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Complexes of some transition metal ions with selected dichlorophenoxyacetic acid

Thermal, spectral and magnetic properties

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Abstract This paper presents the interpretations of data obtained from the investigations of 2,4-dichlorophenoxyacetates of selected lanthanide(III) ions. The compounds of 2,4-dichlorophenoxyacetic acid ion with La(III), Pr(III)–Lu(III) with the formula $Ln(C_8H_5O_3Cl_2)_3 \cdot nH_2O$, where Ln(III) = lanthanides, $n = 2$, 4 or 5 depending on Ln(III) ions, were synthesized and characterized by elemental analysis, FTIR spectroscopy, magnetic and thermogravimetric studies and also by X-ray powder diffraction (XRD) measurements. The compounds crystallize in monoclinic or triclinic systems. The carboxylate groups act as bidentate chelating agents. On heating in air up to 1173 K, the analysed compounds are decomposed in three steps: they are dehydrated to anhydrous salts which next are decomposed to the oxides of respective metals with intermediate formation of the oxychlorides. The enthalpy values of the dehydration process changed from 44.00 to 91.34 kJ mol^{-1}. The magnetic moments of compounds were determined in the ranges of 76–303 K and for some of them at 4.2–303 K.

Keywords 2,4-dichlorophenoxyacetates · Lanthanides · Magnetic properties · Thermal stability

Introduction

2,4-Dichlorophenoxyacetic acid exhibits selective weed killer properties. Therefore, it is used as active substance in many herbicides applied for protection of wheat, rye, barley and oat. This xenobiotic is deliberately introduced by man into the environment in order to increase crops and improve their quality. However, if used unskilfully or excessively, it can pose a threat to the environment. The pesticides and the products of their decomposition pollute the soil, ground and surface waters, agricultural and food products [1–3].

The chlorophenoxyacetic acids and their derivatives as widely used herbicides may form complexes with metal ions present in soil. Those of their compounds being slightly soluble in water may cause retention of metals in soil or in underground parts of the plants and stop their transport to the above-ground sections. This behaviour can reduce the level of pesticides in food or water. The compounds show also the antimicrobial activity [4–10].

The carboxylic group present in the acid molecule may interact with metal ions effecting their properties and biological activity. The lanthanide(III) ions show the interesting biochemical properties; therefore, they may be used in the metabolism investigations. Under temperature changes, the lanthanide ions may migrate from their minerals to soil, water or organic materials and next they may penetrate to plants, animals and also to human organism.

The biological activity of coordination compounds is modulated by many such factors like the following: the nature of group substituted to the basic ligand, type of metal and environment around the central metal ion in complex.

2,4-Dichlorophenoxyacetic acid may form the complexes with metals present in the soil. Therefore, the

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studies of the structures, conditions of the formation and physico-chemical properties of its compounds with various metal ions seem interesting for practical application [1, 10]. As part of our research on carboxylate complexes, we synthesized and investigated also the 2-(4-chlorophenoxy)acetates of lanthanides(III) [11]. These hydrated compounds were characterized by elemental analysis, FTIR spectroscopy, magnetic and thermogravimetric studies and X-ray diffraction (XRD) analysis. In the complex molecules, the carboxylate groups act as bidentate chelating agents. On heating in air to 1273 K, they decompose in three steps. At first, they dehydrate forming at first anhydrous salts and next the oxides of respective metals. The oxychlorides are their intermediate products of thermal destruction. Over the ranges of 76–303 and 1.8–300 K, the magnetic susceptibility of 2-(4-chlorophenoxy)acetates of lanthanides(III) were measured and magnetic moments calculated. The results revealed them to be high-spin complexes with weak ligand fields.

From the review of the available literature on the 2,4-dichlorophenoxyacetates of metal ions, it appears that there are papers on the mixed ligand complexes of 2,4-dichlorophenoxyacetates with Cu(II) and 2,2′- bipyridine and 4,4′- bipyridine [12–14]. Metal(II) compounds of 2,4-dichlorophenoxyacetic acid with *N*-bases, α-aminoacids and bovine serum albumin are described in the articles [13–19]. There are also publications concerning the investigations of 2,4-dichlorophenoxyacetic acid anion with Ag(I), Zn(II), Cu(II), Co(II), Mn(II) and Ni(II) which were characterized by IR and X-ray spectra, TG/DTA and conductometric methods [20–32].

The aim of this paper was to synthesize the complexes of the selected lanthanides(III) such as: La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu with 2,4-dichlorophenoxyacetic acid and to examine their properties such as thermal stability in air at 293–1173 K, magnetic properties in the ranges of 77–303 and 4.2–303 K and to record their FTIR and X-ray spectra. Next our investigations on these compounds will be devoted to examine their biological activity.

Experimental

Materials

All chemicals and solvents used for the synthesis were of commercially available reagent grade and were used without further purification.

2,4-Dichlorophenoxyacetate of ammonium (pH 5) of 0.1 mol L^{-1} concentration was prepared by the addition of NH_3 (aq) solution [25 % pure, Polish Chemical Reagents in Gliwice (Poland)] to 2,4-dichlorophenoxyacetic acid in water solution (99 % pure, Aldrich Chemical Company).

In order to obtain the rare earth element(III) chlorides, $LnCl_3 \cdot nH_2O$, the samples of 0.8 g of lanthanide(III) oxides (99.9 % pure, Aldrich Chemical Company) were digested in the equivalent amounts of concentrated HCl [35–38 % pure, Polish Chemical Reagents in Gliwice (Poland)]. The solutions were constantly heated. The lanthanide(III) chlorides were practically evaporated to dryness. The residue was dissolved in water forming the solutions of lanthanide(III) chlorides, the concentration of which was equal to 0.1 mol L^{-1} and pH 5.

Synthesis

The complexes of lanthanides(III) with 2,4-dichlorophenoxyacetic acid anion were prepared by adding the equivalent quantities of 0.1 mol L^{-1} ammonium salt of 2,4-dichlorophenoxyacetic acid (pH 5) to a warm solutions of lanthanide(III) chlorides and crystallizing at 293 K. For the reaching equilibrium state, the solids were constantly stirred for 1 h. Next they were filtered off, washed with warm water to remove ammonium and chloride ions and dried at 303 K to a constant mass. The sodium salt of 2,4-dichlorophenoxyacetic acid was prepared by the addition of equivalent amount of 0.1 mol L^{-1} ammonium salt of that acid to NaOH solution containing 0.1 g NaOH [analytically pure, Polish Chemical Reagents in Gliwice (Poland)] and crystallizing.

Methods and apparatus applied

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The amounts of Cl and Ln(III) metals were established by X-ray fluorescence XRF method with the use of spectrophotometer of X-ray fluorescence with energy dispersion EDXRF-1510 (Canberra-Packard).

The FTIR spectra of complexes and the products of the final complex decompositions were recorded over the range of 4000–400 cm^{-1} using an M-80 Perkin-Elmer spectrometer. The samples were prepared as KBr discs.

The X-ray diffraction patterns of compounds and the products of decomposition process were taken on a HZG-4 (Carl-Zeiss. Jena) diffractometer with Ni filtered CuK_α radiation. The measurements were made within the range of $2\theta = 4°–80°$ by means of Bragg–Brentano method.

The thermal stabilities and decompositions of the complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow rate of 1 L h^{-1} in the temperature range of 297–1173 K at a heating rate of 5 K min^{-1}. The initial mass of samples of 2,4-dichlorophenoxyacetates of lanthanides(III) used for measurements changed from 5.41 to 4.30 mg. Samples of these compounds were heated in Al_2O_3 crucibles.

Table 1 Elemental analysis data (%) for the lanthanide(III) 2,4-dichlorophenoxyacetates

Complex	C/%		H/%		Cl/%		M/%	
$L = C_8H_5O_3Cl_2^-$	Cald.	Found	Cald.	Found.	Cald.	Found	Cald.	Found
$LaL_3{\cdot}4H_2O$	33.06	33.20	2.64	2.33	24.45	24.30	15.94	15.84
$PrL_3{\cdot}2H_2O$	34.41	34.60	2.27	1.90	25.45	25.25	16.83	16.50
$NdL_3{\cdot}2H_2O$	34.29	34.55	2.26	2.16	25.36	25.34	17.14	17.10
$SmL_3{\cdot}2H_2O$	34.02	34.72	2.24	1.68	25.16	25.10	17.76	17.40
$EuL_3{\cdot}2H_2O$	33.96	34.49	2.24	1.93	25.11	25.10	17.92	18.20
$GdL_3{\cdot}2H_2O$	33.76	33.70	2.23	1.99	24.97	25.00	18.41	18.39
$TbL_3{\cdot}5H_2O$	31.71	31.28	2.75	2.66	23.45	23.20	17.50	18.20
$DyL_3{\cdot}2H_2O$	33.54	34.49	2.21	1.85	24.81	24.93	18.92	18.50
$HoL_3{\cdot}2H_2O$	33.45	34.10	2.20	1.68	24.76	24.50	19.06	18.90
$ErL_3{\cdot}2H_2O$	33.37	34.17	2.20	1.60	24.68	24.60	19.35	18.90
$TmL_3{\cdot}2H_2O$	34.00	34.00	2.19	1.90	24.65	24.48	19.55	19.40
$YbL_3{\cdot}5H_2O$	31.20	32.00	2.70	2.67	23.07	23.00	18.74	18.60
$LuL_3{\cdot}2H_2O$	33.06	33.04	2.18	2.01	24.45	24.40	20.08	20.00

Magnetic susceptibility of polycrystalline samples of 2,4-dichlorophenoxyacetates of lanthanides(III) was investigated at 76–303 K and some of them at 4.2–303 K. The measurements in the range of 76–303 K were carried out using the Gouy's method. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be 1.644×10^{-5} cm^3 g^{-1}. The measurements were made at a magnetic field strength of 9.9 kθe. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [33].

The effective magnetic moment values were calculated from the Eq. 1:

$$\mu_{eff} = 2.83\,(\chi_m \cdot T)^{1/2} \qquad (1)$$

where μ_{eff}—effective magnetic moment, χ_m—magnetic susceptibility per molecule and T—absolute temperature

The measurements in the range of 1.8–303 K were carried out with the use of Quantum Design SQUID-VSM magnetometer. The superconducting agent was generally operated at a field strength ranging from 0 to 7 T. Measurements of samples were made at magnetic field 0–1 T. The SQUID magnetometer was calibrated with the palladium rod sample.

Results

2,4-Dichlorophenoxyacetates of lanthanides(III) were obtained as crystalline products of general formula: $Ln(C_8H_5O_3Cl_2)_3{\cdot}nH_2O$, where Ln(III) = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, $n = 2$, 4 or 5—depends on the Ln(III) ions. The data of the elemental analysis are presented in Table 1.

Infrared spectra

Comparing the IR spectra of lanthanide complexes with that of 2,4-dichlorophenoxyacetic acid, the characteristic band of stretching vibrations of free carboxylic acid at 1730 cm^{-1} disappears and splits into two peaks of asymmetric and symmetric vibrations of COO^- group at 1628–1556 and 1394–1331 cm^{-1}, respectively (Table 2). The magnitudes of separations, $\Delta\nu_{OCO}$, between the frequencies due to ν_{asOCO} and ν_{sOCO} in the spectra of analysed compounds indicate that carboxylate groups act as bidentate chelating ligands [34–37]. The analysis of band frequency values of OCO group allowed to determine the separation of $\nu_{asOCO} - \nu_{sOCO} = \Delta\nu$, value of which is used as a criterion of the carboxylate bonding with metal ions. Taking into account the spectroscopic criteria, especially the Nakamoto criterion [11, 35, 36], the carboxylate ions in the analysed complexes seem to be bidentate chelating. The carboxylate group is bidentate chelating when the $\Delta\nu_{OCO}$ value of studied complex $\ll$ than the $\Delta\nu_{OCO}$ value of the sodium salt [11, 35, 36]. A bidentate bridging structure exists when the $\Delta\nu_{OCO}$ value of the analysed complex $\approx\Delta\nu_{OCO}$ of that of the sodium salt [11, 36]. For monodentate geometry of carboxylate group the $\Delta\nu_{OCO}$ value of the studied complex is considerably larger than the $\Delta\nu_{OCO}$ of the sodium salt. The values of $\Delta\nu_{OCO}$ for analysed 2,4-dichlorophenoxyacetates of Ln(III) are smaller ($\Delta\nu_{OCO} = 246$–210 cm^{-1}) than that for 2,4-dichlorophenoxyacetate of Na(I) ($\Delta\nu_{OCO} = 284$ cm^{-1}). The different

Table 2 Wavenumbers cm^{-1} of OCO, M–O, C–Cl and O–H in the FTIR spectra of 2,4-dichlorophenoxyacetates of lanthanides(III)

Complex $L = C_8H_5O_3Cl_2^-$	ν_{OH}	$\nu_{as(OCO)}$	$\nu_{s(OCO)}$	$\Delta\nu_{(OCO)}$	ν_{C-Cl}	ν_{M-O}
$LaL_3 \cdot 4H_2O$	3428	1568	1332	236	724	472
$PrL_3 \cdot 2H_2O$	3412	1580	1348	232	764	472
$NdL_3 \cdot 2H_2O$	3410	1628	1392	236	796	472
$SmL_3 \cdot 2H_2O$	3400	1584	1340	244	796	468
$EuL_3 \cdot 2H_2O$	3319	1556	1340	216	768	467
$GdL_3 \cdot 2H_2O$	3320	1624	1382	242	752	467
$TbL_3 \cdot 5H_2O$	3384	1584	1348	236	769	468
$DyL_3 \cdot 2H_2O$	3577	1556	1331	225	769	440
$HoL_3 \cdot 2H_2O$	3380	1584	1342	242	796	458
$ErL_3 \cdot 2H_2O$	3336	1584	1338	246	796	468
$TmL_3 \cdot 2H_2O$	3566	1585	1341	244	769	440
$YbL_3 \cdot 5H_2O$	3404	1584	1360	224	722	442
$LuL_3 \cdot 2H_2O$	3040	1604	1394	210	720	440

values of $\Delta\nu_{OCO}$ for complexes may suggest that carboxylate groups have various symmetry connected with the delocalization of 4*f* electrons in the lanthanide series.

The bands with the maximum at 3577–3040 cm^{-1}, characteristic for ν(OH) vibrations, confirmed the presence of crystallization of water molecules in the complexes. The bands of C-H were observed at 2930–2919 cm^{-1} and those of the ring vibrations at 1624, 1476 and 1104 cm^{-1}. The C–Cl vibration bands occurred at 796–720 cm^{-1}, while those of the asymmetric and symmetric ν(C–O–C) vibrations are at 1288–1260 cm^{-1} and 1048–1044 cm^{-1}, respectively. The bands at 472–440 cm^{-1} indicate the ionic metal–oxygen stretching bond vibrations [38, 39]. The separations of the ν_{asOCO} and ν_{sOCO} modes ($\Delta\nu_{OCO} = \nu_{asOCO} - \nu_{sOCO}$) may also serve as the criterion for the evaluation of the metal–oxygen nature bond. For analysed complexes, these values are smaller ($\Delta\nu_{OCO} = 246$–210 cm^{-1}) than that of the sodium salt ($\Delta\nu_{OCO} = 1620$–$1336 = 284$ cm^{-1}). Therefore, it indicates the smaller degree of ionic M–O bond in 2,4-dichlorophenoxyacetates compared to that of the sodium salt.

X-ray powder diffraction

From the X-ray powder diffraction of 2,4-dichlorophenoxyacetates of lanthanides(III), it follows that they are crystalline compounds (as an example Fig. 1). The structures of analysed complexes were not determined since suitable single crystals were not obtained. The trials to obtain them by the recrystallization process from various solvents (H_2O, alcohols, DMSO and DMF) and additionally with various metals/ligand ratios were undertaken, but they did not give the expecting results.

In order to estimate the unit cell parameters, the X-ray powder diffraction of analysed compounds were used for their determination applying the Dicvol 06 programme (Table 3). From the obtained results, it follows that all analysed complexes form low symmetry compounds. 2,4-Dichlorophenoxyacetates of La(III) and Nd(III) crystallized in triclinic system, while those of the rest of them in monoclinic one.

The values of *a*, *b* and *c* for La(III) complex unit cell are equal to 11.5951, 12.1635 and 15.0942 Å, respectively, and for Nd(III) compound they are 5.6537, 12.5261 and 15.0375 Å.

The values of their angles are following: $\alpha = 67.2300°$, $\beta = 71.984°$, $\gamma = 76.432°$ for 2,4-dichlorophenoxyacetate of La(III) and $\alpha = 83.082°$, $\beta = 87.349°$ and $\gamma = 86.900°$ for that of Nd(III).

In the case of monoclinic system of complexes, the values of unit cells change from 7.9670 Å [Gd(III) complex] to 21.9371 Å [for Yb(III) complex] for *a*, from 4.8430 Å [Lu(III) complex] to 20.0728 Å [Sm(III) compound] for *b* and from 10.1840 Å [Gd(III)] to 25.2047 Å [Pr(III)] for *c* parameters.

In the series of monoclinic complexes, the values of β angles change from 94.8850° for Sm(III) compound to 112.3490° for Lu(III) one (Table 3).

Generally, the values of the volumes of elementary unit cells are greater for 2,4-dichlorophenoxyacetates of heavy lanthanides than those for light ones, which is probably connected with the greater values of ionic potentials for heavy lanthanides compared to those of light ones (the dependence of *V* vs. *Z* may show the “gadolinium break”).

The greater ionic potentials, the greater polarization and greater covalent bonds may be expected between central ion and ligands. The values of unit cell volumes for complexes of Tb(III) and Yb(III) are similar being equal to 2865.29 and 2825.46 $Å^3$, respectively, which is probably connected with the contents of 5 water molecules in complex molecule.

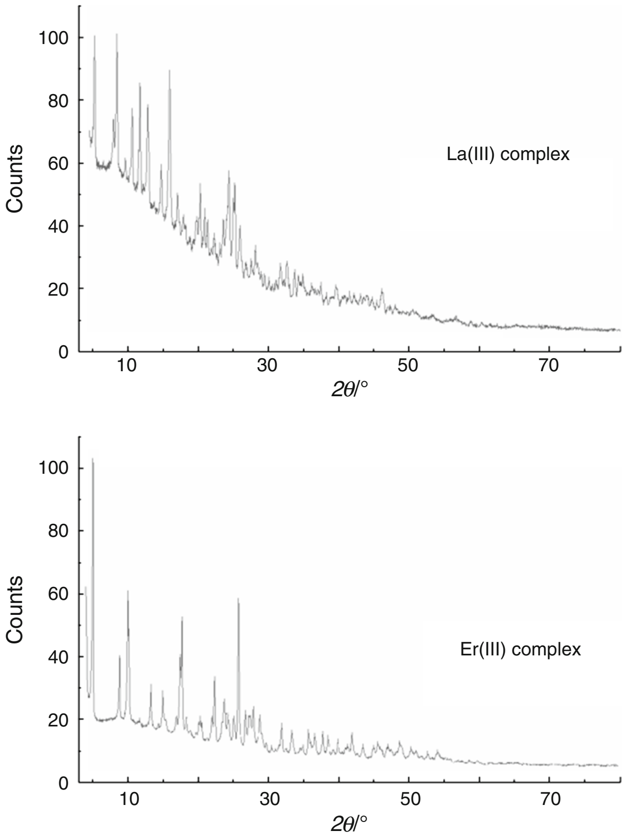

Fig. 1 X-ray diffraction patterns of 2,4-dichlorophenoxyacetates of La(III) and Er(III)

Thermal analysis

The thermal stability of the lanthanide(III) 2,4-dichlorophenoxyacetates was studied in air in the range of 293–1173 K (as an example Fig. 2; Table 4). The TG, DTG and DSC curves were recorded using the DSC/TG technique. All the complexes are hydrated. They lose water molecules between 305 and 451 K. The dehydration process of the compounds is connected with endothermic effects (DSC curves). The complexes dehydrate in one step losing two, four or five molecules of water and form anhydrous compounds. The mass losses calculated from TG curves being equal to 3.53 and 9.90 % correspond to the loss of 2, 4 and 5 molecules of water (theoretical values change from 4.04 to 9.91 %).

From the initial decomposition temperature data, it appears that Sm(III) and Eu(III) complexes with their highest values are the most thermally stable compounds whereas those of Pr(III), Nd(III) and Yb(III) are the least ones in the group of analysed 2,4-dichlorophenoxyacetates of lanthanides(III). The energetic effects accompanying the hydration processes were also determined. The enthalpy values, ΔH, change from 44.00 to 91.34 and from 16.79 to 32.00 kJ mol^{-1} per one molecule of water. Its different

Table 3 Data of unit cell parameters (*α*, *β*, *γ*, *a*, *b*, *c* and *V*) obtained for 2,4-dichlorophenoxyacetates of Ln(III) with the use of dicvol 06 programme

	La(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)	Gd(III)	Tb(III)	Dy(III)	Ho(III)	Er(III)	Tm(III)	Yb(III)	Lu(III)
a/Å	11.5951	15.2352	5.6537	9.8225	10.1214	7.9670	20.1090	21.2093	10.1368	21.7883	12.8705	21.9371	21.8539
b/Å	12.1635	6.4007	12.5261	20.0728	17.7395	17.784	6.6038	5.5863	17.8792	7.5933	10.1915	5.9847	4.8430
c/Å	15.0942	25.2047	15.0375	12.0636	10.6870	10.1840	23.1622	22.8669	13.6090	19.1660	20.5582	22.6975	23.3370
α/°	67.230	90	83.082	90	90	90	90	90	90	90	90	90	90
β/°	71.984	96.658	87.349	94.885	95.565	97.387	111.397	108.361	96.981	111.436	103.832	108.525	112.349
γ/°	76.432	90	86.900	90	90	90	90	90	90	90	90	90	90
V/Å^3	1850.59	2441.29	1054.78	2369.87	1909.80	1430.95	2865.29	2571.38	2448.17	2951.60	2618.41	2825.46	2284.47

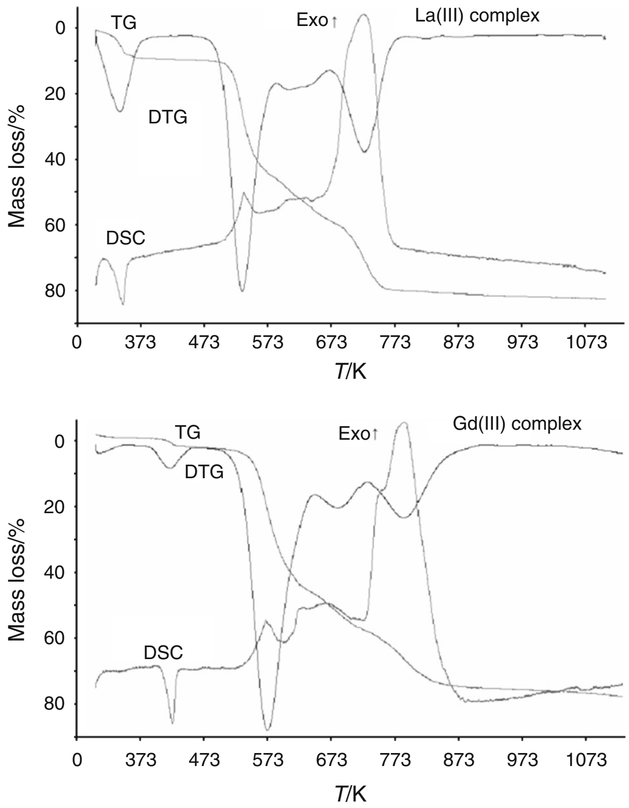

Fig. 2 TG, DTG and DSC curves of La(III) and Gd(III) complexes in air atmosphere

values may suggest that the water molecules are coordinated with different strengths depending on their various positions in the complex coordination spheres. 2,4-Dichlorophenoxyacetate of Lu(III) shows the highest value while that of Yb(III) the least one. The anhydrous complexes of lanthanides(III) in their second step of decomposition form oxychlorides being intermediate products releasing gradually one by one the parts of ligands in the range of 438–1023 K with the strong exothermic effects (DSC curves).

The mass losses calculated from TG curves indicate the oxychloride formations. In the third stage of decomposition, the intermediate products, LnOCl, are decomposed to the oxides of appropriate metals: Ln_2O_3 for La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu and Pr_6O_{11} and Tb_4O_7. The found masses change from 13.40 to 19.50 % (theoretical values from 13.83 to 21.22 %). The final temperature values of their formation are in the range of 923–1173 K.

The final mass losses determined from TG curves change from 80.50 to 86.60 % (theoretical values are 78.78 and 86.17 %). The residue obtained as the oxide metals was verified by comparing their FTIR spectra and diffractograms with those of the pure oxides.

The results indicate that the thermal decompositions of 2,4-dichlorophenoxyacetates of lanthanides(III) in air proceed in the following ways (Schemas 2 and 3):

$$\mathrm{LnL_3 \cdot \mathit{n}H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3, (Ln(III) = La, Nd - Gd,\ Dy{-}Lu)} \tag{2}$$

$$\mathrm{Pr(Tb)L_3 \cdot \mathit{n}H_2O \rightarrow Pr(Tb)L_3 \rightarrow Pr(Tb)OCl \rightarrow Pr_6O_{11}(Tb_4O_7)} \tag{3}$$

$n = 2, 4, 5$ depends on the kind of central ions.

Table 4 Temperature ranges of thermal mass losses of lanthanide(III) 2,4-dichlorophenoxyacetates in air at 293–1173 K

Complex	ΔT_1/K	Mass loss/%		n	ΔT_2/K	Mass loss/%		Residue mass/%		T_K/K	ΔH/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}
$L = C_8H_5O_3Cl_2^-$		Cald.	Found			Cald.	Found	Cald.	Found			
$LaL_3 \cdot 4H_2O$	316–362	8.23	8.58	4	523–801	81.50	81.55	18.50	18.45	973	85.53	21.38
$PrL_3 \cdot 2H_2O$	305–408	4.30	5.06	2	523–873	83.64	83.90	16.36	16.10	923	57.31	28.65
$NdL_3 \cdot 2H_2O$	305¯383	4.28	4.30	2	523–618	80.10	80.90	20.02	19.01	923	57.11	28.56
$SmL_3 \cdot 2H_2O$	401–428	4.23	4.13	2	491–827	83.50	82.91	16.50	17.09	923	48.57	24.28
$EuL_3 \cdot 2H_2O$	402–444	4.24	4.51	2	462–840	86.17	86.60	13.83	13.40	923	50.32	25.16
$GdL_3 \cdot 2H_2O$	323–428	4.22	4.18	2	438–718	78.78	80.50	21.22	19.50	1173	60.57	30.28
$TbL_3 \cdot 5H_2O$	324–373	9.91	9.84	5	523–873	83.60	83.29	16.40	16.70	973	91.34	18.26
$DyL_3 \cdot 2H_2O$	398–451	4.19	3.82	2	523–923	83.70	84.20	16.30	15.80	1023	63.26	31.63
$HoL_3 \cdot 2H_2O$	390–451	4.18	4.53	2	473–873	85.80	86.60	14.20	13.40	923	53.26	26.63
$ErL_3 \cdot 2H_2O$	390–430	4.17	3.53	2	573–1023	83.41	82.50	16.59	17.50	1023	44.00	22.00
$TmL_3 \cdot 2H_2O$	390–420	4.16	3.67	2	554–873	83.27	83.02	16.73	16.98	973	48.14	24.07
$YbL_3 \cdot 5H_2O$	305–351	9.75	9.90	5	473–790	84.00	84.70	16.00	15.30	923	83.99	16.79
$LuL_3 \cdot 2H_2O$	310–360	4.04	4.12	2	480–800	83.65	83.60	16.35	16.40	933	64.00	32.00

ΔT_1, temperature range of dehydration process; n, number of water molecules lost in one step; ΔT_2, temperature range of anhydrous complex decomposition; T_K, final temperature of decomposition process; $\Delta H°$, enthalpy value for one molecule of water

From the obtained results it follows that the water molecules may be lattice or coordinated water despite of their loss at a low temperature [40–43]. All dihydrated complexes contain probably two coordinated water molecules in the inner sphere yielding coordination number 8. The coordination number of lanthanide ions may change from 6 to 12 or to higher value depending on lanthanide(III) ions and the ligand sizes [35].

The initial dehydration temperature values for all complexes indicate that the water molecules may be outer sphere water because they are released below 423 K (305–402 K) [41, 43], but in fact they may be also coordinated water being bounded with different strength in the inner complex coordination yielding the small value of initial dehydration temperature [40, 41, 43].

In the case of complexes of Dy(III), Er(III) and Tm(III), the peaks observed at 483, 480 and 473 K on the DSC curves, respectively, indicate the melting or polymorphic changes.

The data obtained from the determination of the complete structure of these complexes can give fair information on the position of water molecules in the compounds, but their monocrystals have not been yet determined. However, attempts to prepare them have still been done.

The FTIR spectra recorded for the gaseous products released during complex decompositions revealed them to be molecules of H_2O, CO_2, CO, CH_4, hydrocarbons and hydrogen chloride. For all the analysed complex decompositions, the bands at 4000–3500 and 1700–1500 cm^{-1} (348–481 K) confirmed the presence of H_2O molecules in the products. At higher temperatures, the bands at 2250–2500 and 600–760 cm^{-1} result from CO_2 vibrations, while the bands observed at 2000–2220 cm^{-1} are characteristic for CO. The absorbance peak of methane (CH_4) appears around 3000 cm^{-1} and HCl in the range of 3060–2650 cm^{-1} [44, 45].

Magnetic properties

For estimating the character of metal–ligand bonding in the complexes and to find the reasons why their colours are typical for Ln(III) ions, the magnetic susceptibilities of the 2,4-dichlorophenoxyacetates were determined over the range of 76–303 K. The magnetic susceptibilities of the complexes were also investigated between 1.8 and 303 K in order to know whether the nature of atomic magnetic interactions changed at low temperatures.

The complexes obey the Curie–Weiss law (Fig. 3) [46, 47]. For all of them, the Weiss constant values, θ_m, had a negative sign, which may result from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [46–52]. The experimentally determined effective magnetic moment, μ_{eff}, values for the 2,4-dichlorophenoxyacetates at 76 and 303 K are given in Table 5. In the lanthanide(III) 2,4-dichlorophenoxyacetates, the paramagnetic central ions remain practically unaffected by the diamagnetic ligands around them. The 4*f* electrons are well (although not totally) shielded from external fields by the overlying $5s^2$ and $5p^6$ shells. Therefore, the states arising from the various $4f^n$ configurations tend to remain nearly invariant for a given ion. The spin-orbit coupling constants are quite large (order of 1000 cm^{-1}). The states of the $4f^n$ configurations are approximated by a Russell–Saunders coupling [48]. The lanthanide ions have ground state with a single well-defined value of the total angular momentum, *J*, with the next lowest *J* state at energies many times kT (at ordinary temperatures equal to $\sim$200 cm^{-1}) above, hence virtually unpopulated. Therefore, the susceptibilities and magnetic moments should be given straightforwardly by formulas considering only this one well-defined *J* state, and indeed such calculations give results that are with only two exceptions, in good agreement with experimental values. From Sm(III) and Eu(III) ions, it appears that the first excited *J* state is sufficiently close to the ground state for this state (and in the case of Eu(III) even the second and third excited states) to be appreciably populated at ordinary temperatures. Since these excited states have higher *J* values than the ground state, the actual magnetic moments are higher than those calculated by considering the ground

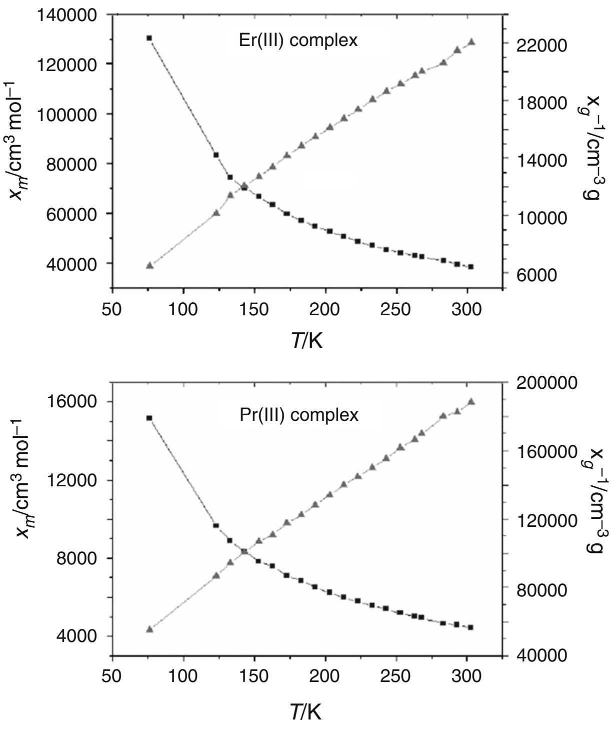

Fig. 3 Relationship of χ_m and χ_g^{-1} versus *T* for 2,4-dichlorophenoxyacetates of Er(III) and Pr(III)

Table 5 Effective magnetic moment μ_{eff}/μ_B, values for the Ln(III) 2,4-dichlorophenoxyacetates at 76 and 303 K

Trivalent ion	$T = 76$ K	$T = 303$ K	Trivalent ion	$T = 76$ K	$T = 303$ K
Pr	3.04	3.29	Tb	9.67	9.97
Nd	2.84	3.09	Dy	10.39	10.87
Sm	0.89	1.29	Ho	8.96	9.88
Eu	2.57	3.59	Er	8.90	9.66
Gd	8.26	8.12	Tm	6.95	7.54
			Yb	2.00	3.54

Table 6 Magnetic moment values μ_{eff} of lanthanide(III) ions calculated by Hund and Van Vleck [47, 49, 53] and those obtained experimentally for Ln(III) 2,4-dichlorophenoxyacetates at room temperature

Trivalention	Configuration	μ_{eff}/μ_B		
		Calculated by Hund	Calculated by Van Vleck	Experimental
Pr	f^2	3.58	3.62	3.29
Nd	f^3	3.62	3.68	3.09
Sm	f^5	0.84	1.55–1.65	1.29
Eu	f^6	0.00	3.40–3.51	3.59
Gd	f^7	7.94	7.94	8.12
Tb	f^8	9.70	9.70	9.97
Dy	f^9	10.60	10.60	10.87
Ho	f^{10}	10.60	10.60	9.88
Er	f^{11}	9.60	9.60	9.66
Tm	f^{12}	7.60	7.60	7.54
Yb	f^{13}	4.50	4.50	3.54

states only. Calculations taking into account the population of excited state afford results in good agreement with experiment [48].

Because the 4*f* orbitals are so well shielded from the surroundings of the ions, the various states arising from the $4f^n$ configurations are split by external fields only to the extent ~ 100 cm^{-1}. Thus, when electronic transition, called *f*–*f* transitions, occurs from one *J* state of an f^n configuration to another *J* state of this configuration, the absorption bands are extremely sharp. They are similar to those for free atoms and are quite unlike the broadbands for *d*–*d* transitions. As the colours are due to the *f*–*f* transition, they are virtually independent of the environment of the ions [48].

The magnetic properties may be taken as those of the ground state alone, and the lanthanide(III) ions in the complexes act in the same manners as free ions. The values of μ_{eff} determined for all 2,4-dichlorophenoxyacetates (except Eu) (Table 5) were similar to those calculated for Ln(III) ions by Hund and Van Vleck (Table 6) [11, 49].

The values of magnetic moments determined for the complexes indicate that the energies of 4*f* electrons in the central ions are not changed compared to those in the free lanthanide ions. Therefore, the colours of these complexes determined by rare earth (III) ions remain the same as those in the free lanthanides [11, 52]. The metal–ligand bonding in these analysed lanthanide(III) compounds is mainly electrostatic in nature [11, 52].

The magnetic properties of Ho(III) were also studied over the temperature range of 1.8–303 K. Plots of magnetic susceptibility χ_m^{-1} and of the product $\chi_m T$ versus T are shown in Fig. 4. The thermal dependence of χ_m^{-1} obeys the Curie–Weiss law over the whole temperature range. From the shape of the dependence of the $\chi_m T$ versus T curve, it follows that it decreases on cooling in the range of 303–1.8 K. Between 303 and 48 K, the decrease is very slow showing the saturation paramagnetic state, while it is drastic between 48 and 1.8 K. The value of $\chi_m T$ for Ho(III) 2,4-dichlorophenoxyacetate at room temperature was 11.30 cm^3 mol^{-1} K, which is similar to that calculated theoretically for the free Ho(III) ion, 11.60 cm^3 mol^{-1} K [47, 53, 54]. At 1.8 K, the $\chi_m T$ value was 6.16 cm^3 mol^{-1} K. The decrease in the $\chi_m T$ versus T curve in the range of 48–1.8 K indicates a negative θ value, which may confirm the antiferromagnetic intermolecular interactions. Therefore, the magnetic moment value of the Ho(III)

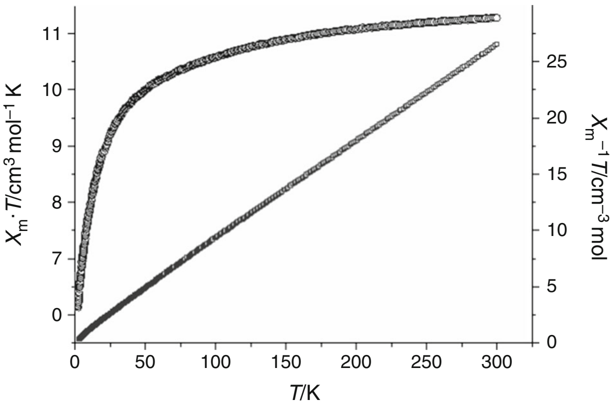

Fig. 4 Relationship of $\chi_m T$ and χ_m^{-1} versus T for 2,4-dichlorophenoxyacetate of Ho(III)

complex was equal to 7.00 (1.8 K) and 8.96 μ_B (283 K). Next, this value increases to 9.88 μ_B (303 K) which is connected with the change in the unpaired electron order. This value is similar to that of the free Ho(III) ion value (10.60 μ_B) [47, 53].

Conclusions

From the obtained results, it follows that the lanthanide(III) 2,4-dichlorophenoxyacetates were prepared as di-, four and pentahydrates with colours typical for respective Ln(III) ions, having their origin in the lowest energy *f–f* electronic transitions of the central ions. The Lu–O bonds are electrostatic in nature. The compounds are crystalline complexes. They crystallized in monoclinic or triclinic systems. On heating in air to 1173 K they decompose in three steps. At first, they dehydrate to form anhydrous complexes, which further decompose to the oxides of the corresponding metal(III) with the intermediate formation of LnOCl. The values of μ_{eff} experimentally determined for all analysed 2,4-dichlorophenoxyacetates of Ln(III) are close to those theoretically calculated by Van Vleck but in the case of Hund also for most of them however with the exception of Sm(III) and Eu(III) complexes. The enthalpy values of dehydration processes were in the range of 44.00–91.34 and 16.79–32.00 kJ mol^{-1} per one molecule of water.

As a continuation of our studies on lanthanide complexes with chlorophenoxyacetic acids and taking into account the presence and positions of one or two Cl substituents in benzene ring, the properties of 2-(4-chlorophenoxy)acetates and 2,4-dichlorophenoxyacetates of lanthanide elements were compared for investigating the influence of the substituent positions in benzene ring on their physico-chemical characterization.

From the IR spectra analysis [11], it follows that the bands of $\nu_{asymOCO}$ and ν_{symOCO} appear at a lower wavenumber values for 4-chlorophenoxyacetates of Ln(III) compared to those in the IR spectra of Ln(III) 2,4-dichlorophenoxyacetates. Also the C–Cl vibration bands have higher values for 2,4-dichlorophenoxyacetates than those in 4-chlorophenoxyacetate IR spectra. This difference is connected with the various inductive and mesomeric effects of the substituents on the electron density of the system. The influence of the substituents on the reactions of aromatic compounds is described by Hammett's constant δ whose value depends on the substituent character and its position on the aromatic ring. The greater its value, the stronger electrons are attracted by the given substituent. The δ values for Cl substituent are $\delta_m = +0.373$ and $\delta_p = +0.227$. In 2-(4-chlorophenoxy)acetates, the presence of the Cl in the *para* position stabilizes the aromatic ring since the inductive effect of the Cl substituent decreases the electron density in benzene ring. In the case of 2,4-dichlorophenoxyacetates of Ln(III), the presence of Cl in *ortho* position does not stabilize the system because of the steric effect [55–59].

The 2-(4-chlorophenoxy)acetates of Ln(III) contain less water molecules compared to those of 2,4-dichlorophenoxyacetates of those elements.

The thermal stabilities of Ln(III) 2-(4-chlorophenoxy)acetates are higher than those for 2,4-dichlorophenoxyacetates. Also the values of ΔH per one molecule of water are greater for 4-chlorophenoxyacetates (60.20–21.43 kJ mol^{-1}) in comparison with those for 2,4-dichlorophenoxyacetates (32.00–16.79 kJ mol^{-1}).

The magnetic moment values measured in the range of 77–303 K for 2-(4-chlorophenoxy)acetates and 2,4-dichlorophenoxyacetates of Ln(III) are higher for 2-(4-chlorophenoxy)acetates than those for 2,4-dichlorophenoxyacetates, which depends on the kind of ligands forming the complex molecules.

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