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4-CHLORO-2-METHOXYBENZOATES OF HEAVY LANTHANIDES(III) AND YTTRIUM(III)

Thermal, spectral and magnetic behaviour

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4-Chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) were obtained as mono-, di-, tri- or tetrahydrates with metal to ligand ratio of 1:3 and general formula $Ln(C_8H_6ClO_3)_3 \cdot nH_2O$, where n=1 for Ln=Er, n=2 for Ln=Tb, Dy, Tm, Y, n=3 for Ln=Ho and n=4 for Yb and Lu. The complexes were characterized by elemental analysis, FTIR spectra, TG, DTA and DSC curves, X-ray diffraction and magnetic measurements.

The carboxylate group appears to be a symmetrical bidentate chelating ligand. All complexes are polycrystalline compounds. The values of enthalpy, ΔH, of the dehydration process for analysed complexes were also determined. The solubilities of heavy lanthanide(III) 4-chloro-2-methoxybenzoates in water at 293 K are of the order of 10^{-4} mol dm^{-3}. The magnetic moments were determined over the range of 76–303 K. The results indicate that there is no influence of the ligand field of 4f electrons on lanthanide ions and the metal ligand bonding is mainly electrostatic in nature.

Keywords: *4-chloro-2-methoxybenzoates, complexes of rare earth, magnetic susceptibility determinations, spectrochemical and thermal stability investigations*

Introduction

The preparation and investigations of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) are presented in this paper. We decided to take this subject because the carboxylates play an important role in inorganic and bioinorganic chemistry. Many their complexes with metal cations in a great number of various biological processes are a component of vitamins and drugs [1, 2]. Carboxylates of d- and 4f ion elements are also used in the modern techniques as electric materials.

From the survey of literature it follows that there are papers that concern the complexes of methoxy- and chloromethoxybenzoic acid anions with d- and 4f metal ion elements [3–14]. The compounds described in the above mentioned papers were synthesized and characterized by elemental analysis, FTIR and FIR spectra recorded over the ranges 4000–400 and 600–100 cm^{-1}, respectively. Their thermogravimetric studies, X-ray diffraction and magnetic investigations were presented as well. 4-Chloro-2-methoxybenzoic acid is a white crystalline solid sparingly soluble in cold water [15]. The complexes of light lanthanides(III) with 4-chloro-2-methoxybenzoic acid were prepared and investigated [16], but those of heavy lanthanides(III) have not been obtained so far.

The aim of this work was to obtain them in solid-state and to examine some of their properties such as: thermal stability in static and dynamic air during heating to 1173 K, magnetic properties, the way of coordination of carboxylate groups, crystalline forms and the analysed complex solubilities in water.

Thermal characterizations let us evaluate the assumed position of crystallization water molecules in outer or inner spheres of coordination, determine the endothermic or exothermic effects connected with such processes as: dehydration, melting, crystallization, oxidation, reduction and estimate the strength of bonding between atoms or groups of atoms and ions. The magnetic susceptibility were measured to estimate the nature of metal ligand bonding and to get information why colours of the complexes are typical for central metal ions. The solubility determination is valuable because it informs about the practical use of the acid for separation of metal ions by extraction or ion-exchange chromatographic method.

Experimental

Materials

The complexes of 4-chloro-2-methoxybenzoic acid anion with heavy lanthanides(III) were prepared by

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the addition of equivalent quantities of 0.1 M ammonium 4-chloro-2-methoxybenzoate (pH≈5) to a hot solution containing the rare earth element nitrates(V) 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 to a constant mass. The 4-chloro-2-methoxybenzoate of Na was prepared by the addition of equivalent amount of 4-chloro-2-methoxybenzoate to NaOH solution containing 0.1 g NaOH and crystallizing.

Methods

The contents of carbon and hydrogen in complexes were determined by elemental analysis using CHN 2400 Perkin Elmer analyzer and the content of chlorine by the Schöniger method. The contents of rare earth elements were established by oxalic method (Table 1). The value of the order of solubility of rare earth element oxalates in water (293 K) is equal to 10^{-6} mol dm^{-3} [17].

The FTIR spectra of complexes were recorded over the range of 4000–400 cm^{-1} using a FTIR 1725X Perkin-Elmer spectrometer. The samples for the FTIR spectra were prepared as KBr discs. Some of the results are presented in Table 2.

The X-ray diffraction patterns of complexes and the intermediate and final products of decomposition process were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range of 2θ=4–80° by means of the Debye–Scherrer–Hull method. The relationships between I/I_0 and 2θ for these complexes are presented in Fig. 1.

The thermal stability and decomposition of the 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 TG – 100 mg, DTG and DTA sensitivities were regulated by computer Derill programme (Table 3, Fig. 2). The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration.

Table 1 Elemental analysis data of heavy lanthanide(III) and Y(III) 4-chloro-2-methoxybenzoates and their solubility in water at 293 K

Complex $L=C_8H_6ClO_3^-$	C/% calcd. (found)	H/% calcd. (found)	Cl/% calcd. (found)	*M*/% calcd. (found)	Solubility/mol dm^{-3}
$TbL_3·2H_2O$	38.17 (38.23)	2.78 (2.83)	14.12 (14.10)	21.07 (21.00)	$7.5·10^{-4}$
$DyL_3·2H_2O$	38.14 (38.10)	2.91 (2.81)	14.10 (14.10)	21.52 (21.57)	$4.3·10^{-4}$
$HoL_3·3H_2O$	37.14 (37.02)	3.09 (3.05)	13.73 (13.72)	21.27 (21.37)	$3.2·10^{-4}$
$ErL_3·H_2O$	38.83 (38.17)	2.69 (2.79)	14.35 (14.34)	22.55 (22.45)	$3.3·10^{-4}$
$TmL_3·2H_2O$	37.82 (37.90)	2.90 (2.89)	13.98 (13.92)	22.19 (22.20)	$2.8·10^{-4}$
$YbL_3·4H_2O$	35.94 (35.95)	3.24 (3.12)	13.29 (13.39)	21.59 (21.59)	$1.5·10^{-4}$
$LuL_3·4H_2O$	35.84 (35.84)	3.23 (3.17)	13.26 (13.18)	21.78 (21.64)	$1.3·10^{-4}$
$YL_3·2H_2O$	42.51 (42.58)	3.25 (3.26)	15.73 (15.27)	13.10 (13.00)	$3.0·10^{-4}$

Table 2 Frequencies (cm^{-1}) of the absorption bands of COO$^-$ for 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III), sodium and that of CO for 4-chloro-2-methoxybenzoic acid

Complex $L=C_8H_6ClO_3^-$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\Delta\nu_{COO^-}$	ν_{C-Cl}	ν_{M-O}	$\nu_{C=O}$
$TbL_3·2H_2O$	1550	1430	125	688	416	–
$DyL_3·2H_2O$	1550	1420	130	690	416	–
$HoL_3·3H_2O$	1524	1424	100	686	424	–
$ErL_3·H_2O$	1528	1424	104	710	420	–
$TmL_3·2H_2O$	1524	1424	100	710	418	–
$YbL_3·4H_2O$	1530	1428	102	706	422	–
$LuL_3·4H_2O$	1528	1424	104	710	422	–
$YL_3·2H_2O$	1520	1420	100	686	420	–
NaL	1604	1376	228	670	–	–
HL	–	–	–	–	–	1728

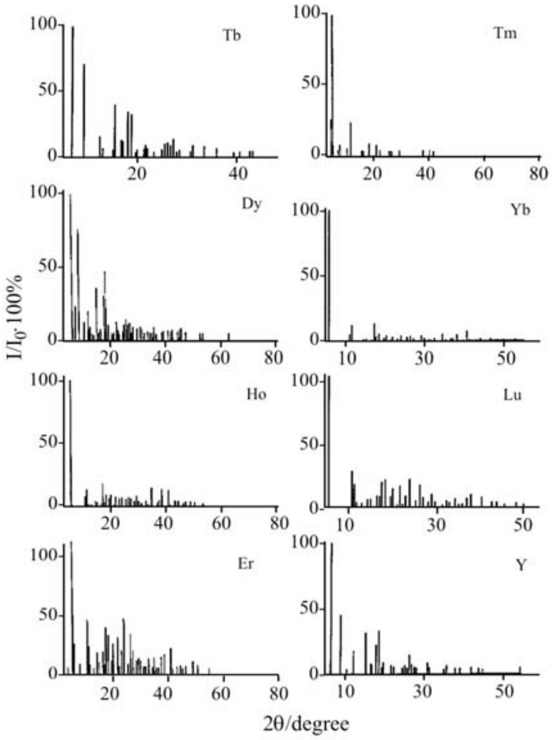

Fig. 1 Dependence of I/I_0 *vs.* 2θ for heavy lanthanide(III) 4-chloro-2-methoxibenzoates

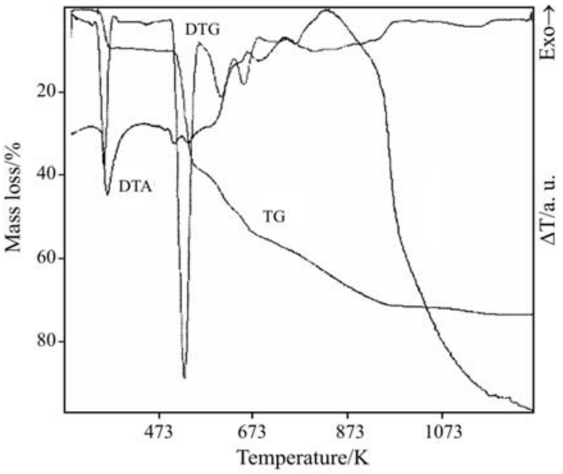

Fig. 2 TG, DTG and DTA curves for Ho(III) 4-chloro-2-methoxibenzoate

In order to calculate the energetic effects of dehydration process, to compare the ways of thermal decompositions of complexes in air and to ascertain if they are reproducible during measurements using various methods, the thermogravimetric analysis of DSC/TG was also performed at 293–673 K using a differential thermoanalyser TG-DTA-DSC Setsys 16/18 Setaram at a heating rate of 1 K $\min^{-1}$ (Table 4). The experiments were carried out under air flow at a rate of 75 mL $\min^{-1}$. The initial masses of samples of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) used for measurements change from 6.2 mg for Tb(III) complex to 6.5 mg for Yb(III) complex. The samples were heated in platinum crucibles without cover.

Magnetic susceptibilities of polycrystalline samples of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were made at a magnetic field strength of 9.9 kOe. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility of $1.644\cdot10^{-5}$ cm^3 g^{-1} was taken [18]. The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [19]. The temperature-independent paramagnetism of rare earth ions was assumed to be zero. Magnetic moments were calculated from the Eqs (1) and (2):

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

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

where μ_{eff} – magnetic moment, χ_M – magnetic susceptibility, T – temperature [K], Q – Weiss constant.

Table 3 Temperature range of thermal stability of heavy lanthanide(III) and yttrium(III) 4-chloro-2-methoxybenzoates in air

Complex $L=C_8H_6ClO_3^-$	ΔT_1/K	Mass loss/% calcd. (found)	n	ΔT_2/K	Mass loss/% calcd. (found)	T_K/K
$TbL_3\cdot2H_2O$	350–401	4.80 (4.80)	2	505–974	70.9 (70.4)	1170
$DyL_3\cdot2H_2O$	354–474	4.76 (4.00)	2	510–998	75.3 (75.0)	1110
$HoL_3\cdot3H_2O$	347–506	6.96 (7.20)	3	573–843	75.60 (76.0)	1100
$ErL_3\cdot H_2O$	337–516	2.42 (2.82)	1	573–847	74.20 (74.4)	1113
$TmL_3\cdot2H_2O$	357–532	4.72 (4.80)	2	576–836	74.66 (74.60)	1103
$YbL_3\cdot4H_2O$	353–378	8.92 (8.67)	4	533–923	75.42 (75.88)	1083
$LuL_3\cdot4H_2O$	348–378	8.96 (8.91)	4	533–893	75.24 (75.21)	1030
$YL_3\cdot2H_2O$	353–383	4.72 (4.80)	2	513–943	83.33 (83.25)	1010

ΔT_1 – temperature range of dehydration process, n – number of crystallization water molecules being lost in one endothermic step, ΔT_2 – temperature range of anhydrous complex decomposition, T_K – temperature of the oxide formation

Table 4 The results of thermogravimetric analysis of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) in the DSC/TG system

Complex L=$C_8H_6ClO_3^-$	Δ*T*/K	Mass loss/%	Δ*H*/kJ mol^{-1}
$TbL_3·2H_2O$	344–359	4.80	35.30
$DyL_3·2H_2O$	348–398	4.00	88.86
$HoL_3·3H_2O$	312–340	7.20	171.10
$ErL_3·H_2O$	310–340	2.82	65.40
$TmL_3·2H_2O$	307–338	4.80	44.89
$YbL_3·4H_2O$	311–342	8.67	182.40
$LuL_3·4H_2O$	304–338	8.95	196.20
$YL_3·2H_2O$	322–345	4.80	84.30

Δ*T* – temperature range of dehydration process,
Δ*H* – enthalpy for dehydration process

Some of the results are given in Table 4.

The solubility of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) in water at 293 K was determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic method [17] (Table 1).

Results and discussion

The complexes of 4-chloro-2-methoxybenzoic acid with heavy lanthanides(III) and yttrium(III) were synthesized as crystalline products with a metal to ligand ratio of 1:3 and a general formula $Ln(C_8H_6ClO_3)_3·nH_2O$ (where *Ln*=Tb–Lu, Y and *n*=4 for Yb, Lu, *n*=3 for Ho, *n*=2 for Tb, Dy, Tm, Y and *n*=1 for Er). Their colours are those typical of the appropriate trivalent ions, which is connected with the similar electron density in the system. In these molecules the f→f electronic transition of the central ions are those of the lowest energy and therefore, the absorption occurs at relatively high wavelengths that depends on the nature of the metal ion. The compounds were characterized by elemental analysis (Table 1) and IR spectra (Table 2). All heavy lanthanide(III) 4-chloro-2-methoxybenzoates show similar solid-state IR spectra.

However, the characteristic frequencies related to the carbonyl group are changed markedly in going from acid to salts. The band of the –COOH group at 1728 cm^{-1}, present in the acid spectrum, completely disappears in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of the COO^- occur at 1550–1520 and 1430–1420 cm^{-1}, respectively. The bands with the maxima at 3490–3416 cm^{-1} characteristic for ν_{OH} vibrations [20] and the narrow band of δ_{H_2O} at 1610 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands of C–H asymmetric and symmetric stretching vibrations of CH_3 groups are observed at 2950–2944 and 2840 cm^{-1}, respectively. The bands of $\nu_{C–C}$ ring vibrations appear at 1584–1576, 1480, 1184–1180, 1025–1016 cm^{-1}. The valency $\nu_{C–Cl}$ vibration bands occur at 710–686 cm^{-1} and the bands at 424–416 cm^{-1} confirm the metal–oxygen bond [20–25]. The maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- for 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and sodium salt are presented in Table 2. The magnitudes of separation, $\Delta\nu_{OCO}$, between the frequencies of $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ in the complexes are lower ($\Delta\nu_{OCO}$=130–100 cm^{-1}) than in the sodium salt ($\Delta\nu_{OCO}$=228 cm^{-1}), which indicates a smaller degree of ionic bond in the heavy lanthanide(III) 4-chloro-2-methoxybenzoates. The shifts of the frequencies $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ are lower and higher, respectively, than those for sodium 4-chloro-2-methoxybenzoate. Accordingly, the carboxylate ion appears to be a symmetrical bidentate, chelating ligand [26, 27].

In order to examine the external crystalline forms of heavy lanthanide(III) 4-chloro-2-methoxybenzoates, the X-ray powder diffraction measurements were made. The diffractogram analysis suggests that they are polycrystalline compounds with low symmetry, large size of the unit sizes and different structures [28].

In the order to determine the temperature ranges of their thermal stabilities and decompositions during heating in air, to estimate the intermediate and final products of their decompositions and to evaluate the types of processes that occur during heating the thermal stability of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) was studied in air (Tables 3 and 4; Figs 2 and 3). TG, DTG, DTA and DSC curves were recorded using two measurement methods (DTA/TG and DSC/TG techniques). From TG, DTG, DTA and T curves it was found that complexes are hydrates with the ratio of metal:ligand 1:3. 4-Chloro-2-methoxybenzoates contain from 1 to 4 molecules of crystallization water. The complexes are stable up

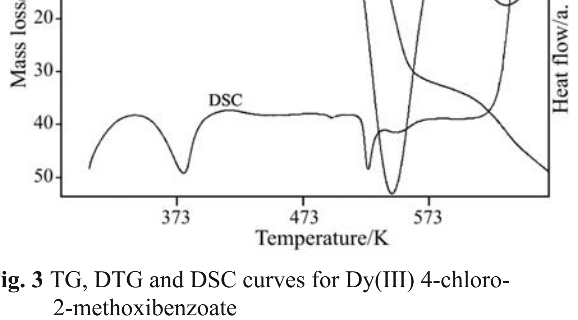

Fig. 3 TG, DTG and DSC curves for Dy(III) 4-chloro-2-methoxibenzoate

to 337–357 and 304–348 K, respectively (Tables 3 and 4). Next in the range of 337–532 and 304–398 K they dehydrate in one step losing all molecules of crystallization water and form anhydrous compounds. The mass losses calculated from TG curves changing from 2.82 to 8.91% correspond to the loss of 1 to 4 molecules of water (theoretical values are 2.42 and 8.96%). Dihydrate of 4-chloro-2-methoxybenzoate of Tm(III) is the most thermally stable complex since its initial temperature of dehydration T_i is equal to 357 K, while monohydrate of 4-chloro-2-methoxybenzoate of Er(III) is the least thermally stable complex (T_i=337 K). The dehydration process is accompanied by endothermic effect in the DTA curves. The values of enthalpy, ΔH, of the dehydration process for complexes were determined (Table 4). They change from 35.30 to 192.2 kJ mol^{-3} for Tb(III) and Lu(III) complexes, respectively, and they correspond to the energy of the bonding of the proper numbers of water molecules. The water molecules may be coordinated to the central ions with different strengths and they are situated in various places of complex coordination spheres. The anhydrous compounds are stable up to 505–576 K. In the temperature range of 513–780 K they gradually, one by one, release the parts of ligands and form oxychlorides, LnOCl. The decomposition of organic ligand is connected with strong exothermic effect in DTA curve. In the range of 790–1170 K the oxychlorides of lanthanides(III) are decomposed to the oxides of respective metals. The theoretical values of mass losses are equal to 70.9–83.33% and those calculated from TG curves 70.4–83.25%. The most thermally stable is the anhydrous complex of Tm(III), the initial temperature of decomposition of which is equal to 576 K, whereas the least thermally stable is that of Tb(III) (T_2=505 K). The temperatures of oxide formations change their values from 1170 (Tb_4O_7) to 1010 K (Y_2O_3).

The final and intermediate products of decompositions were identified roentgenographically, also by elemental analysis and FTIR spectra. The X-ray and FTIR spectra of lanthanide oxides being the final products of complex decompositions were compared with those obtained by roasting the lanthanide(III) oxalates.

The thermal stability of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) were also studied in air by DSC/TG technique (Table 4). The obtained results confirmed their decompositions as hydrates with the formulae established previously on the basis of the results obtained from thermal stability investigations with the use of DTA/TG technique.

Considering the temperatures at which the dehydration process of the complexes takes place and the way by which it proceeds, it is possible to assume that the water molecules are differently bound in the complex coordination spheres [29–31]. The IR spectra recorded for analysed compounds may also suggest that the water molecules are probably bounded by hydrogen bound, probably, in outer-sphere of complex.

The detailed data obtained from the determination of the complete structures of these complexes can give fair answer concerning above assumption. However, their monocrystals have not been obtained, so far, but attempts to obtain them have been made.

The results indicate that the thermal decomposition of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) in air proceeds in the following way:

$$LnL_3 \cdot nH_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_4O_7$$

where (Ln=Tb)

$$LnL_3 \cdot nH_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3$$

where (Ln=Dy, Ho, Er, Tm, Yb, Lu, Y)

$$L^-=C_8H_6O_3Cl;\ n=1–4$$

These two methods used for the investigations (DTA/TG and DSC/TG) let state that the complexes decompose in the same way and they contain identical numbers of water molecules.

The solubility of 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) in water (at 293 K) was also determined (Table 1). It is in the order of 10^{-4} mol dm^{-3}. Tb(III) 4-chloro-2-methoxybenzoate is the most soluble salt, while that of Lu(III) the least soluble one. From the solubility data it appears that 4-chloro-2-methoxybenzoic acid cannot be used for the separation of heavy lanthanide ions by ion-exchange chromatography or by extraction methods because of the low order of solubility values of analysed complexes.

In order to estimate the nature of metal ligand bonding in lanthanide complexes and try to know the reason why the colours of 4-chloro-2-methoxybenzoates of heavy lanthanides and yttrium are typical of Ln^{3+} ions the magnetic susceptibility of 4-chloro-2-methoxybenzoates was determined over the range of 76–303 K. The complexes obey Curie–Weiss law (Table 5).

A plot of the inverse of the magnetic susceptibility χ_M determined for all complexes yields a straight line. For all complexes the values of the Weiss constants, Q, have a negative sign. It probably results from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [32–35]. In these complexes the central ions remain unaffected by diamagnetic ligands coordinated around them so the f-electrons causing their paramagnetism are well separated from outside influences. Therefore the values of μ_{eff} determined for all complexes are close to those calculated for Ln^{3+} ions by Hund and Van Vleck (Tables 5

Table 5 Magnetic data of heavy lanthanide(III) 4-chloro-2-methoxybenzoates

$TbL_3\cdot 2H_2O$ $\Theta=-12$ K			$DyL_3\cdot 2H_2O$ $\Theta=-6$ K			$HoL_3\cdot 3H_2O$ $\Theta=-11$ K			$ErL_3\cdot H_2O$ $\Theta=-5$ K			$TmL_3\cdot 2H_2O$ $\Theta=-10$ K			$YbL_3\cdot 4H_2O$ $\Theta=-48$ K		
T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B
77	133861	9.72	76	152503	9.63	76	153213	9.68	76	115148	8.37	76	74278	6.72	77	24460	4.96
120	88260	9.64	123	94926	9.67	113	111642	10.05	123	72998	8.48	123	48873	6.94	122	17067	4.85
134	80905	9.69	133	86169	9.58	123	103319	10.09	133	67140	8.46	133	44654	6.90	133	15730	4.81
144	74285	9.60	143	79823	9.56	133	95758	10.10	143	62443	8.46	143	41561	6.90	143	14943	4.82
153	70608	9.63	153	74916	9.58	143	88373	10.06	153	58734	8.48	153	39498	6.96	149	14157	4.77
166	64724	9.57	163	70432	9.59	153	83227	10.10	163	55372	8.50	163	37061	6.96	168	13370	4.83
177	62296	9.68	173	66624	9.61	163	77320	10.05	173	52060	8.49	173	35186	6.98	172	12977	4.85
185	58840	9.61	183	62817	9.60	173	72532	10.02	183	48217	8.49	183	33592	7.02	182	12662	4.80
192	57369	9.65	193	61421	9.74	183	70250	10.15	193	47041	8.53	193	32092	7.04	199	12190	4.96
221	50014	9.63	203	58713	9.77	193	66446	10.13	203	44989	8.55	203	30874	7.08	206	11640	4.93
233	47072	9.59	213	56048	9.78	203	62956	10.12	213	43088	8.57	213	29561	7.10	216	11168	4.94
238	45601	9.53	223	53848	9.81	213	59644	10.09	223	41825	8.64	223	28811	7.17	226	11011	5.00
246	44865	9.50	233	51394	9.79	223	56244	10.02	233	40194	8.66	233	27799	7.20	238	10617	5.01
255	42659	9.53	243	49491	9.81	233	53738	10.01	243	38636	8.67	243	27030	7.25	246	10145	4.97
267	41188	9.57	253	47968	9.86	243	51724	10.03	253	37375	8.70	253	26638	7.35	258	9280	4.86
277	38981	9.48	263	46445	9.89	253	49934	10.06	263	26337	8.75	263	25155	7.28	270	9044	4.54
288	37510	9.47	273	44879	9.91	263	48144	10.07	273	35002	8.75	273	24312	7.29	282	8730	4.87
296	36775	9.58	283	43525	9.93	273	46881	10.13	283	34162	8.80	283	24461	7.45	296	8336	4.87
298	35304	9.62	293	42256	9.96	283	45459	10.15	293	33099	8.81	293	23093	7.36			
			303	40860	9.96	293	44206	10.19	303	32134	8.83	303	22418	7.38			
						303	42722	10.18									

$L=C_8H_6ClO_3^-$

Table 6 Values of μ_{eff} for the heavy lanthanides determined by Hund and Van Vleck and *calculated for heavy lanthanide 4-chloro-2-methoxybenzoates at 303 K

Ln^{3+}	Ground term.	Calcd. by Hund μ_{eff}	Van Vleck μ_{eff}	μ_{eff}/BM*
Tb^{3+}	$^7F_6$	9.70	9.70	9.62
Dy^{3+}	$^7H_{15/2}$	10.60	10.60	9.96
Ho^{3+}	$^5I_8$	10.60	10.60	10.18
Er^{3+}	$^4I_{15/2}$	9.60	9.60	8.83
Tm^{3+}	$^3H_6$	7.60	7.60	7.38
Yb^{3+}	$^2F_{7/2}$	4.50	4.50	4.87
Lu^{3+}	$^1S_0$	0.00	0.00	0.00

and 6) [35]. In the lanthanide ions 4f electrons are in an inner shell having a radius that is equal to 0.35 Å [35]. This value seems to be very small compared to the radius of the $5s^2p^6$ closed shell being equal to 1 Å. Therefore, the 4f electrons interact only weakly with the electrons of the surrounding atoms and they are almost unaffected by the chemical environment. Their energy levels stay the same as in the free ions. For most of the lanthanide ions the ground state is separated by several hundreds of cm^{-1} from the next higher lying state and the magnetic properties can be taken as those of the ground state alone. Taking this fact into account lanthanide ions in the compounds act in the same way as the free ions [35–39]. From the values of magnetic moments determined for the complexes it appears that the energies of 4f electrons in the central ions are not changed compared to those in the free lanthanide ions. Therefore, the colours of the complexes stay the same as those in the free lanthanide ions. The electron density in the molecules makes the $f \rightarrow f$ electronic transitions of central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths. The analytical, magnetic and spectral data suggest that in 4-chloro-2-methoxybenzoates of heavy lanthanides the lanthanide ions probably exhibit a coordination numbers eight, nine and ten depending on the position of water molecules in the complex. The coordination numbers of Ln^{3+} ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. The trivalent lanthanide ions exhibit a wide variety of stereochemistries on the basis of their varying coordination numbers from six to twelve. This coordination variation in lanthanide complexes is well established and may be ascribed to the steric factors and electrostatic force of attraction and repulsion rather than to the direction of bonds by the deep seated 4f orbitals of metal ions. The 4f orbitals of lanthanide ions are effectively shielded by the $5s^25p^6$ octet. Therefore, the metal ligand bonding in lanthanide(III) complexes is mainly electrostatic in nature [40].

Conclusions

From the obtained results it appears that 4-chloro-2-methoxybenzoates of heavy lanthanides(III) and yttrium(III) were synthesized as hydrated complexes. Their colours are typical for the particular Ln(III) ions 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 Ln–O bond is mainly electrostatic in nature. The complexes are crystalline compounds that on heating in air to 1173 K decompose in three steps. In the first step they dehydrate to form anhydrous complexes that next decompose to the oxides of the appropriate metals with intermediate formation of LnOCl. The values of μ_{eff} calculated for all compounds are close to those obtained for Ln^{3+} by Hund and Van Vleck. There is no influence of the ligand field of 4f electrons on lanthanide ions. From the obtained results it follows that the various substituents and their different positions in benzene ring influence the hydration degree, thermal stability of complexes their solubility in water and dentates of carboxylates groups, but the ratio of metal ion: ligand in complexes, their colours stay the same [5–14]. The changes in the values presented above are probably connected with the various influences of inductive, mesomeric and steric effects on the electron density of the system depending on their positions in benzene ring. The investigations of the influence of substituents in benzene ring on the properties of complexes are also the aim of our studies.

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