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THERMAL AND SPECTRAL BEHAVIOUR OF 5-CHLORO-2-METHOXYBENZOATES OF HEAVY LANTHANIDES AND YTTRIUM

W. Ferenc and B. Bocian

Department of General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University
Pl 20-031, Lublin, Poland

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Abstract

5-Chloro-2-methoxybenzoates of heavy lanthanides and yttrium were obtained as di- or tetrahydrates with a metal to ligand ratio of 1:3 and general formula: $Ln(C_8H_6ClO_3)_3 \cdot nH_2O$, where n=2 for *Ln*=Tb, Dy, Y and n=4 for *Ln*=Ho, Er, Tm, Yb, Lu. The complexes were characterized by elemental analysis, IR and FIR spectra, thermogravimetric studies, X-ray diffraction and magnetic measurements. The carboxylate group appears to be a symmetrical, bidentate, chelating ligand. All complexes are polycrystalline compounds. Their thermal stabilities were determined in air and in nitrogen atmospheres. When heated they dehydrate to form anhydrous salts which next in air are decomposed to the oxides of the respective metals while in nitrogen to the mixtures of carbon and oxides or carbon and oxychlorides of respective metals. The complexes are more stable in air than in nitrogen.

The solubilities of yttrium and heavy lanthanide 5-chloro-2-methoxybenzoates in water at 293 K are of the order of 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 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: 5-chloro-2-methoxybenzoates, magnetic susceptibility determinations, rare earth complexes, spectrochemical and thermal stability investigations

Introduction

According to literature survey compounds of 5-chloro-2-methoxybenzoic acid with various metal ions have been scarcely studied. A paper only deals with its complexes with light lanthanides [1]. The complexes were synthesized as penta- or monohydrates and characterized by elemental analysis, IR and FIR spectra.The thermogravimetric studies, X-ray diffraction and magnetic measurements were also presented. 5-Chloro-2-methoxybenzoic acid is a white crystalline solid sparingly soluble

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in cold water, that is stable up to 199°C after which it decomposes with the melting point temperature.

The complexes of heavy lanthanides and yttrium with 5-chloro-2-methoxybenzoic acid have not been prepared and investigated so far. Therefore, we decided to obtain them in solid state and to examine some of their physico-chemical properties including thermal stability in air and nitrogen during heating to 1273 and 1173 K, respectively. Taking the presence of methoxy- group in benzene ring into account, the properties of 5-chloro-2-methoxybenzoates of rare earth elements were compared with those of 2-methoxybenzoates. The comparison lets us estimate the influence of the position of substituents in aromatic ring on the properties of the complexes.

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, know the mechanism of decomposition, 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.

Experimental

The complexes of 5-chloro-2-methoxybenzoic acid with heavy lanthanides and yttrium were prepared by the addition of equivalent quantities of 0.1 M ammonium 5-chloro-2-methoxybenzoate (pH~5) to a hot solution containing the rare earth element nitrates 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.

Table 1 Analytical data of yttrium and heavy lanthanide 5-chloro-2-methoxybenzoates

Complex	H/%		C/%		Cl/%		M/%	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$TbL_3 \cdot 2H_2O$	2.92	2.73	38.32	38.15	14.17	14.03	21.15	21.00
$DyL_3 \cdot 2H_2O$	2.91	2.76	38.14	37.94	14.10	14.01	21.52	21.23
$HoL_3 \cdot 4H_2O$	3.27	3.11	36.29	36.22	13.42	13.18	20.78	20.63
$ErL_3 \cdot 4H_2O$	3.27	3.27	36.19	36.42	13.38	13.79	21.01	21.08
$TmL_3 \cdot 4H_2O$	3.26	3.10	36.11	36.01	13.36	13.07	21.18	21.01
$YbL_3 \cdot 4H_2O$	3.24	3.12	35.94	35.95	13.29	13.39	21.59	21.59
$LuL_3 \cdot 4H_2O$	3.23	3.17	35.84	35.84	13.26	13.18	21.78	21.64
$YL_3 \cdot 2H_2O$	3.25	3.26	42.51	42.58	15.72	15.37	13.12	13.04

$L=C_8H_6ClO_3$

The contents of carbon and hydrogen in complexes were determined by elemental analysis using a 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 ranges 4000–400 and 600–100 cm^{-1} using M-80 and Perkin Elmer 180 spectrophotometers, respectively. Samples for IR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Nujol mulls sandwiched between polyethylene plates (Table 2, Fig. 1).

Table 2 Frequencies (cm^{-1}) of the absorption bands of COO$^-$ for 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides and sodium and that of CO for 5-chloro-2-methoxybenzoic acid

Complex	ν(C=O)	ν_{as}(OCO)	ν_s(OCO)	Δν(OCO)	ν(C–Cl)	ν(M–O)
$TbL_3 \cdot 2H_2O$	–	1548	1420	128	688	416
$DyL_3 \cdot 2H_2O$	–	1552	1420	132	688	416
$HoL_3 \cdot 4H_2O$	–	1528	1428	100	688	424
$ErL_3 \cdot 4H_2O$	–	1528	1428	100	712	420
$TmL_3 \cdot 4H_2O$	–	1528	1428	100	712	420
$YbL_3 \cdot 4H_2O$	–	1532	1428	104	708	424
$LuL_3 \cdot 4H_2O$	–	1528	1424	104	712	424
$YL_3 \cdot 2H_2O$	–	1528	1420	108	688	424
NaL	–	1560	1404	156	670	–
HL	1728	–	–	–	695	–

$L=C_8H_6ClO_3$

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 2Θ=4–80° by means of the Debye–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 1273 K with a sensitivity TG-100 mg, DTG and DTA sensitivities were regulated by computer Derill programme. The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration.

The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10 K min^{-1}. The samples were heated at the following sensitivities: TG-100 mg, DTA-1/10, DTG-1/5. The nitrogen flowed through gas washers filled with pyrogallol and silica gel at a rate of 115 cm^3 min^{-1}. The results are presented in Table 3. The nature of the solid products of decomposition was established from the TG curves and confirmed by IR and X-ray spectra.

Magnetic susceptibilities of polycrystalline samples of 5-chloro-2-methoxybenzoates of heavy lanthanides were measured by the Gouy method using a sensitive

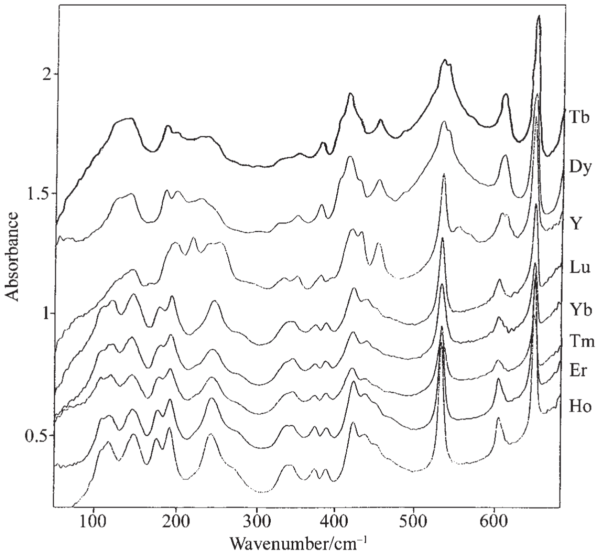

Fig. 1 Far-infrared spectra of 5-chloro-2-methoxybenzoates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III)

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 of $16.44\cdot10^{-6}$ (cm^{-3} g^{-1}) was taken [2]. The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [3]. The temperature-independent paramagnetism of rare earth ions was assumed to be zero. Magnetic moments were calculated from the equations:

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

$$\mu_{\mathrm{eff}}=2.83[\chi_{\mathrm{M}}(T-\Theta)]^{1/2}$$

Some of the results are given in Table 4.

The solubility of 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides 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 3).

Results and discussion

The complexes of 5-chloro-2-methoxybenzoic acid with yttrium and heavy lanthanides were obtained as crystalline products with a metal to ligand ratio of 1:3 and a general formula $Ln(C_8H_6ClO_3)_3\cdot nH_2O$ (where Ln=Tb–Lu, Y and n=4 for Ho–Lu and n=2 for Tb, Dy, Y). Their colours are those typical of the appropriate trivalent ions (it means for: Ho-cream, Er-salmon and Tb, Dy, Tm, Yb, Lu-white), which is connected with the similar electron density in the system. In these molecules the f→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, Fig. 1). All heavy lanthanide and yttrium 5-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^- group occur at 1552–1528 and 1428–1420 cm^{-1}, respectively. The bands with the maxima at 3480–3384 cm^{-1} characteristic of ν(OH) vibrations [4, 5] and narrow bands of $\delta(H_2O)$ at 1600 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 ν(C–C) ring vibrations appear at 1584–1576, 1480, 1184–1180, 1020–1016 and 207–185 cm^{-1}. The valency ν(C–Cl) vibration bands occur at 712–670 and the bands at 424–416 cm^{-1} confirm the metal–oxygen bond [6–15]. Their regular shifts are not observed in the spectra. Probably 5-chloro-2-methoxybenzoic acid forms with the heavy lanthanides complexes of similar stability and the same type. The bands in the range 129–120 cm^{-1} are connected with the O–H...O stretching vibrations and they change their shapes in the series of heavy lanthanide complexes. It probably results from the higher degree of hydration in tetrahydrates of 5-chloro-2-methoxybenzoates of Ho(III), Er(III), Tm(III), Yb(III), Lu(III) than in the dihydrates of Tb(III), Dy(III) and Y(III). Probably the molecules of crystallization water are in the outer-sphere of coordination forming the hydrogen bond [10, 11]. The bands at 150–145 cm^{-1} confirm the internal C–C torsion vibrations. The bands at 249–240 cm^{-1} due to the aromatic ring vibrations are shifted to higher frequencies from Tb to Lu with the decrease of ionic radii of elements. The bands of $\rho(H_2O)$ vibrations appear at 532 cm^{-1} and they change their shapes in the series of heavy lanthanides depending on the numbers of crystal water molecules. The maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- for 5-chloro-2-methoxybenzoates of the heavy lanthanides, yttrium and sodium are presented in Table 2. The magnitudes of separation, $\Delta\nu$, between the frequencies ν_{as}(OCO) and ν_s(OCO) in the complexes are lower ($\Delta\nu$=132–100 cm^{-1}) than in the sodium salt ($\Delta\nu$=156 cm^{-1}) which indicates a smaller degree of ionic bond in yttrium and the heavy lanthanide 5-chloro-2-methoxybenzoates. In the case of 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides the shifts of the frequencies ν_{as}(OCO) and ν_s(OCO) are lower and higher, respectively, than those for sodium 5-chloro-2-methoxybenzoate. Accordingly, the carboxylate ion appears to be a symmmetrical, bidentate chelating ligand [8, 16, 17].

In order to estimate the external crystalline forms of yttrium and the heavy lanthanide 5-chloro-2-methoxybenzoates, the X-ray powder diffraction measurements were made. The diffractogram analysis suggests that they are polycrystalline compounds and their crystal structures are different in essential features [18]. The

Table 3 Temperature range of thermal stability of heavy lanthanide and yttrium 5-chloro-2-methoxybenzoates in air and nitrogen atmospheres and their solubility in water at 293 K

Complex	ΔT_1/K	Mass loss/%		n	A(Air) N(N_2)	ΔT_2/K	Mass loss/%		T_k/K	Ln_2O_3/%		Residue/%	Solubility/ mol dm^{-3}
		calcd.	found				calcd.	found		calcd.	found		
$TbL_3 \cdot 2H_2O$	348–388	4.80	4.95	2	A	493–883	73.87	73.87	1193	26.13	26.13		$2.57 \cdot 10^{-3}$
	353–383		4.75		N	513–713						39.00	
$DyL_3 \cdot 2H_2O$	363–393	4.77	4.67	2	A	508–923	75.30	75.21	1218	24.70	24.79		$2.47 \cdot 10^{-3}$
	353–383		5.00		N	503–703						32.00	
$HoL_3 \cdot 4H_2O$	343–378	9.07	8.99	4	A	498–923	76.18	76.21	1208	23.82	23.79		$2.23 \cdot 10^{-3}$
	333–373		9.24		N	493–713						31.80	
$ErL_3 \cdot 4H_2O$	348–378	9.05	9.24	4	A	518–923	75.97	75.88	1113	24.03	24.12		$1.88 \cdot 10^{-3}$
	333–373		8.94		N	513–693						28.85	
$TmL_3 \cdot 4H_2O$	353–373	9.03	9.24	4	A	533–958	75.81	75.55	1103	24.19	24.45		$1.76 \cdot 10^{-3}$
	343–373		8.98		N	523–713						26.87	
$YbL_3 \cdot 4H_2O$	353–378	8.92	8.67	4	A	533–923	75.42	75.88	1083	24.58	24.12		$1.52 \cdot 10^{-3}$
	343–373		9.00		N	523–723						40.00	
$LuL_3 \cdot 4H_2O$	348–378	8.96	8.91	4	A	533–893	75.24	75.21	1033	24.76	24.79		$1.67 \cdot 10^{-3}$
	343–373		8.78		N	523–723						25.00	
$YL_3 \cdot 2H_2O$	353–383	4.72	4.80	2	A	513–943	83.33	83.25	1148	16.67	16.75		$3.01 \cdot 10^{-3}$
	343–383		4.91		N	518–718						30.35	

$L=C_8H_6ClO_3$; 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 complexes may have the different crystal structures which have not been determined because their single crystals have not been obtained so far. The anhydrous 5-chloro-2-methoxybenzoates of the heavy lanthanides appear to be less crystalline than the hydrated ones but no changes of their crystal structures were observed. The structure of all heavy lanthanide oxides obtained from the ignition of the oxalates and

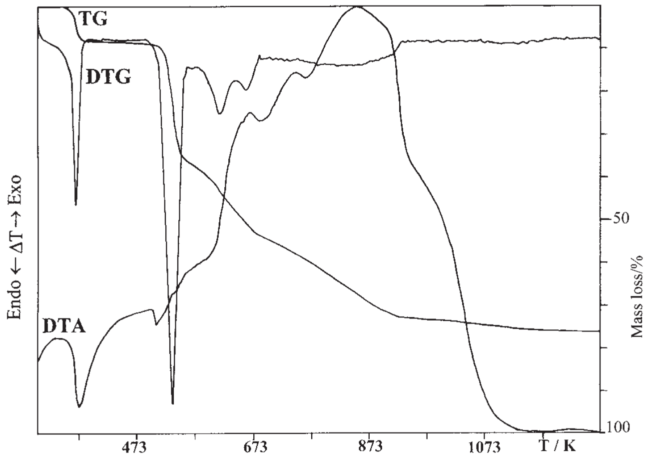

Fig. 2 TG, DTG and DTA curves of holmium 5-chloro-2-methoxybenzoate in air atmosphere

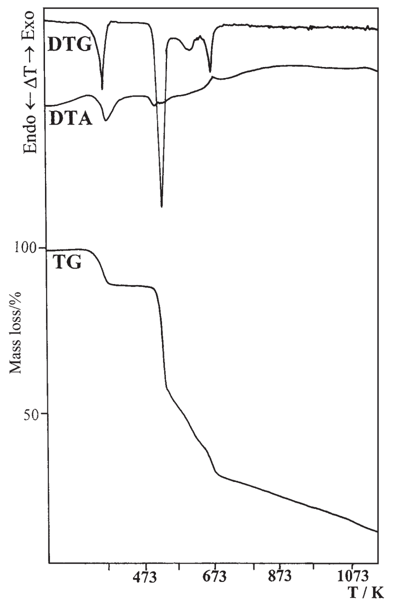

Fig. 3 TG, DTG and DTA curves of holmium 5-chloro-2-methoxybenzoate in nitrogen atmosphere

5-chloro-2-methoxybenzoates remains the same irrespectively of the way of their formation [19].

The thermal stability of the yttrium and heavy lanthanide 5-chloro-2-methoxybenzoates was studied in air and nitrogen atmospheres (Table 3, Figs 2, 3). Heated in air they decompose in two steps. The complexes are stable up to 343–363 K. Next in the temperature range 343–393 K they dehydrate in one step losing four (Ho, Er, Tm, Yb, Lu) and two (Y, Tb, Dy) molecules of crystallization water and form anhydrous complexes. The mass loss calculated from TG curves being equal to 4.67 and 9.24% corresponds to the loss of 2 or 4 molecules of water (theoretical values 4.72 and 9.07%). The anhydrous 5-chloro-2-methoxybenzoates of heavy lanthanides(III) in the range 493–958 K are decomposed to the oxides of appropriate metals. The temperature of oxide formations decreases from 1218 (Dy_2O_3) to 1033 K (Lu_2O_3). The dehydration process is connected with an endothermic effect seen in DTA curves while the combustion of the organic ligand with an exothermic one. For example, TG, DTG and DTA curves of 5-chloro-2-methoxybenzoate of Ho during heating in air was presented in Fig. 2. 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 [20–23]. The IR and FIR spectra recorded for 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides 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 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides in air proceeds in the following steps:

$$LnL_3\cdot 4H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3 \quad \text{(for } Ln\text{=Ho–Lu)}$$

$$LnL_3\cdot 2H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3 \quad \text{(for } Ln\text{=Y, Tb, Dy)}$$

The thermal stability of yttrium and heavy lanthanide 5-chloro-2-methoxybenzoates was studied also in nitrogen atmosphere (Table 3, Fig. 3). The complexes of Ho(III)–Lu(III) were found to be tetrahydrates (the found mass loss calculated from TG curves are equal to 8.78–9.24% and theoretical 8.92–9.07%) while those of Tb(III), Dy(III) and Y(III) are dihydrates (the found loss of mass is equal to 4.75–5.00 and theoretical 4.72–4.80%). The complexes being heated to 1173 K decompose in two steps. In the first step, in the range 333–383 K, they are dehydrated to form anhydrous complexes. The dehydration process is accompanied by endoeffect observed in DTA curves. For tetrahydrates of 5-chloro-2-methoxybenzoates of Ho(III), Er(III), Tm(III), Yb(III), Lu(III) the initial dehydration temperature values are lower (333–343 K) compared to those in air (343–353 K), which suggests them to be more stable in air than in nitrogen. Next, in the range 493–723 K, all anhydrous complexes further decomposed. The combustion of organic ligands is connected with an exoeffect seen in DTA curves. Figure 3 presents the TG, DTG and DTA curves of

5-chloro-2-methoxybenzoate of Ho during heating in nitrogen atmosphere. The values of initial decomposition temperatures of anhydrous complexes of Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) in nitrogen are lower (493–523 K) than those in air, which suggests them to be more stable in air than in nitrogen. The final products of decomposition of 5-chloro-2-methoxybenzoates of yttrium and heavy lanthanides are the mixtures of the respective metal oxides and carbon (Table 3). The contents of mixture were identified by X-ray powder diffraction [18, 19].

The solubilities of 5-chloro-2-methoxybenzoates of heavy lanthanides in water at 293 K were measured (Table 3). They are in the order of 10^{-3}mol dm^{-3}. The ytterbium 5-chloro-2-methoxybenzoate is the least soluble salt while that of yttrium is the most soluble one.

The thermal stability of 5-chloro-2-methoxybenzoates of heavy lanthanides in air was compared with that of 2-methoxybenzoates of those elements [24]. 2-Methoxybenzoates seem more stable than 5-chloro-2-methoxybenzoates. It is probably connected with the influence of Cl position in benzene ring on an electron density in the system. 2-Methoxybenzoates of heavy lanthanides are better soluble than 5-chloro-2-methoxybenzoates [25]. Their solubilities are in the orders of 10^{-2} mol dm^{-3}. The difference in the values of the orders results from the influence of various mesomeric and inductive effects of Cl on electron density in benzene ring.

In order to estimate the nature of metal ligand bonding in lanthanide complexes and try to know the reason why the colours of 5-chloro-2-methoxybenzoates of heavy lanthanides and yttrium are typical of Ln^{3+} the magnetic susceptibility of 5-chloro-2-methoxybenzoates was determined over the range 77–298 K. The complexes obey Curie–Weiss law (Table 4). A plot of the inverse of the magnetic susceptibility χ_M de-

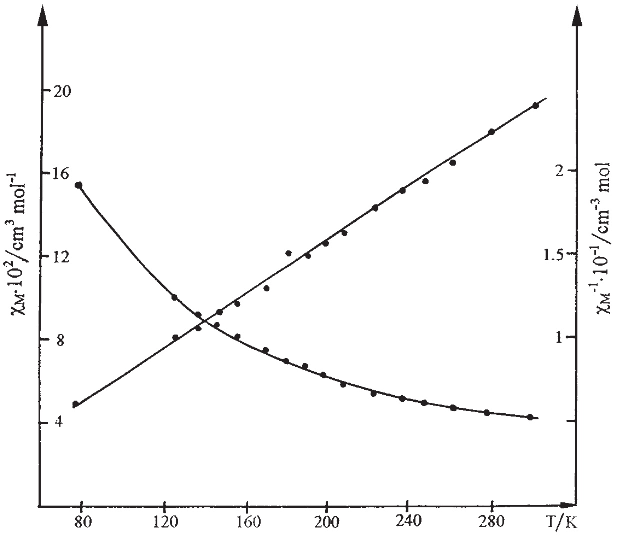

Fig. 4 Relationship between χ_M and χ_M^{-1} *vs.* T for 5-chloro-2-methoxybenzoate of holmium

termined for all complexes yields a straight line. In Fig. 4 the relationship between χ_M and χ_M^{-1} and T for 5-chloro-2-methoxybenzoate of Ho is presented. For all complexes the values of the Weiss constants, Θ have a negative sign. It probably results from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [26–31]. 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 4 and 5) [31]. In the lanthanide ions 4f electrons are in an inner shell having a radius that is equal to 0.35 Å [32]. This value seems to be very small compared to the radius of the $5s^25p^6$ 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 [31–35]. 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 5-chloro-2-methoxybenzoates of heavy lanthanides the lanthanide ions probably exhibit a coordination number six or 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 complexes is mainly electrostatic in nature [32, 36].

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

$TbL_3{}^{a}\cdot 2H_2O$			$DyL_3\cdot 2H_2O$			$HoL_3\cdot 4H_2O$		
Θ^{b}= –11 *K*			Θ = –5 *K*			Θ = –10 *K*		
T/K	$\chi\cdot 10^6$	μ/BM	*T*/K	$\chi\cdot 10^6$	μ/BM	*T*/K	$\chi\cdot 10^6$	μ/BM
77	133861	9.72	77	164000	10.37	77	154434	10.38
120	88260	9.64	130	101200	10.46	124	98545	10.30
134	80905	9.69	134	96500	10.36	135	91072	10.30
144	74285	9.60	147	90200	10.47	145	87180	10.42
153	70608	9.63	154	84000	10.34	156	82043	10.46
166	64724	9.57	168	74720	10.17	169	73948	10.32
177	62296	9.68	178	72290	10.29	180	65541	10.01
185	58840	9.61	198	70200	10.68	188	66164	10.27
192	57369	9.65	204	69340	10.77	198	63828	10.34
221	50014	9.63	206	65010	10.48	208	59469	10.22
233	47072	9.59	217	60022	10.33	224	55188	10.20
238	45601	9.53	225	58521	10.38	239	52775	10.29
246	44865	10.00	235	54559	10.23	249	50596	10.28
255	42659	9.53	243	52620	10.22	262	47871	10.24
267	41188	9.57	257	50120	10.25	278	44213	10.13
277	38981	9.48	266	49720	10.38	298	41877	10.20
288	37510	9.47	276	47490	10.33			
296	36775	9.58	291	45221	10.35			
298	35304	9.62						

$ErL_3\cdot 4H_2O$			$TmL_3\cdot 4H_2O$			$YbL_3\cdot 4H_2O$		
Θ = – 6 *K*			Θ = –12 *K*			Θ = – 47 *K*		
T/K	$\chi\cdot 10^6$	μ/BM	*T*/K	$\chi\cdot 10^6$	μ/BM	*T*/K	$\chi\cdot 10^6$	μ/BM
77	134297	9.46	77	73226	7.24	77	24460	4.96
129	78860	9.25	130	47515	7.37	122	17067	4.85
139	72614	9.20	139	42591	7.20	133	15730	4.81
149	67929	9.20	151	39778	7.23	143	14943	4.82
159	64025	9.22	160	36730	7.14	149	14157	4.77
169	59340	9.14	170	34386	7.11	166	13370	4.83
182	53094	8.97	178	32823	7.10	174	12977	4.85
193	52313	9.16	204	28915	7.11	183	12662	4.80
203	49190	9.10	214	26571	6.98	198	12190	4.96
213	47628	9.17	224	25789	7.02	207	11640	4.93
223	45286	9.14	232	25008	7.12	218	11168	4.94
232	42944	9.08	250	23445	7.10	228	11011	5.00
242	41382	9.10	252	22663	7.09	239	10617	5.01
252	39820	9.46	260	21882	7.11	247	10145	4.97
262	38259	9.10	270	21100	7.06	260	9280	4.86
272	36697	9.08	276	20319	7.12	270	9044	4.54
282	35136	9.04	296	19537	7.00	280	8730	4.87
296	33574	9.05				295	8336	4.87

[a] *L*=$C_8H_6ClO_3$; [b] Θ=Weiss constant

Table 5 Values of μ_{eff} for the heavy lathanides determined by Hund and Van Vleck and *calculated for heavy lanthanide 5-chloro-2-methoxybenzoates at 298 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	10.58
Ho^{3+}	$^5I_8$	10.60	10.60	10.60
Er^{3+}	$^4I_{15/2}$	9.60	9.60	9.58
Tm^{3+}	$^3H_6$	7.60	7.60	7.48
Yb^{3+}	$^2F_{7/2}$	4.50	4.50	4.48
Lu^{3+}	$^1S_0$	0.00	0.00	0.00

Conclusions

On the basis of the results obtained it appears that 5-chloro-2-methoxybenzoates of heavy lanthanides and yttrium were synthesized as hydrated complexes. Their colours 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 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 and nitrogen to 1173 K decompose in two steps. In the first step they dehydrate to form anhydrous complexes that next in air decompose to the oxides of the appropriate metals or in nitrogen to the mixtures of metal oxides and carbon. The complexes are more stable in air than in nitrogen atmosphere.

* * *

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