

THERMAL, SPECTRAL AND MAGNETIC BEHAVIOUR OF 4-CHLORO-2-METHOXYBENZOATES OF LIGHT LANTHANIDES(III)

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4-Chloro-2-methoxybenzoates of light lanthanides(III) were obtained as mono-, di- or trihydrates with metal to ligand ratio of 1:3 and general formula $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot n\text{H}_2\text{O}$, where $n=1$ for $\text{Ln}=\text{Ce}, \text{Pr}$, $n=2$ for $\text{Ln}=\text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ and $n=3$ for $\text{Ln}=\text{La}$. The complexes were characterized by elemental analysis, IR spectra, thermogravimetric studies, X-ray diffraction and magnetic measurements. The carboxylate group appears to be a symmetrical bidentate, chelating ligand. All complexes seem polycrystalline compounds. Their thermal stabilities were determined in air. When heated they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. The solubilities of light lanthanide(III) 4-chloro-2-methoxybenzoates in water at 293 K are of the order of $10^{-5} \text{ mol dm}^{-3}$. The magnetic moments were determined over the range of 77–300 K. They obey the Curie–Weiss law. The values of μ_{eff} calculated for all compounds are close to those obtained for Ln^{3+} by Hund and Van Vleck. 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 earths, magnetic susceptibility determinations, spectrochemical and thermal stability investigations

Introduction

The preparation and investigations of 4-chloro-2-methoxybenzoates of light lanthanides(III) were presented in this paper because, on one hand, the carboxylates play an important role in inorganic and bioinorganic chemistry and then again many metal cations in a great number of various biological processes, especially six-membered ring system, are a component of several vitamins and drugs [1, 2]. Moreover, carboxylates of d - and $4f$ ion elements depending on their magnetic properties as magnets may be used in the modern branches of techniques and technology as electric materials.

According to literature survey compounds of various organic ligands, also chloromethoxy- and methoxybenzoic acids have been studied. There are papers that deal with their complexes with d - and mainly $4f$ metal ion elements [3–14]. The complexes were synthesized and characterized by elemental analysis, IR and FIR spectra. Their thermogravimetric studies, X-ray diffraction and magnetic measurements were also presented. 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 have been prepared and investigated. The aim of this work was to obtain them in solid-state and to examine some of their physico-chemical properties including thermal stability in air during

heating to 1173 K. Generally, in our experiments the complexes obtained in the solid-state are characterized by elemental analysis, IR spectral data, thermogravimetric studies and X-ray diffraction measurements. Thermal characterizations let us evaluate the assumed position of crystallization water molecules in outer or inner spheres of coordination, determine the endo- or exo-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.

Experimental

Materials

The complexes of 4-chloro-2-methoxybenzoic acid anion with light lanthanides(III) were prepared by the addition of equivalent quantities of 0.1 M ammonium 4-chloro-methoxybenzoate (pH~5) to a hot solution containing the rare earth element nitrates(V) and crystallizing at 293 K. In order to obtain the rare earth element nitrates(V) (with the exception of Ce(III), that was used as $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) the oxides of lanthanides(III) (the sample mass 0.8 g) were dissolved

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in the equivalent amounts of concentrated HNO₃. The solutions were constantly heated. The lanthanide(III) nitrates(V) were practically evaporated to dryness to eliminate the excess of acid. The residue was dissolved in water forming the solutions of light lanthanide nitrates(V), the concentrations of which were equal to 0.1 M and pH~5. To the hot solution of nitrates(V) the equivalent amounts of 0.1 M ammonium 4-chloro-2-methoxybenzoate were added. 4-Chloro-2-methoxybenzoate of ammonium (pH~5) was prepared by the addition of concentrated solution of NH₄OH to 4-chloro-2-methoxybenzoic acid. In order to reach the equilibrium state the solids were heated for 1 h at 333–343 K with constant stirring. Next they 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 0.1 M ammonium 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 analyser and the content of chlorine by

Schöniger method. The contents of rare earth elements were established by oxalic method (Table 1).

The IR and FIR spectra of complexes were recorded over the range 4000–400 and 600–100 cm⁻¹ using M-80 and Perkin-Elmer 180 spectrometers, respectively. Samples for IR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Nujol mulls sandwiched between polyethylene plates (Table 2).

The X-ray diffraction patterns of complexes and the products of decomposition process were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range 2θ=4–80° by means of the Debye–Scherrer–Hull method.

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. 1). The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration.

Table 1 Analytical data of light lanthanide(III) 4-chloro-2-methoxybenzoates

Complex <i>L</i> = C ₈ H ₆ ClO ₃ ⁻	H/%		C/%		Cl/%		M/%	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
LaL ₃ ·3H ₂ O	3.20	3.06	38.43	38.76	14.21	14.14	18.53	18.04
CeL ₃ ·H ₂ O	2.80	2.54	40.31	40.32	14.90	14.50	19.59	19.32
PrL ₃ ·H ₂ O	2.80	2.54	40.26	40.32	14.88	14.62	19.69	19.51
NdL ₃ ·2H ₂ O	2.99	2.90	39.10	39.18	14.46	14.20	19.57	18.94
SmL ₃ ·2H ₂ O	2.82	2.82	38.61	38.89	14.28	14.20	20.16	20.15
EuL ₃ ·2H ₂ O	2.81	2.62	38.76	39.70	14.25	14.18	20.33	20.43
GdL ₃ ·2H ₂ O	2.79	2.70	38.45	38.48	14.15	14.10	20.88	20.83

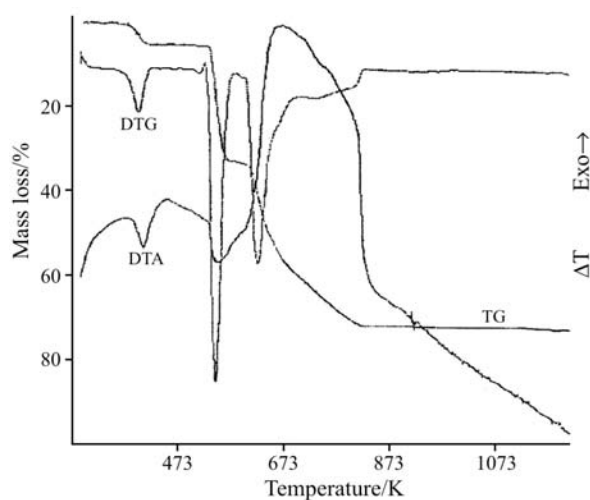
Table 2 Frequencies (cm⁻¹) of the absorption bands of COO⁻ for 4-chloro-2-methoxybenzoates of light lanthanides(III), sodium and that of CO for 4-chloro-2-methoxybenzoic acid

Complex <i>L</i> = C ₈ H ₆ ClO ₃ ⁻	ν _{C=O}	ν _{as(OCO)}	ν _{s(OCO)}	Δν _{OCO}	ν _{C-Cl}	ν _{M-O}
LaL ₃ ·3H ₂ O	–	1592	1424	168	720	424
CeL ₃ ·H ₂ O	–	1592	1420	172	692	424
PrL ₃ ·H ₂ O	–	1580	1424	156	682	424
NdL ₃ ·2H ₂ O	–	1592	1436	156	700	424
SmL ₃ ·2H ₂ O	–	1600	1425	175	690	415
EuL ₃ ·2H ₂ O	–	1600	1425	175	690	410
GdL ₃ ·2H ₂ O	–	1600	1440	160	720	410
NaL	–	1592	1404	188	680	–
HL	1728	–	–	–	–	–

Table 3 Temperature range of thermal stability of light lanthanide(III) 4-chloro-2-methoxybenzoates in air atmosphere and their solubility in water at 293 K

Complex $L = C_8H_6ClO_3$	$\Delta T_1/K$	Mass loss/%		n	$\Delta T_2/K$	Mass loss/%		$\Delta H/kJ\ mol^{-1}$	Solubility/ $mol\ dm^{-3}$
		calcd.	found			calcd.	found		
$LaL_3 \cdot 3H_2O$	362–377	7.20	7.10	3	517–925	78.30	78.2	67.20	$5.68 \cdot 10^{-5}$
$CeL_3 \cdot H_2O$	339–362	2.84	2.90	1	673–940	75.30	75.0	25.40	$4.89 \cdot 10^{-5}$
$PrL_3 \cdot H_2O$	339–355	2.84	2.86	1	510–829	75.90	75.0	82.40	$4.92 \cdot 10^{-5}$
$NdL_3 \cdot 2H_2O$	384–503	4.90	5.10	2	517–829	77.20	76.80	47.14	$7.61 \cdot 10^{-5}$
$SmL_3 \cdot 2H_2O$	373–400	4.80	5.00	2	504–848	76.53	76.30	51.20	$8.42 \cdot 10^{-5}$
$EuL_3 \cdot 2H_2O$	372–423	4.80	4.90	2	495–897	76.37	75.80	53.20	$6.64 \cdot 10^{-5}$
$GdL_3 \cdot 2H_2O$	371–416	4.80	4.95	2	502–904	75.83	75.40	52.30	$9.24 \cdot 10^{-5}$

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, ΔH – enthalpy for dehydration process

**Fig. 1** TG, DTG and DTA curves for 4-chloro-2-methoxybenzoate of Nd(III)

In order to calculate the energetic effects of dehydration processes, 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 293–1173 K using a differential thermoanalyser TG-DTA-DSC Setsys 16/18 Setaram at a heating rate of $1\ K\ min^{-1}$ (Table 3). The experiments were carried out under air flow at a rate of $75\ mL\ min^{-1}$. The initial mass of samples of 4-chloro-2-methoxybenzoates of light lanthanides(III) used for measurements are following: La(III) – 6.2 mg; Ce(III) – 6.2 mg; Pr(III) – 6.3 mg; Nd(III) – 6.4 mg; Sm(III) – 6.2 mg; Eu(III) – 6.5 mg; Gd(III) – 6.1 mg. The samples were heated in platinum crucibles without cover.

Magnetic susceptibilities of polycrystalline samples of 4-chloro-2-methoxybenzoates of light 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 $1.644 \cdot 10^{-5}\ cm^{-3}\ g^{-1}$ was taken [16]. The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [17]. The temperature-independent paramagnetism of rare earth ions was assumed to be zero. Magnetic moments were calculated from the Eqs (1) and (2):

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

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

Some of the results are given in Table 4.

The solubility of 4-chloro-2-methoxybenzoates of light lanthanides(III) in water at 298 K was determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic method (Table 3).

Results and discussion

The complexes of 4-chloro-2-methoxybenzoic acid with light lanthanides(III) were obtained as crystalline products with a metal ion to ligand ratio of 1:3 and a general formula $Ln(C_8H_6ClO_3)_3 \cdot nH_2O$ (where $Ln=La-Gd$ and $n=3$ for La, $n=2$ for Nd, Sm, Eu, Gd and $n=1$ for Ce, Pr). Their colours are those typical of the appropriate trivalent ions (it means: La, Ce, Eu, Gd – white, Pr – greenish, Nd – pink, Sm – cream) which is connected with the similar electron density in the system. In these molecules the $f \rightarrow f$ electronic transitions 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), IR and FIR spectra (Table 2). All light 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

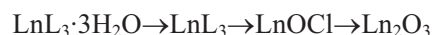
Table 4 Magnetic data of light lanthanide(III) 4-chloro-2-methoxybenzoates complex $L = C_8H_6ClO_5$

CeL ₃ ·H ₂ O Θ = -46			PrL ₃ ·H ₂ O Θ = -42			NdL ₃ ·2H ₂ O Θ = -25			SmL ₃ ·2H ₂ O Θ = 86			EuL ₃ ·2H ₂ O Θ = -724			GdL ₃ ·2H ₂ O Θ = 7.62		
T/K	χ _M ·10 ⁶	μ _{eff} /μ _B	T/K	χ _M ·10 ⁶	μ _{eff} /μ _B	T/K	χ _M ·10 ⁶	μ _{eff} /μ _B	T/K	χ _M ·10 ⁶	μ _{eff} /μ _B	T/K	χ _M ·10 ⁶	μ _{eff} /μ _B	T/K	χ _M ·10 ⁶	μ _{eff} /μ _B
77	6920	2.66	77	14962	3.82	77	17398	3.84	77	2103	1.70	77	5086	5.92	77	83043	7.58
125	4720	2.64	132	10159	3.81	134	10992	3.78	130	1596	1.74	130	5014	6.05	132	49124	7.42
137	4482	2.66	144	9450	3.85	142	10282	3.77	138	1378	1.72	139	4650	5.86	142	46859	7.44
147	4168	2.74	152	9138	3.85	152	9965	3.84	152	1625	1.70	152	4506	5.86	150	43056	7.34
162	3776	2.64	162	8593	3.81	164	8858	3.74	162	1232	1.70	158	4506	5.85	162	39402	7.32
170	3540	2.61	166	8427	3.83	174	8384	3.73	174	1231	1.74	169	4430	5.84	168	38305	7.36
182	3384	2.58	174	7797	3.77	186	8067	3.74	186	1087	1.72	178	4506	5.92	179	37250	7.46
185	3384	2.62	185	7640	3.80	196	7830	3.76	198	1016	1.72	190	4360	5.87	189	33222	7.25
198	3224	2.64	197	7320	3.82	205	7119	3.79	203	1015	1.71	198	4285	5.84	196	32166	7.26
210	2990	2.62	207	7008	3.81	215	6960	3.70	209	1017	1.73	208	4215	5.84	206	30734	7.26
222	2912	2.64	210	6930	3.82	230	6644	3.76	222	1018	1.76	217	4212	5.86	216	29418	7.28
234	2833	2.58	218	6692	3.83	230	6328	3.78	232	1015	1.79	228	4140	5.84	227	27802	7.23
242	2676	2.64	230	6534	3.87	250	6168	3.77	242	944	1.78	238	4070	5.85	236	27049	7.28
254	2597	2.66	240	6142	3.82	260	5933	3.79	252	942	1.82	248	4072	5.86	244	26462	7.30
262	2518	2.68	246	6142	3.86	268	5616	3.77	258	941	1.82	256	3940	5.83	250	24852	7.19
272	2440	2.66	257	5826	3.83	280	5380	3.74	268	652	1.62	266	3995	5.86	259	24149	7.22
278	2360	2.64	267	5668	3.85	294	5068	3.74	294	582	1.64	278	3925	5.84	268	23539	7.24
298	2282	2.69	277	5432	3.83				293	3852	5.85	278	22539	7.21			
			293	5196	3.88							293	21199	7.23			

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 $1600\text{--}1580$ and $1436\text{--}1420\text{ cm}^{-1}$, respectively. The bands with the maxima at $3490\text{--}3416\text{ cm}^{-1}$ characteristic for ν_{OH} vibrations [18, 19] and the narrow band of $\delta_{\text{H}_2\text{O}}$ 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 $2950\text{--}2944$ and 2840 cm^{-1} , respectively. The bands of $\nu_{\text{C-C}}$ ring vibrations appear at $1584\text{--}1576$, 1480 , $1184\text{--}1180$, $1025\text{--}1016$ and $201\text{--}185\text{ cm}^{-1}$. The valency $\nu_{\text{C-Cl}}$ vibration bands occur at $720\text{--}680$ and the bands at $424\text{--}410\text{ cm}^{-1}$ confirm the metal-oxygen bond [18–24]. Their regular shifts are not observed in the spectra. Probably 4-chloro-2-methoxybenzoic acid forms with the light lanthanide(III) complexes of similar stability and the same type. The bands in the range of $129\text{--}120\text{ cm}^{-1}$ are connected with the O–H...O stretching vibrations and they change their shapes in the series of light lanthanide(III) complexes depending on the degree of hydration in the compounds. Probably the molecules of crystallization water are in the outer-sphere of coordination forming the hydrogen bond [22, 23]. The bands at $180\text{--}150\text{ cm}^{-1}$ confirm the internal C–C torsion vibrations. The bands at $250\text{--}245\text{ cm}^{-1}$ due to the aromatic ring vibrations are shifted to higher frequencies from La to Gd with the decrease of ionic radii of elements. The bands of $\rho_{\text{H}_2\text{O}}$ vibrations appear at 530 cm^{-1} . The maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- for 4-chloro-2-methoxybenzoates of light lanthanides(III) and sodium salt are presented in Table 2. The magnitudes of separation, $\Delta\nu$, between the frequencies of $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ in the complexes are lower ($\Delta\nu_{\text{OCO}}=175\text{--}156\text{ cm}^{-1}$) than in the sodium salt ($\Delta\nu_{\text{OCO}}=188\text{ cm}^{-1}$), which indicates a smaller degree of ionic bond in the light lanthanide(III) 4-chloro-2-methoxybenzoates. The shifts of the frequencies ν_{asOCO} and ν_{sOCO} 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 [21, 25, 26].

In order to examine the external crystalline forms of light 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 [27]. However their crystal structures have not been determined because no single crystals have been obtained.

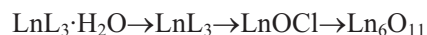
The thermal stability of light lanthanide(III) 4-chloro-2-methoxybenzoates was studied in air (Table 3, Fig. 1). TG, DTG and DSC curves were recorded using two methods of measurements (DTA/TG and DSC/TG techniques). Heating to 1173 K the complexes decompose in two (cerium complex) and three steps. They are stable up to $339\text{--}384\text{ K}$. Next in the range of $339\text{--}503\text{ K}$ these compounds dehydrate in one step losing all water molecules and form anhydrous complexes. The mass losses calculated from TG curves being equal to 2.86 and 7.10% correspond to the loss of 1 and 3 molecules of water (theoretical values 2.84 and 7.20%). The numbers of crystallization water molecules were found to be practically the same irrespective of the used measurement methods. The energetic effects accompanying the dehydration processes were calculated. The enthalpy values, ΔH , change from 25.4 to 82.4 kJ mol^{-1} for Ce(III) and Pr(III) complexes, respectively. Its values may suggest that the water molecules are coordinated to the central ions with different strengths and they are situated in various places of complex coordination spheres. The anhydrous complexes of light lanthanides(III) in the range of $495\text{--}940\text{ K}$ are decomposed to the oxides of appropriate metals with the intermediate formation of LnOCl (with the exception of Ce(III) complex that is directly decomposed to CeO_2). In the temperature range of $495\text{--}680\text{ K}$ they gradually, one by one, release the parts of ligands and form oxychlorides, LnOCl . The dehydration process is connected with an endothermic effect seen in the DTA curves while the combustion of the organic ligand with an exothermic one (Fig. 1). 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 outer-sphere of complex coordination [28–30]. The IR and FIR spectra recorded for analysed compounds may also suggest that the molecules of water are probably bounded by hydrogen bond 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 light lanthanides(III) in air proceeds in the following ways:



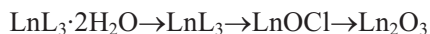
where $\text{Ln}=\text{La}$



where $\text{Ln}=\text{Ce}$



where $Ln=Pr$



where $Ln=Nd, Sm, Eu, Gd$.

In the series of investigated compounds the most thermally stable is complex of Nd(III) ($T=384$ K) whereas those of Ce(III) and Pr(III) are the least thermally stable ($T=339$ K). These two thermal methods (with various parameters) used in presented investigations let state that the complexes decompose in the same way and they contain identical numbers of water molecules. The data are comparable.

The solubility of 4-chloro-2-methoxybenzoates of light lanthanides(III) in water (at 293 K) was also determined (Table 3). It is in the order of 10^{-5} mol dm⁻³. Gd(III) 4-chloro-2-methoxybenzoate is the most soluble salt, while that of Ce(III) the least soluble one. From the solubility data, it appears that 4-chloro-2-methoxybenzoic acid cannot be used for the separation of light lanthanide(III) 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 reasons why their colours are typical of Ln³⁺ the magnetic susceptibility of 4-chloro-2-methoxybenzoates was determined over the range of 77–300 K. The complexes obey Curie–Weiss law (Table 4). For all compounds the values of the Weiss constant, θ , have a negative sign. It probably results from the antiferromagnetic spin or form a crystal field splitting of the paramagnetic spin state [31–34]. In 4-chloro-2-methoxybenzoates of light lanthanides(III) the paramagnetic central ions remain practically unaffected by diamagnetic ligands coordinated around them. The f -electrons causing their paramagnetism are well separated from outside influences and they do not participate in the formation of M–O bond. They are in an inner shell characterized by radius 0.35 Å [35] to be very small in comparison with the radius of the 5s²5p⁶ closed shell (~1 Å). Their energy levels are the same as in the free ions. For most of the lanthanide ions the ground state is separated by several hundred of cm⁻¹ from the next higher lying state. Therefore the magnetic properties can be taken as those of the ground state alone. Taking into account this fact lanthanide ions in the compound act in the same way as the free ions. The values of μ_{eff} determined for all 4-chloro-2-methoxybenzoates (except for europium) are close to those calculated for Ln³⁺ ions by Hund and Van Vleck (Table 5). Their values at room temperature for analysed complexes are following: 2.69 μ_{β} for Ce; 3.88 μ_{β} for Pr; 3.74 μ_{β} for Nd; 1.64 μ_{β} for Sm; 5.85 μ_{β} for Eu and 7.23 μ_{β} for Gd [34]. Lanthanum(III) 4-chloro-2-methoxybenzoate is diamagnetic in nature as expected.

Table 5 Values of μ_{eff} for the light lanthanides determined by Hund and Van Vleck and calculated for light lanthanide(III) 4-chloro-2-methoxybenzoates at 298 K*

Ln ³⁺	Ground term	Calculated		
		μ_{eff} by Hund	μ_{eff} by Van Vleck	$\mu_{\text{eff}}/\mu_{\beta}^*$
La ³⁺	¹ S ₀	0.00	0.00	0.00
Ce ³⁺	² F _{5/2}	2.54	2.56	2.69
Pr ³⁺	³ H ₄	3.58	3.62	3.88
Nd ³⁺	⁴ J _{9/2}	3.62	3.68	3.74
Sm ³⁺	⁶ H _{5/2}	0.84	1.55–1.65	1.64
Eu ³⁺	⁷ F ₀	0.00	3.40–3.51	5.85
Gd ³⁺	⁸ S _{7/2}	7.94	7.94	7.23

The higher value of μ_{eff} for Eu(III) 4-chloro-2-methoxybenzoate compared to that given by Hund may suggest the possible interaction of the ligand field with central ion or may be connected with the multiplet – splitting. The first excited state in europium ion is sufficiently close in energy to the ground state (even the second and third ones) to be appreciably populated at room temperature [34–37]. Since the excited states have higher J values than the ground state, the actual magnetic moments is higher than those calculated by using the J for the ground state. With the exception of Sm(III) and Eu(III) the multiplet widths of lanthanons are very wide compared to kT at room temperature while those for Sm(III) and Eu(III) are comparable to kT [34, 36]. 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. Thus, the colours of the complexes stay the same as those in the free lanthanide ions. The electron density in the molecules makes the f – f electronic transitions of the central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths. The $4f$ orbitals of lanthanide ions effectively shielded by the 5s²5p⁶ octet. Therefore the metal ligand bonding in lanthanide complexes is mainly electrostatic in nature [38, 39].

Conclusions

On the basis of the results obtained it appears that 4-chloro-2-methoxybenzoates of light lanthanides(III) were synthesized as hydrated complexes. Their colours are typical for the particular Ln(III) ion, i.e. white for La, Ce, Eu, Gd, cream for Sm, green for Pr and violet for Nd, 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 two (Ce complex) or 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 Ln³⁺ 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 [8–14]. 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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