bands arising from asymmetric and symmetric vibrations of the COO^- group occurring, at 1530 – 1524 and 1430 – 1412 cm^{-1} , respectively. The bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups, $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$, are observed at the 2970 – 2920 and 2840 – 2810 cm^{-1} respectively. The bands of $\nu(\text{C}=\text{C})$ ring vibrations appear at 1595 – 1580 , 1100 and 1030 cm^{-1} . The bands at 1150 – 1130 cm^{-1} are attributed to the $\delta(\text{C}-\text{H})$ deformation vibrations and those of the $-\text{C}-\text{O}-\text{C}-$ symmetric vibrations of the $-\text{C}-\text{O}-\text{C}-$, $\nu_s(\text{COC})$, occur at 1040 – 1025 cm^{-1} . The bands observed at 905 – 605 cm^{-1} are associated to out-of-plane deformation ring vibration, $\phi(\text{C}-\text{C})$, and out-of-plane C–H bond vibrations, $\gamma(\text{C}-\text{H})$.

The bands at 910 – 800 cm^{-1} are assigned to the (C–H) vibrations (in 1,2,4,5-substituted ring). The bands at 450 – 425 cm^{-1} results from $\nu(\text{M}-\text{O})$ stretching vibrations [2–4, 15–25]. The bands with the maxima at 3470 – 3450 cm^{-1} characteristic for $\nu(\text{OH})$ vibrations and narrow bands of $\delta(\text{H}_2\text{O})$ at 1620 – 1610 cm^{-1} confirm the presence of crystallization water molecules in the analysed complexes. The oscillation ring vibrations result in the bands at 387 – 378 cm^{-1} . The bands at 287 – 259 cm^{-1} correspond to the $\nu(\text{M}-\text{O})$ vibrations [25]. The bands at 129 – 119 cm^{-1} are due to the $\text{O}-\text{H}\cdots\text{O}$ stretching vibrations [26, 27] and they change their shapes according to the atomic number of the central ions and degree of hydration in the 2,4,5-trimethoxybenzoates. The bands at 137 – 135 cm^{-1} confirm the internal C–C torsion [26, 27].

Table 2 presents the maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- group for 2,4,5-trimethoxybenzoates of heavy lanthanides(III), yttrium(III) and sodium. The magnitude of the separation, $\Delta\nu_{\text{COO}^-}$ between the frequencies of ν_{asCOO^-} and ν_{sCOO^-} in these complexes are lower ($\Delta\nu_{\text{COO}^-} = 116$ – 100 cm^{-1}) than in the sodium salt ($\Delta\nu_{\text{COO}^-} = 172 \text{ cm}^{-1}$), which indicates a smaller degree of ionic bond in the heavy lanthanide(III) 2,4,5-trimethoxybenzoates. For 2,4,5-trimethoxybenzoates of heavy lanthanides(III) the shifts of the frequencies ν_{asCOO^-} and ν_{sCOO^-} are lower and higher, respectively, than those for sodium 2,4,5-trimethoxybenzoate. Accordingly, the carboxylate ion in the analysed complexes appears to be a symmetrical, bidentate, chelating ligand [25, 27]. Probably the methoxy-group may also coordinate with central ion. It results from the interpretation of FTIR spectra analysis. The band positions of $-\text{OCH}_3$ group vibrations in the spectra of complexes are changed in comparison with those in the acid spectrum.

The analysis of the diffractograms suggests that the heavy lanthanides(III) and yttrium(III) 2,4,5-trimethoxybenzoates are polycrystalline compounds. The structures of the compounds have not been determined because single crystals have not been obtained.

The thermal stability of the 2,4,5-trimethoxybenzoates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) was studied in air atmosphere in the temperature range 293 – 1273 K . Some results are presented in Table 3. The results reveal that the complexes of heavy lanthanides(III) and yttrium(III) are hydrated compounds. These results were also confirmed by the elemental analysis (Table 1) and FTIR spectra. 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) heated in air to 1273 K are stable up to 303 – 380 K . Next during heating they decompose in two steps. In the temperature range 303 – 425 K they dehydrate and form anhydrous salts that on further heating decompose to the oxides of

the appropriate metals. Dihydrates of Tb(III), Dy(III), Ho(III) lose in one step two molecules of water while trihydrates of Er(III), Tm(III), Yb(III), Lu(III) and Y(III) the three of them. The dehydration process is associated with an endothermic effect on DTA curves. The mass losses calculated from TG curves being equal to 4.32–6.69% correspond to the loss of 2 or 3 molecules of water (theoretical values are 4.32–6.95%). The anhydrous 2,4,5-trimethoxybenzoates of yttrium(III) and heavy lanthanides(III) in the temperature range 510–970 K are decomposed to the oxides of appropriate lanthanides. The mass losses calculated from TG curves are equal to 69.46–79.11% (the theoretical values are 68.75–78.55%). The combustion of the organic ligand is accompanied by strong exo-effect. The temperatures of the thermal stability of complexes do not change regularly with the increasing atomic number of elements. 2,4,5-Trimethoxybenzoate of Lu(III) is the most thermally stable ($T_1=380$ K) while the least thermally stable is complex of Tb(III) ($T_1=303$ K). Heavy lanthanides(III) and yttrium(III) 2,4,5-trimethoxybenzoates are decomposed directly to the oxides of the respective metals as final products of their decomposition. The oxides of these elements are formed at 990–930 K. The temperature of oxide formation is the highest for Dy_2O_3 (990 K) and the lowest for Yb_2O_3 (930 K).

The values of enthalpy of the dehydration process for 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III), ΔH , were determined using DSC technique (Table 3). These values are in the range 170.50–94.85 kJ mol⁻¹ and they seem to be in good agreement with the supposed losses of 2 or 3 molecules of water, respectively, depending on the position of water molecules in the complex lattice, the strength of their bonding in its sphere and on the various interactions in their surroundings.

The FTIR spectra of the gaseous products evolved during the decomposition of the 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) are presented in Table 4. Their interpretation reveals them to be the molecules of H₂O, CO₂, CO and hydrocarbons [16–18, 23–25].

The solubilities of 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) in water (at 293 K) were measured (Table 2). They are in the order of 10⁻³–10⁻⁴ mol dm⁻³. The yttrium(III) 2,4,5-trimethoxybenzoate is the most soluble salt while that of terbium(III) the least soluble one.

The magnetic susceptibility of the heavy lanthanide(III) 2,4,5-trimethoxybenzoates was measured in the temperature range of 77–300 K. The values of the Weiss constant, θ , are negative for all of the complexes which may be caused by small antiferromagnetic spin interactions in the complexes that are

higher at room temperatures than at lower ones or a crystal field splitting of the paramagnetic spin state [29, 30]. This may probably result from the presence of superexchange magnetic interactions between paramagnetic centres of different molecules of the complexes in the crystal lattice. The paramagnetic central ions in the compounds investigated remain virtually unaffected by the surrounding ligands. The 4f electrons causing their paramagnetism are well protected from outside influences and do not participate in the formation of the Ln–O bond. Instead, they only weakly interact with the electrons of the surrounding atoms and are located in an inner shell of a radius of 0.35 Å [31]. This value is very small in comparison with the radius of the 5s²5p⁶ closed shell equals to ca. 1 Å. The ground state of the lanthanide ions is separated by several hundreds of cm⁻¹ from the first higher-lying state. Hence the magnetic properties in the ground state can be expected to be identical for bounded and non-bounded lanthanide ions. The 2,4,5-trimethoxybenzoates of heavy lanthanides(III) obey the Curie–Weiss law (Fig. 2). The values of μ_{eff} determined for all the complexes are close to those calculated for Ln(III) ions by Hund and van Vleck (Table 5). Lutetium 2,4,5-trimethoxybenzoate is, as expected, diamagnetic.

The above presented data indicate that the Ln–O bond in the heavy lanthanide(III) 2,4,5-trimethoxybenzoates is predominantly of an electrostatic nature since 4f orbitals of the lanthanide ions are effectively polarized by the 5s²5p⁶ octet [31, 32].

Conclusions

On the basis of the results obtained it appears that 2,4,5-trimethoxybenzoates of heavy lanthanides(III) were synthesized as di- or trihydrated complexes. Their colours are typical for the particular *M*(III) ion, i.e. white for Tb, Dy, Tm, Yb, Lu, Y, cream for Ho and salmon for Er, having their origin in the lowest energy of f→f electronic transitions of the central ions. Their energies are not radically changed in comparison with the free lanthanide ions, therefore the colours of the compounds are the same as those for the free lanthanide ions. The M–O bond is mainly electrostatic in nature. The carboxylate group in the analysed complexes appears to have a symmetrical, bidentate, chelating character. The complexes are polycrystalline compounds that on heating in air to 1273 K decompose in two steps. In the first step they dehydrate to form anhydrous complexes that next decompose to the oxides of the appropriate metals. The gaseous products evolved during the decomposition of the 2,4,5-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) are the molecules of H₂O, CO₂, CO and hydrocarbons. The values of enthalpy of the dehydration process confirm the losses

of two or three molecules of water. The values of the enthalpy depend also on the position of water molecules in the space lattice of a complex, their strength of bonding in its sphere that is determined by the various interactions in their surroundings.

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