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# COMPLEXES OF HEAVY LANTHANIDES AND YTTRIUM WITH 3,4-DIMETHOXYBENZOIC ACID

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## Abstract

The complexes of yttrium and heavy lanthanides with 3,4-dimethoxybenzoic acid of the formula: $Ln(C_9H_9O_4)_3 \cdot nH_2O$, where $Ln$=Y(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III), and $n$=4 for Tb(III), Dy(III), $n$=3 for Ho(III), and $n$=0 for Er(III), Tm(III), Yb(III), Lu(III) and Y(III) have been prepared and characterized by elemental analysis, IR spectroscopy, thermogravimetric and magnetic studies and X-ray diffraction measurements. The complexes have colours typical of $Ln^{3+}$ ions (Ho – cream, Tb, Dy, Yb, Lu, Y – white, Er – salmon). 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 hydrated 3,4-dimethoxybenzoates decompose in two steps while those of anhydrous only in one stage. The tetrahydrates of Tb and Dy and trihydrate of Ho 3,4-dimethoxybenzoates are firstly dehydrated to form anhydrous salts that next are decomposed to the oxides of the respective metals. The complexes of Er, Tm, Yb, Lu and Y are directly decomposed to the oxides of the appropriate elements. The solubility in water at 293 K for yttrium and heavy lanthanides is in the order of $10^{-4}$–$10^{-3}$ mol dm$^{-3}$. The magnetic moments of the complexes were determined over the range 77–298 K. They obey the Curie-Weiss law. The values of $\mu_{eff}$ calculated for all compounds are close to those obtained for $Ln^{3+}$ by Hund and van Vleck. The results show that there is no influence of the ligand field on 4f electrons of lanthanide ions in these polycrystalline compounds and 4f electrons do not take part in the formation of M–O bonding.

**Keywords:** 3,4-dimethoxybenzoates of rare earth elements, magnetic moments of 3,4-dimethoxybenzoates, solubility of complexes, thermal stability of complexes

## Introduction

A literature survey indicated that the compounds of 3,4-dimethoxybenzoic acid with various cations have been relatively seldom studied. Papers exist on its complexes with the following cations only: $Na^+$, $Ag^+$ and $Ba^{2+}$ [1]. The 3,4-dimethoxybenzoate of Na(I) forms dihydrate, that of Ba(II) hexahydrate while that of Ag(I) is anhydrous complex. 3,4-Dimethoxybenzoic acid of the formula $C_9H_{10}O_4$ is a white, crystalline solid, sparingly soluble in water and readily soluble in alcohol and ether. Its dissociation constant is equal to $3.6 \cdot 10^{-5}$ (25°C) and its melting point is 181°C [2].

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There are no information about the solid-state properties of the complexes of 3,4-dimethoxybenzoic acid with yttrium and heavy lanthanides. Therefore, we decided to synthesize them in the solid state and to examine some of their physicochemical properties, that is thermal stability in air during heating to 1273 K, solubility in water at 293 K, and to present their IR spectral characterization 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 determining its final or intermediate products, to establish 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. In our investigations on thermal stability of the complexes during heating in air to 1273 K we did not study the kinetics of the decomposition process under non-isothermal condition and we tried to estimate the activation energy of dehydration reaction using only Fotieev-Pletniev method. The close investigations connected with the kinetics of the decomposition process and the comparison of the various methods for more real determination of the activation energy of dehydration process are the aims of our future works.

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 method.

The magnetic moments of 3,4-dimethoxybenzoates of yttrium and heavy lanthanides were determined in order to estimate the nature of M–O bond in these complexes.

**Table 1** Analytical data of 3,4-dimethoxybenzoates of heavy lanthanides and yttrium

| Complex<br>*L*=$C_9H_9O_4$ | H/% | | C/% | | Ln/% | |
|---|---|---|---|---|---|---|
| | calcd. | found | calcd. | found | calcd. | found |
| $TbL_3\cdot 4H_2O$ | 4.52 | 4.48 | 41.83 | 41.85 | 20.52 | 20.58 |
| $DyL_3\cdot 4H_2O$ | 4.49 | 4.40 | 41.64 | 41.68 | 20.88 | 20.78 |
| $HoL_3\cdot 3H_2O$ | 4.33 | 4.38 | 42.49 | 42.58 | 21.63 | 21.63 |
| $ErL_3$ | 3.79 | 3.80 | 45.58 | 45.57 | 23.53 | 23.49 |
| $TmL_3$ | 3.81 | 3.80 | 45.51 | 45.53 | 23.70 | 23.73 |
| $Ybl_3$ | 3.79 | 3.79 | 45.25 | 45.24 | 24.14 | 24.15 |
| $LuL_3$ | 3.78 | 3.80 | 45.13 | 45.15 | 24.34 | 24.28 |
| $YL_3$ | 4.29 | 4.30 | 51.20 | 51.25 | 14.19 | 14.09 |

## Experimental

3,4-Dimethoxybenzoates of yttrium and heavy lanthanides were prepared by the addition of the equivalent quantities of 0.1 M ammonium 3,4-dimethoxybenzoate (pH≈5) to a hot solution containing the heavy lanthanide element nitrates and by crystallizing at 293 K. The solids formed were 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 using CHN 2400 Perkin Elmer analyser. The contents of the yttrium and heavy lanthanide elements were established by oxalic acid method (Table 1).

The IR spectra of complexes were recorded over the range 4000–400 $cm^{-1}$ using M-80 spectrophotometer. Samples were prepared as KBr discs. Some of the results are presented in Table 2.

**Table 2** Spectroscopic data of 3,4-dimethoxybenzoates of heavy lanthanides, yttrium and Na and 3,4-dimethoxybenzoic acid ($cm^{-1}$), their solubility in water at 293 K and solubility products

| Complex $L$=$C_9H_9O_4$ | $\nu_{C=O}$ | $\nu_{as\,COO^-}$ | $\nu_{s\,COO^-}$ | $\Delta\nu_{COO^-}$ | Solubility/ $M$ | Solubility products/ $mol^4\,dm^{-12}$ |
|---|---|---|---|---|---|---|
| $TbL_3{\cdot}4H_2O$ | – | 1520 | 1410 | 110 | $6.6{\cdot}10^{-4}$ | $5.0{\cdot}10^{-12}$ |
| $DyL_3{\cdot}4H_2O$ | – | 1520 | 1410 | 110 | $1.1{\cdot}10^{-3}$ | $4.2{\cdot}10^{-11}$ |
| $HoL_3{\cdot}3H_2O$ | – | 1520 | 1410 | 110 | $1.5{\cdot}10^{-3}$ | $1.4{\cdot}10^{-10}$ |
| $ErL_3$ | – | 1520 | 1415 | 105 | $1.6{\cdot}10^{-3}$ | $1.6{\cdot}10^{-10}$ |
| $TmL_3$ | – | 1550 | 1415 | 135 | $1.2{\cdot}10^{-3}$ | $6.2{\cdot}10^{-11}$ |
| $YbL_3$ | – | 1550 | 1415 | 135 | $7.5{\cdot}10^{-4}$ | $8.6{\cdot}10^{-12}$ |
| $LuL_3$ | – | 1530 | 1415 | 135 | $6.3{\cdot}10^{-4}$ | $4.3{\cdot}10^{-12}$ |
| $YL_3$ | – | 1525 | 1415 | 105 | $1.6{\cdot}10^{-3}$ | $2.0{\cdot}10^{-10}$ |
| NaL | 1700 | 1560 | 1400 | 160 | – | – |
| HL | – | – | – | – | – | – |

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered $CuK_\alpha$ radiation. The measurements were made within the range of $2\theta=4–80°$ by means of the Deby'e-Scherrer-Hull method.

The thermal stability and decomposition of the prepared complexes were determined by Paulik-Paulik-Erdey Q-1500D derivatograph with 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 samples (100 mg) were heated in platinum crucibles in static air to 1173 K with a sensitivity 100 mg, DTG and DTA sensitivities were regulated by computer Derill programme. The products of decomposition were calculated from the TG curves and verified by the diffraction pattern registration (Table 3).

The solubility of 3,4-dimethoxybenzoates of yttrium and heavy lanthanide elements in water at 298 K was determined by measuring the concentration of $Ln^{3+}$ ions in a saturated solution by the oxalic acid method (Table 2).

Magnetic susceptibility of polycrystalline samples of 3,4-dimethoxybenzoates was measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were made at a magnetic field strength of 9.9 kθe. The calibrant employed was $CoHg(SCN)_4$, for which the magnetic susceptibility [3] was taken $1.644{\cdot}10^{-5}$ $cm^3\,g^{-1}$. The correction for diamagnetism of the constituent atoms was calculated by use of

**Table 3** Temperature of dehydration and decomposition of 3,4-dimethoxybenzoates of heavy lanthanides and yttrium

| Complex $L$=$C_9H_9O_4$ | $\Delta T_1$/K | Mass loss/% | | $n$ | $\Delta T_2$/K | Mass loss/% | | $T_K$/K | $E_a$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | calcd. | found | | | calcd. | found | | |
| $TbL_3 \cdot 4H_2O$ | 373–573 | 9.30 | 9.30 | 4 | 573–883 | 72.89 | 72.90 | 1033 | 132.2 |
| $DyL_3 \cdot 4H_2O$ | 383–593 | 9.25 | 9.15 | 4 | 598–918 | 73.58 | 74.00 | 973 | 73.2 |
| $HoL_3 \cdot 3H_2O$ | 373–593 | 7.08 | 7.10 | 3 | 603–918 | 73.33 | 73.50 | 993 | 92.5 |
| $ErL_3$ | – | – | – | – | 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 | – |

$\Delta T_1$=temperature range of dehydration process; $n$=number of crystallization water molecules being lost in one endothermic step; $\Delta T_2$=temperature range of decomposition of anhydrous complex; $T_K$=temperature of the oxide formation; $E_a$=energy activation of dehydration reaction

Pascal's constants [4]. The magnetism of the samples was found to be field independent. The temperature-independent paramagnetism of the lanthanide ions was assumed to be zero. The magnetic moments were calculated from the equations:

$$\mu=2.83(\chi_{\mathrm{M}}T)^{1/2}$$

$$\mu=2.83[\chi_{\mathrm{M}}(T-\theta)]^{1/2}$$

The magnetic moments calculated for 3,4-dimethoxybenzoates of heavy lanthanides at 298 K are presented in Table 4.

**Table 4** Values of $\mu_{\mathrm{eff}}$ for lanthanides determined by Hund and van Vleck and 3,4-dimethoxybenzoates of heavy lanthanides at 298 K* ($\mu$/BM)

| $Ln^{3+}$ | Ground term | $\mu_{\mathrm{eff}}$ calculated by | | $\mu_{\mathrm{eff}}$ (BM)* |
|---|---|---|---|---|
| | | Hund | van Vleck | |
| $Tb^{3+}$ | $^7F_6$ | 9.70 | 9.70 | 9.68 |
| $Dy^{3+}$ | $^7H_{15/2}$ | 10.60 | 10.60 | 10.65 |
| $Ho^{3+}$ | $^5I_8$ | 10.60 | 10.60 | 10.68 |
| $Er^{3+}$ | $^4I_{15/2}$ | 9.60 | 9.60 | 9.64 |
| $Tm^{3+}$ | $^3H_6$ | 7.60 | 7.60 | 7.58 |
| $Yb^{3+}$ | $^2F_{7/2}$ | 4.50 | 4.50 | 4.46 |
| $Lu^{3+}$ | $^1S_0$ | 0.00 | 0.00 | 0.00 |

## Results and discussion

3,4-Dimethoxybenzoates of yttrium and heavy lanthanides were obtained as crystalline hydrated or anhydrous products with a metal to ligand ratio of 1:3 and general formula: $Ln(C_9H_9O_4)_3\cdot nH_2O$, where $Ln$=Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III). For Tb(III), Dy(III) $n$=4, for Ho(III) $n$=3, and for Er(III), Tm(III), Yb(III), Lu(III), Y(III) $n$=0.

The colours of the complexes are those typical of the appropriate trivalent $Ln^{3+}$ ions (it means for Tb, Dy, Tm, Yb, Lu and Y – white, Ho – cream, Er – salmon), which is connected with the electron density in the system [5–8].

The complexes were characterized by elemental analysis (Table 1) and IR spectra. All 3,4-dimethoxybenzoates of heavy lanthanides and yttrium show similar solid state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salts. The band of the COOH group at 1700 cm$^{-1}$ present in the acid spectrum, disappears in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of the $COO^-$ group occur at 1550–1520 and 1415–1410 cm$^{-1}$, respectively [9–12]. The bands with the maxima at 3540–3530 cm$^{-1}$ characteristic of $\nu$(OH) vibrations and narrow band $\delta(H_2O)$ at 1600 cm$^{-1}$ confirm the presence of crystallization water in the complexes of Tb(III), Dy(III) and Ho(III). The bands of C–H antisymmetric stretching of $CH_3$ groups are observed at 2930–2925 cm$^{-1}$

whereas their symmetric stretching at 2830–2825 $cm^{-1}$. The symmetric deformation vibration bands of $CH_3$ group occur at 1325–1320 $cm^{-1}$. The presence of $–OCH_3$ groups in benzene ring is confirmed by the bands at 1250–1245 $cm^{-1}$. The skeletal ring mode region is observed at 1610–1450 $cm^{-1}$. The =C–H bond stretches appear at 3015–3000 $cm^{-1}$ and out-of-plane C–H bonding in the range 945–645 $cm^{-1}$. The bands typical of the aromatic ring vibrations are insignificantly shifted compared to the respective bands in 3,4-dimethoxybenzoic acid which indicates that the Ln(III) ions weakly influence the benzene ring. The bands due to metal-oxygen bond appear at 545–540 $cm^{-1}$ and they are not regularly shifted in the spectra. Probably 3,4-dimethoxybenzoic acid forms complexes with rare earth elements that have the similar stability [13]. Table 2 presents the maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the $COO^-$ for 3,4-dimethoxybenzoates of yttrium and heavy lanthanides and sodium and of CO group for 3,4-dimethoxybenzoic acid [9–14]. The magnitudes of separation, $\Delta\nu$, between the frequencies $\nu_{as\,OCO^-}$ and $\nu_{s\,OCO^-}$ in the complexes are lower ($\Delta\nu$= 135–105 $cm^{-1}$) than in sodium salt ($\Delta\nu$=160 $cm^{-1}$) which indicates a smaller degree of ionic bond in the rare earth element 3,4-dimethoxybenzoates. For 3,4-dimethoxybenzoates of yttrium and heavy lanthanides the shifts of the frequencies $\nu_{as\,OCO^-}$ and $\nu_{s\,OCO^-}$ are lower and higher,

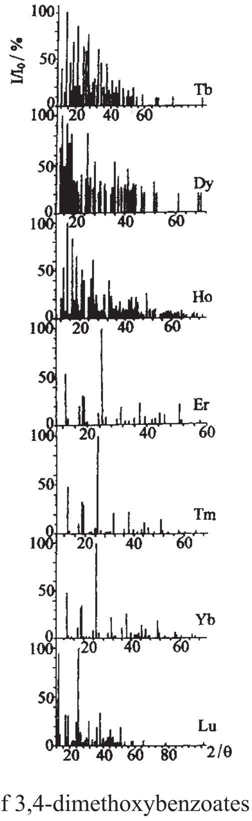

**Fig. 1** Radiograms of 3,4-dimethoxybenzoates of heavy lanthanides

respectively than those for sodium 3,4-dimethoxybenzoate. Accordingly, the carboxylate ion appears to be a symmetrical, bidentate, chelating ligand [9, 11, 14].

The diffractogram analysis suggests that 3,4-dimethoxybenzoates are polycrystalline compounds with various symmetry and different structures (Fig. 1). They form two groups of isostructural compounds. The hydrated 3,4-dimethoxybenzoates of Tb(III), Dy(III) and Ho(III) of low symmetry belong to the one of them while those of anhydrous ones (Er, Tm,Yb) having the higher symmetry belong to the second isostructural group. The structures of the complexes have not been determined because single crystals have not been obtained. 3,4-Dimethoxybenzoates of yttrium and heavy lanthanides heated to 1273 K form the oxides of the respective metals having the same structures as the oxides obtained from the ignition of rare earth element oxalates [15].

The thermal stability of yttrium and heavy lanthanide 3,4-dimethoxybenzoates was studied in the range 273–1273 K (Table 3). The results obtained from their thermal decomposition reveal them to be tetrahydrates (Tb, Dy), trihydrate (Ho) and anhydrous salts (Er, Tm, Yb, Lu, Y), as it was established on the basis of elemental analysis (Tables 1 and 3). All 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 Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are stable up to 563–618 K and then they are decomposed to the oxides of appropriate metals that are formed at 863–983 K. The mass loss calculated from TG curves are equal to 72.36–80.00% (theoretical: 72.31–82.02%).

The TG, DTG and DTA curves of erbium 3,4-dimethoxybenzoate is presented in Fig. 2. The mass loss of the complex starts at 618 K. The sudden decrease in mass occurs in the range 618–868 K and the TG curve does not proceed horizontally. The loss in mass determined from TG curve is 72.99% (calculated value is 73.09%). That decrease in mass is ascribed to the oxidation of organic ligand and the formation of $Er_2O_3$. The peak in DTG curve connected with the mass loss is observed. The oxidation process is connected with the strong exoeffect in the DTA curve. After this, above 868 K the TG curve

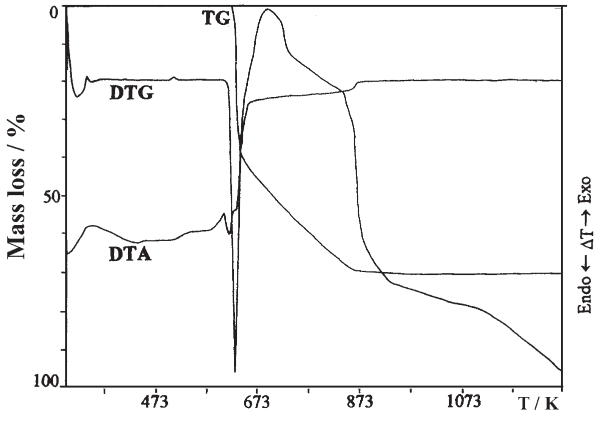

**Fig. 2** TG, DTG and DTA curves of 3,4-dimethoxybenzoate of Er

is horizontal again, which corresponds to $Er_2O_3$ formation. Tetrahydrates of Tb(III), Dy(III) and trihydrate of Ho(III) are stable up to 373–383 K and then loosing all molecules of crystallization water in one step (373–593 K) they form anhydrous complexes, that at 573–918 K are decomposed to the oxides of respective metals. The found mass losses estimated from TG curves are equal to 7.10–9.30% (theoretical: 7.08–9.30%) and 72.90–74.00% (calculated: 72.89–73.58%) for dehydration processes and the formations of oxides, respectively. In the series of hydrated complexes the most thermally stable is the complex of dysprosium that releases water at 383 K while the least thermally stable ones are 3,4-dimethoxybenzoates of Tb and Ho. In the case of anhydrous 3,4-dimethoxybenzoates of Er(III), Tm(III), Yb(III), Lu(III) and Y(III) the least thermally stable complexes are those of thulium and lutetium that start to decompose at 563 K, while the most thermally stable is the complex of erbium that decomposes at 618 K.

The dehydration process is connected with an endothermic effect whereas the combustion of organic ligand with exothermic one in the DTA curve [16]. Considering the temperatures at which the dehydration process takes place and the way by which it proceeds it is possible to assume that the molecules of water of crystallization are of the outer-sphere water. According to Nikolaev *et al.* [17] and Singh *et al.* [18] water eliminated below 423 K can be considered as water of crystallization whereas the water eliminated above 423 K may be that coordinated to the central ion. In our investigations water is assumed to be crystallization water which was also confirmed by IR studies. From TG and DTA curves the activation energies of dehydration reactions were calculated with Fotieev and Pletniev method [19] using the equation (in Table 3, $E_a$):

$$E_a = \frac{RT_{max}^2 \Delta m}{m_0 \Delta T}$$

where: $R$ – gas constant; $T_{max}$ – temperature of maximum of the mass loss; $m_0$ – the mass loss at $T_{max}$; $m$ – the mass loss at $T$; $T$ – given temperature; $\Delta m=m-m_0$; $\Delta T=T_M-T$.

The different values of activation energies may suggest that molecules of outer-sphere water are coordinated with different forces depending on their position in the coordination sphere. It has the smallest value for dysprosium 3,4-dimethoxybenzoate while the highest one for that of terbium.

The results indicate that the decomposition of 3,4-dimethoxybenzoates of yttrium and heavy lanthanides in air during their heating to 1273 K proceeds in the following ways:

$LnL_3 \cdot 4H_2O \rightarrow LnL_3 \rightarrow Tb_4O_7, Dy_2O_3$ for *Ln*=Tb, Dy

$LnL_3 \cdot 3H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3$ for *Ln*=Ho

$LnL_3 \rightarrow Ln_2O_3$ for *Ln*=Er, Tm, Yb, Lu and Y

The oxides of rare earth elements were identified by X-ray powder diffraction [15] and the measurements revealed them to be $Ln_2O_3$ for *Ln*=Dy, Ho, Er, Tm, Yb, Lu, Y and $Tb_4O_7$ for *Ln*=Tb.

The solubilities of 3,4-dimethoxybenzoates of yttrium and heavy lanthanides in water (at 293 K) were measured and their solubility products determined (Table 2). They are in the orders of: $10^{-4}$–$10^{-3}$ mol dm$^{-3}$ and $10^{-12}$–$10^{-10}$ mol$^4$ dm$^{-12}$ respectively. The 3,4-dimethoxybenzoates of erbium and yttrium are the best soluble complexes while that of lutetium the least soluble one. The solubility order of 3,4-dimethoxybenzoates of Tb, Yb and Lu is less than that determined for benzoates, 3-methoxy- and 4-methoxybenzoates of rare earth elements ($10^{-3}$ mol dm$^{-3}$) [20–23]. In view of the values of the complex solubilities, it would seem that 3,4-dimethoxybenzoic acid cannot be used for the separation of the heavy lanthanides by ion-exchange chromatography or by extraction methods because its complexes formed with them are not easily soluble.

The magnetic susceptibility of heavy lanthanide 3,4-dimethoxybenzoates was determined over the range 77–298 K. The values of the Weiss constant, $\theta$, for all complexes were found to have a negative sign, which probably arises from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [24, 25]. In these complexes, the paramagnetic central ions remain virtually unaffected by the diamagnetic ligands coordinated around them. The 4f electrons causing their paramagnetism are well separated from outside influences and they do not participate in the formation of the M–O bond; they may interact only weakly with the electrons of the surrounding atoms. They are in an inner shell characterized by a radius $r \approx 0.35$ [26], which is very small in comparison with the radius of the $5s^25p^6$ closed shell (≈1 Å). Therefore their energy levels are the same as in the free ions due to the very effective shielding by overlapping $5s^25p^6$ shell. For the lanthanide ions the ground state is separated by several hundreds of cm$^{-1}$ from the next higher-lying state. Thus the magnetic properties can be taken as those of the ground state alone, making lanthanide ions in a compound act in the same way as the free ion. The 3,4-dimethoxybenzoates of the heavy lanthanides and yttrium obey the Curie-Weiss law. The values of magnetic moments determined for the complexes suggest that the energies of $\mu_{eff}$ are close to those calculated for $Ln^{3+}$ ions by Hund and van Vleck (Table 4). The obtained results reveal that in these complexes the M–O bond is mainly electrostatic in nature since the 4f orbitals of lanthanide ions are effectively shielded by the $5s^25p^6$ octet and the energies of 4f electrons in the central ions are not radically changed compared to those in the free lanthanide ions [26–31]. Therefore the colours of the complexes are the same as those for the free lanthanide ions.

## Conclusions

Anhydrous and hydrated complexes of 3,4-dimethoxybenzoates of yttrium and heavy lanthanides were synthesized. The amount of crystalline water decreases with the decrease of ionic radii of elements. The colours of the complexes are typical of the particular Ln(III) ion, i.e. white for Tb, Dy, Tm, Yb, Lu and 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 in the central ions are not radically changed in the complexes in comparison with the free lanthanide ions. Therefore the colours of 3,4-dimethoxybenzoates are the same as those for the free lanthanide ions and the Ln–O bond is mainly electrostatic in nature. The complexes are crystalline compounds of various symmetry, which on heating in air to 1273 K decompose in various ways yielding the oxides of the appropriate elements. From the solubility values determined in water at 293 K it follows that the 3,4-dimethoxybenzoic acid cannot be used for the separation of the heavy lanthanides by ion-exchange chromatography or by extraction methods because its complexes formed with them are not easily soluble.

## References

1 Beilsteins Handbuch der Organischen Chemie, Bd. X. Springer Verlag, Berlin 1927, p. 393.
2 R. T. Morrison and R. N. Boyd, Chemia organiczna, PWN, Warszawa 1996, p. 670.
3 B. N. Figgs and R. S. Nyholm, J. Chem. Soc., (1958) 4190.
4 E. König, Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Berlin 1966, p. 24.
5 P. Karrer, Chemia organiczna, T. 2, PWN, Warszawa 1985, p. 206.
6 H. A Staab, Einführung in die theoretische organische Chemie, Verlag Chemie, Weinheim 1962, p. 355.
7 A. Bartecki, Barwa związków metali, Wydawnictwo Politechniki Wrocławskiej, Wrocław 1993, p. 37.
8 J. Shorter, Correlation Analysis in Organic Chemistry. An Introduction to Linear Free-Energy Relationships, Clarendon Press, Oxford 1973, p. 55.
9 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley,Toronto 1968, p. 191.
10 K. Nakamoto and P. J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, Wiley, New York 1968, p. 73.
11 R. C. Mehrotra and R. Bohra, Metal Carboxylates, Academic Press, London 1983, p. 48.
12 L. J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hull, London 1975, p. 72.
13 K. Burger, Coordination Chemistry: Experimental Methods, Akadémiai K., Budapest 1973, p. 53.
14 B. S. Manhas and A. K. Trikha, J. Indian Chem. Soc., 59 (1982) 315.
15 P. Pascal, Noveau Traité de Chimie Minérale, VII, Mason et C$^{ie}$, Paris 1959, p. 777.
16 D. N. Todor, Thermal Analysis of Minerals, Abacus Press, Tunbridge Wells, 1976, p. 55.
17 A. V. Nikolaev, V. A. Logvienko and L. I. Myachina, Thermal Analysis, Vol. 2, Academic Press, New York 1989, p. 72.
18 B. Singh, B. V. Agarwala, P. L. Mourya and A. K. Dey, J. Indian Chem. Soc., 59 (1992) 1130.
19 Ch. A. Cherchas and T. P. Jezierskaya, Izv. Akad. Nauk. SSSR, 1 (1977) 45.
20 L. N. Bondarieva, L. M. Dvornikowa and L. A. Gucu, Zh. Neorg. Khim., 19 (1974) 2659.
21 W. Brzyska and W. Ożga, Thermochim. Acta, 214 (1993) 261.
22 W. Brzyska and W. Ferenc, Zesz. Nauk. Politech. Śląsk., 5 (1985) 113.
23 W. Brzyska and W. Błaszczak, Ann. Univ. Marie Curie-Skłodowska Sect. A A, Vol.34. 6 (1979) 45.
24 C. I. O'Conner, Progress in Inorganic Chemistry, Wiley, New York 1982, p. 204.

25 C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier and P. Rey, Angev. Chem., 26 (1989) 913.
26 S. P. Sinha, Systematics and Properties of the Lanthanides, D. Reidel, Dordrecht 1983, p. 256.
27 I. H.van Vleck, Theory of Electronic and Magnetic Susceptibilities, Oxford University Press, Oxford 1932, p. 239.
28 A. T. Baker, A. M. Hammer and S. E. Livingstone, Transition Met. Chem., 9 (1984) 423.
29 A. M. Hammer and S. E. Livingstone, Transition Met. Chem., 8 (1993) 298.
30 R. Earnshow, Introduction to Magnetochemistry, Academic Press, London 1956, p. 1.
31 D. J. Karraker, J. Chem. Ed., 47 (1970) 424.