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COMPLEXES OF 4-CHLOROPHENOXYACETATES OF ND(III), GD(III) AND HO(III)

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Abstract: The complexes of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) have been synthesized as polycrystalline hydrated solids, and characterized by elemental analysis, spectroscopy, magnetic studies and also by X-ray diffraction and thermogravimetric measurements. The analysed complexes have the following colours: violet for Nd(III), white for Gd(III) and cream for Ho(III) compounds. The carboxylate groups bind as bidentate chelating (Ho) or bridging ligands (Nd, Gd). On heating to 1173K in air the complexes decompose in several steps. At first, they dehydrate in one step to form anhydrous salts, that next decompose to the oxides of respective metals. The gaseous products of their thermal decomposition in nitrogen were also determined and the magnetic susceptibilities were measured over the temperature range of 76-303K and the magnetic moments were calculated. The results show that 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) are high-spin complexes with weak ligand fields. The solubility value in water at 293K for analysed 4-chlorophenoxyacetates is in the order of 10^{-4} mol/dm³.

Keywords: 4-chlorophenoxyacetates, thermal stability, magnetic properties of Nd(III), Ho(III) and Gd(III).

Introduction

The carboxylates play an important role in inorganic and bioinorganic chemistry. Many metal cations are a component of several vitamins and drugs [1,2]. The carboxylates of d- and f- ion elements may be used as electric materials in the modern branches of techniques and technology. They may have also applications as precursors in superconducting ceramic and magnetic field productions and may be used as catalysts, pigments, solvents, food preservatives and plastics productions.

Metal carboxylates are applied for the productions of high degree purity of metal oxides and polycarboxylic acids are used for supermolecular compound synthesis, which in many cases, form with metal ions the molecular polymers containing

in their structures, pores and channels owing to them they appear catalytic and adsorption properties. Therefore they may be used for the adsorption of inorganic gases such as: argon, nitrogen and hydrocarbons or small molecules of another inorganic compounds. Polycarboxylic acids may also form the molecules with two- and three-dimensional structures, yielding special magnetic and luminescence properties which let them be used in optical and electronic industries [3-10].

4-Chlorophenoxyacetic acid is a white solid hardly soluble in water ($K=7,9 \cdot 10^{-4}$) and easily soluble in ether and ethanol [10,11]. It is used as growth hormone for plants [12]. In some papers the details of its molecular structure was presented [13-15]. Literature survey informs that its complexes with Li(I), Cu(II), Co(II), Mn(II) and

Ni(II) ions were synthesized and their properties were studied [10,16,17].

As a continuation of our studies on chlorophenoxyacetates and also on carboxylates [10,18-30] we decided to synthesize 4-chlorophenoxyacetates with Nd(III), Gd(III) and Ho(III) and to study some of those of their properties not to have been investigated so far, such as magnetic properties in the range of 76-303K, thermal stability in air at 293-1173K, solubility in water at 293K and to record their FTIR spectra.

Thermal stability investigations give information about the process of dehydration about the ways of decompositions, and the magnetic susceptibility measurements let study the kinds of the manner of central ion coordination. The determination of the solubility is valuable because it informs about the practical use of acid for separation of transition metal ions by extraction or ion-exchange chromatographic methods.

Table 1. Elemental analysis data of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates and their solubility in water at 293K.

Complex L- = C ₈ H ₆ ClO ₃	H/%		C/%		Cl/%		M/%		Solubility mol·dm ⁻³
	calcd	found	calcd	found	calcd	found	calcd	found	
NdL ₃ ·2H ₂ O	3.00	2.77	39.10	38.96	14.50	14.48	19.60	22.70	5,3 · 10 ⁻⁴
GdL ₃ ·2H ₂ O	2.90	2.79	38.40	38.94	14.20	14.18	20.90	19.50	7,6 · 10 ⁻⁴
HoL ₃ ·3H ₂ O	3.10	2.88	37.10	37.16	14.10	14.08	21.80	21.20	8,5 · 10 ⁻⁴

The contents of M³⁺ were established gravimetrically and by XRF method using spectrometer of X-ray fluorescence with energy dispersion EDXRF-1510 (CANBERRA firm).

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

The FTIR spectra of the intermediate and final products obtained from the complex thermal decompositions were also registered.

Experimental details

The 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) were prepared by the addition of the equivalent quantities of 0,1 mol·dm⁻³ ammonium 4-chlorophenoxyacetate (pH ≈ 5) to a hot solution containing the 0,1 mol·dm⁻³ Nd(III), Gd(III) and Ho(III) nitrates (V) and crystallizing at 293K (1h). The solids formed were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303K to a constant mass.

The contents of carbon and hydrogen in the complexes and in the intermediate and final products obtained from their thermal decompositions were determined by elemental analysis using a CHN 2500 Perkin-Elmer analyzer and the content of chlorine by the Schöniger method (Table 1).

Table 2. Wavenumbers (cm⁻¹) of COO⁻ bands in the analysed complexes of Nd(III), Gd(III), Ho(III), and Na(I), and that of the COOH band in 4-chlorophenoxyacetic acid.

Complex L- = C ₈ H ₆ ClO ₃	ν C=O	ν as OCO	ν sym OCO	Δν OCO	ν C-Cl	ν M-O
NdL ₃ ·2H ₂ O	-	1567	1335	233	507	451
GdL ₃ ·2H ₂ O	-	1572	1337	235	507	452
HoL ₃ ·3H ₂ O	-	1572	1346,1328	226, 244	528, 503	449
H-L	1708	-	-	-	722	-
NaL	-	1615	1344	271	722	449

The X-ray diffraction patterns of hydrated and dehydrated complexes, the intermediate and final products of complex thermal decompositions were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered Cu Kα radiation. The measurements were made within the range 2θ = 4-80° by means of the Debye-Scherrer-Hull method. The relationships between I/I₀ and 2θ for these complexes are presented in Fig.1.

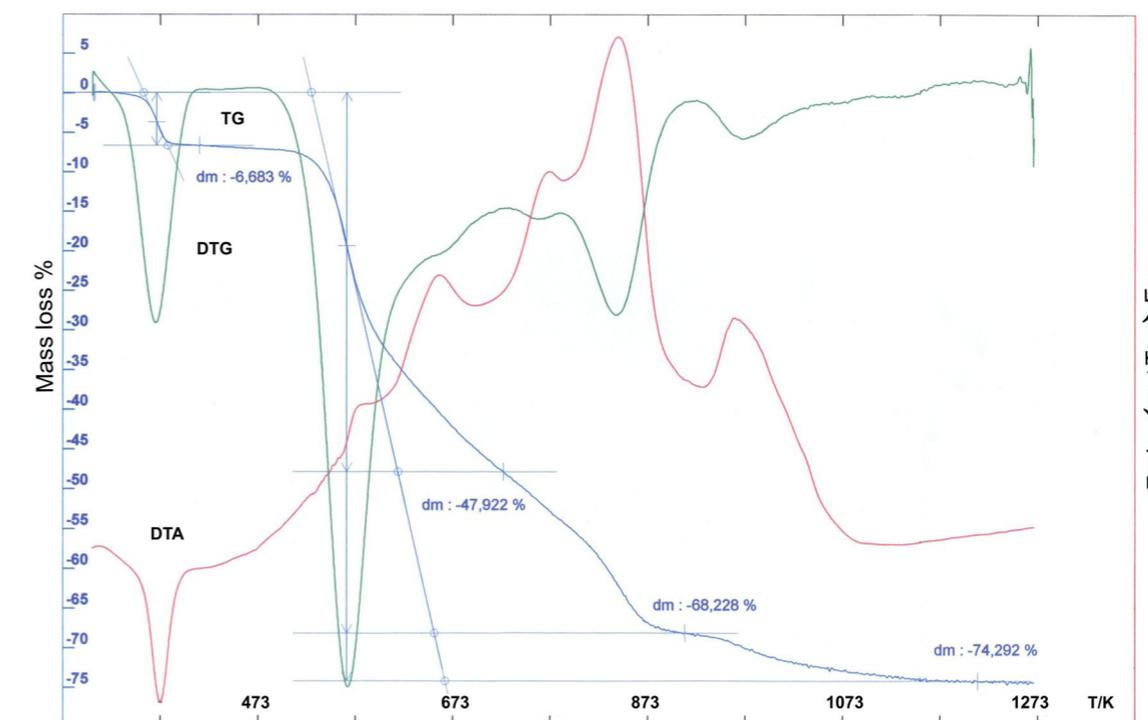


Fig. 1. Dependence of I/I₀ vs 2θ for Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates.

The thermal stability and decomposition of the prepared complexes were determined by Paulik-Paulik-Erday Q-1500D derivatograph with Derill converter, recording TG, DTG, and DTA curves (Fig.2). The measurements were made at a heating rate of 10K min⁻¹ with a full scale. The samples (100mg) were heated in platinum crucibles in static air to 1173K with a sensitivity of TG-100mg. DTG and DTA sensitivities were regulated by a Derill computer program. The products of decomposition

were calculated from TG curves and verified by the diffraction pattern registration and IR spectra. The thermogravimetric analysis of DSC/TG was performed at temperature 323-723K using a differential thermoanalyzer Netzsch STA 409C 3F. The measurements were carried out under nitrogen flow (99,995% purity) and temperature increase rates of 1-12K min⁻¹.

Table 3. Temperature ranges of thermal stability of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates in air.

Complex L = C ₈ H ₆ ClO ₃	$\Delta T_1/K$	Mass loss/%		n H ₂ O	$\Delta T_2/K$	Mass loss/%		Intermediate product	$\Delta H/kJ\cdot mol^{-1}$	$\Delta H_{1H_2O}/kJ\cdot mol^{-1}$	TK/K	Mass of residue/%		Final product of decomposition
		calcd.	found			calcd.	found					calcd.	found	
NdL ₃ ·2H ₂ O	338-416	4,34	4,88	2	553- 873	73,45	72,14	NdOCl	90,8	45,4	1273	22,80	~23,3	Nd ₂ O ₃
GdL ₃ ·2H ₂ O	316-412	4,27	4,81	2	573- 923	72,18	71,42	GdOCl	136,5	68,3	1270	24,30	~24,0	Gd ₂ O ₃
HoL ₃ ·3H ₂ O	312-425	6,96	6,68	3	573- 912	70,20	68,22	HoOCl	156,8	52,3	1223	24,27	24,3	Ho ₂ O ₃

ΔT_1 – temperature range of dehydration process, ΔT_2 – temperature range of anhydrous complex decomposition, n – number of water molecules lost in the one step of dehydration process, ΔH – enthalpy value of dehydration process, T_K – final temperature of decomposition process, ΔH_{1H_2O} – enthalpy value for one molecule of water, T_K – final temperature of decomposition process

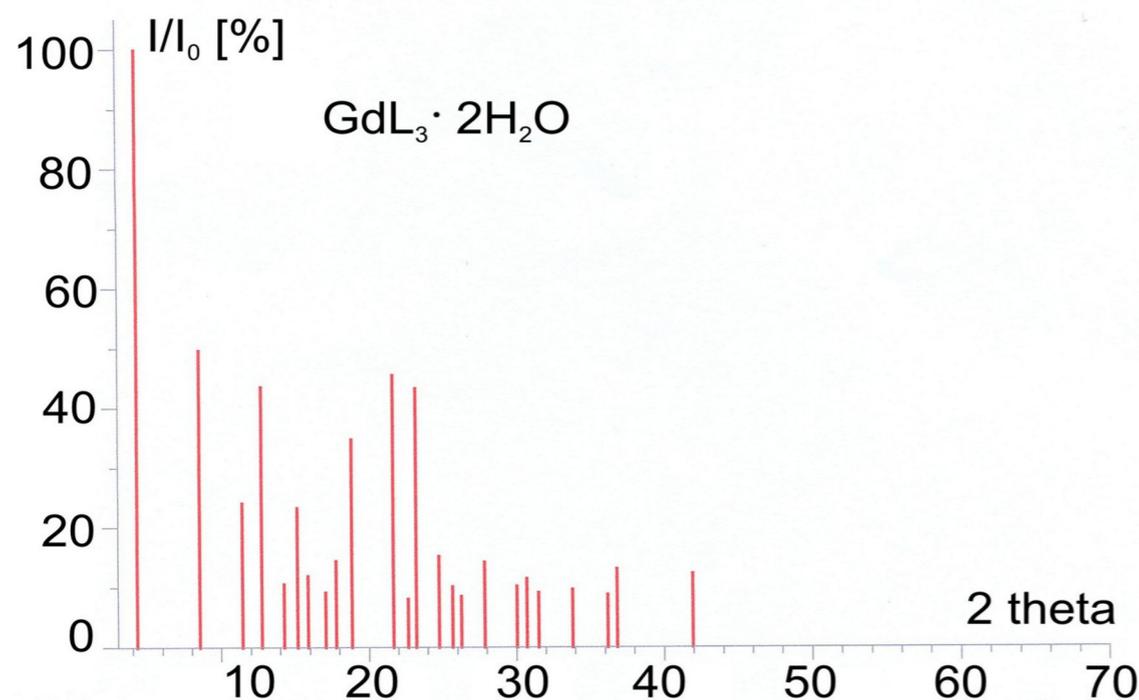


Fig. 2. TG,DTG and DTA curves for Ho(III) 4-chlorophenoxyacetate in air

Magnetic susceptibilities of polycrystalline samples of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) were measured by the Gouy method using a sensitive Cahn RM-2 balance. The samples were placed in a long cylindrical tube which was suspended from an analytical balance. The sample tube was positioned between the poles of the magnet such that one its end was in the region of homogenous field and the other end was in the region of zero field. The force exerted on the sample was a function of the volume occupied by

the sample in the region of the field gradient. This force may be written in scalar form as a function of the isotropic volume susceptibility. Measurements were carried out at a magnetic field strength of 9,9 kOe. The calibrant employed was Hg[Co(SCN)₄] for which the magnetic susceptibility was assumed to be $1,644 \cdot 10^{-5} \text{cm}^3 \text{g}^{-1}$. Correction for diamagnetism of the calibrant atoms was calculated by the use of Pascal's constants [31,32]. Magnetic moments were calculated from Eq.(1):

$$\mu_{\text{eff}} = 2,83 (\chi_M \cdot T)^{1/2} \quad (1)$$

Table 4. Magnetic data for the studied complexes of Nd(III), Gd(III) and Ho(III), L = C₈H₆ClO₃.

NdL ₃ ·2H ₂ O $\theta = -25$			GdL ₃ ·2H ₂ O $\theta = -8,2$			HoL ₃ ·3H ₂ O $\theta = -35$		
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
76	14292	2.95	76	97416	7.70	76	166685	10.07
123	9964	3.13	123	60763	7.74	123	106935	10.26
133	9335	3.15	133	55865	7.71	133	98520	10.24
143	8763	3.17	143	51821	7.70	143	91856	10.26
153	8343	3.20	153	48289	7.69	153	87225	10.34
163	7924	3.22	163	45099	7.67	163	81917	10.34
173	7543	3.23	173	42622	7.68	173	77229	10.34
183	7237	3.26	183	40172	7.67	183	73389	10.37
193	7009	3.29	193	38435	7.71	193	69831	10.39
203	6742	3.31	203	36669	7.72	203	66386	10.39
213	6418	3.31	213	34733	7.70	213	63506	10.41
223	6189	3.32	223	33252	7.71	223	60683	10.41
233	5960	3.33	233	31771	7.70	233	57972	10.40
243	5769	3.35	243	30518	7.71	243	55713	10.41
253	5636	3.38	253	29293	7.70	253	53680	10.43
263	5445	3.39	263	28467	7.74	263	51985	10.46
273	5274	3.40	273	27470	7.75	273	51082	10.57
283	5178	3.43	283	26701	7.78	283	49049	10.54
293	5083	3.45	293	25933	7.80	293	47693	10.58
303	4949	3.47	303	25192	7.82	303	45943	10.56

The solubilities of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) in water were measured at 293K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Nd(III), Gd(III) and Ho(III) were determined using ASA 880 spectrofotometer (Varian). The values of solubilities are presented in Table1.

Results and Discussion

The complexes of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) were obtained as polycrystalline products with a metal ion to ligand ratio of 1:3 and the general formula $M(C_8H_6ClO_3)_3 \cdot nH_2O$, where M(III)= Nd, Gd, Ho and n=2 for Nd and Gd and n=3 for Ho. Their colours are following: violet for Nd(III), cream for Ho(III), and

white for Gd(III) complexes. In these compounds the $f \rightarrow f$ electron transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave lengths that depends on the nature of the metal ion [33,34].

The compounds were characterized by elemental analysis (Table 1), FTIR and FIR spectra (Table 2).

The 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) exhibit similar solid state IR spectra. The band at 1708 cm^{-1} originating from the RCOOH group, presented in the acid spectrum, is replaced in the spectra of complexes by two bands at $1572\text{-}1567\text{ cm}^{-1}$ and $1346\text{-}1328\text{ cm}^{-1}$, which can be ascribed to the asymmetric and symmetric vibrations of COO⁻ group, respectively [35-38].

The bands with the maxima at $3429\text{-}3410\text{ cm}^{-1}$ characteristic for ν_{OH} vibrations [35-40] confirm the presence of crystallization water molecules in the complexes.

The bands of C-H vibrations are observed at $2929\text{-}2918\text{ cm}^{-1}$. The bands of $\nu(\text{C}=\text{C})$ ring vibrations appear at $1624\text{-}1622\text{ cm}^{-1}$, 1494 cm^{-1} , $1177\text{-}1174\text{ cm}^{-1}$, $1111\text{-}1104\text{ cm}^{-1}$ and $1068\text{-}1066\text{ cm}^{-1}$. The valency $\nu(\text{C}-\text{Cl})$ vibration bands occur at $734\text{-}730\text{ cm}^{-1}$ and those of the asymmetric and symmetric $\nu(\text{C}-\text{O}-\text{C})$ at $1082\text{-}1068\text{ cm}^{-1}$ and $1060\text{-}1058\text{ cm}^{-1}$, respectively. The bands at $451\text{-}449\text{ cm}^{-1}$ confirm the ionic metal-oxygen bond [41-50]. These bands change insignificantly their positions which may suggest the different stability of these complexes.

The bands in the range of $118\text{-}106\text{ cm}^{-1}$ are connected with the O-H...O stretching vibrations and they change their shapes according to the rise of atomic number of elements and the degree of hydration in 4-chlorophenoxyacetates. The bands at $138\text{-}122\text{ cm}^{-1}$ confirm the internal C-C torsion vibrations and the bands at $283\text{-}267\text{ cm}^{-1}$ arising from the aromatic ring vibrations also change their shapes.

Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of analysed complexes.

The separations of the $\nu_{\text{as}}(\text{COO}^-)$, and $\nu_{\text{s}}(\text{COO}^-)$ modes in the compounds, $\Delta\nu(\text{COO}^-)$, are smaller than that of the sodium salt ($\Delta\nu_{\text{COO}^-} =$

271 cm^{-1}) indicating a smaller degree of M-O ionic bonds in 4-chlorophenoxyacetates compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of $\nu_{\text{as}}(\text{COO}^-)$, and $\nu_{\text{s}}(\text{COO}^-)$ are lower, and lower or the same, respectively, than those for sodium 4-chlorophenoxyacetate. Accordingly, taking into account the spectroscopic criteria [36-38,49,51] the carboxylate ions appear to be bidentate groups.

In order to estimate the crystalline forms of the 4-chlorophenoxyacetates the X-ray powder diffraction measurements were done. The diffractogram values suggest them to be polycrystalline compounds with various degree of crystallinity [52] (Fig.1)

The thermal stability of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates was studied in air at $293\text{-}1273\text{ K}$ (Table 3. Fig.2).

When heated to 1273 K the Nd(III) complex is dehydrated in one step. In the temperature range of $338 - 416\text{ K}$ it losses two water molecules and forms anhydrous salt. The loss of mass calculated from TG curve is equal to $4,88\%$ (theoretical value is $4,34\%$). The anhydrous salt at $553 - 1273\text{ K}$ is gradually decomposed to Nd_2O_3 that is the final product of complex decomposition. The intermediate compound formed in this range of $553\text{-}873\text{ K}$ is NdOCl. The found mass loss is equal to $72,14\%$ and the calculated value $73,45\%$. The residue mass estimated from TG curve is equal to $23,27\%$ while that theoretically calculated $22,80\%$. The dehydration process is connected with endothermic effect whereas the combustion of the organic ligand is accompanied by exothermic one. The final product of complex decomposition was confirmed by IR spectra and X-ray powder diffractogram.

The dihydrate of Gd(III) 4-chlorophenoxyacetate during heating in air losses the water molecules in one stage in the range of $316 - 412\text{ K}$ and forms anhydrous salt. The final product of complex decomposition was identified by elemental analysis and X-ray powder diffractogram as Gd_2O_3 . The intermediate product of complex decomposition is GdOCl formed at $573\text{-}923\text{ K}$. The found weight loss is equal to $71,42$ and calculated one $72,18\%$. The residue mass estimated from TG curve is $24,0\%$ and theoretically determined $24,30\%$. The dehydration process is connected

with the endoeffect while that of oxidation with exothermic one.

When heated in air to 1173 K the trihydrate of 4-chlorophenoxyacetate of Ho(III) dehydrates in one step at $312 - 425\text{ K}$ and forms anhydrous salt. The mass loss calculated from TG curve being equal to $6,68\%$ corresponds to the loss of three molecules of water (theoretical value is equal to $6,96\%$). The anhydrous 4-chlorophenoxyacetate of Ho(III) at $573 - 1223\text{ K}$ is decomposed to Ho_2O_3 , which is the final product of thermal decomposition. The mass loss calculated from TG curve is equal to $74,29\%$ that corresponds to the Ho_2O_3 formation (calculated value is $75,73\%$). The intermediate product of complex decomposition formed at $573\text{-}912\text{ K}$ is HoOCl. The dehydration process is connected with the endothermic effect seen in DTA curve, while the combustion of the organic ligand is accompanied by exothermic one.

Considering the temperature 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 may be in the outer sphere of complex coordination [41, 53-55].

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-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) in air proceeds in the following way:

$$\text{LnL}_3 \cdot n\text{H}_2\text{O} \rightarrow \text{LnL}_3 \rightarrow \text{LnOCl} \rightarrow \text{Ln}_2\text{O}_3$$

where Ln(III)=Nd, Gd, Ho and $n=2$ for Nd and $n=3$ for Ho.

The values of enthalpy of dehydration process were determined with the use of DSC/TG system under nitrogen atmosphere. They are in the range of $156,80 - 90,81\text{ kJ}\cdot\text{mol}^{-1}$ and $68,25 - 45,4\text{ kJ}\cdot\text{mol}^{-1}$ per one molecule of water. These values indicate that the water molecule is the strongest bounded in the Gd(III) complex while that the weakest in Nd(III) compound. Taking into account

the temperatures of dehydration process it appears that Nd(III) complex is the most thermally stable while Ho(III) has the least thermal stability.

The solubility of analysed compounds was measured (Table 1). It is in the order of $10^{-4}\text{ mol}\cdot\text{dm}^{-3}$. The Ho(III) 4-chlorophenoxyacetate is the most soluble salt, while that of Nd(III) the least soluble one. These compounds are relatively hardly soluble in water and the order value is not sufficient to use 4-chlorophenoxyacetic acid for the separation of some metal ions by ion-exchange chromatography method [10].

The magnetic susceptibility of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) was measured over the range of $76\text{-}303\text{ K}$ (Table 4). The values of the Weiss constant, θ , for analysed complexes were found to have a negative sign which probably arises from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [56-61]. The analysed complexes obey the Curie-Weiss law.

The magnetic moment values experimentally determined at $76\text{-}303\text{ K}$ for Nd(III), Gd(III) and Ho(III) compounds change from $2,95\ \mu_{\text{B}}$ (at 76 K) to $3,47\ \mu_{\text{B}}$ (at 303 K) for Nd(III) complex, from $7,70\ \mu_{\text{B}}$ (at 76 K) to $7,82\ \mu_{\text{B}}$ (at 303 K) for Gd(III), and from $10,07\ \mu_{\text{B}}$ (at 76 K) to $10,56\ \mu_{\text{B}}$ (at 303 K) for Ho(III) 4-chlorophenoxyacetates.

In 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(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 $0,35\text{ \AA}$ [62] to be very small in comparison with the radius of the $5s^25p^6$ closed shell ($\sim 1\text{ \AA}$). 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 4-chlorophenoxyacetates are close to those calculated for Ln^{3+} ions by Hund and Van Vleck (Table 5). Their values at room temperature for analysed complexes are

following: $3,74 \mu_B$ for Nd; $7,23 \mu_B$ for Gd and $10,60 \mu_B$ for Ho [63].

From the values of magnetic moments determined for the complexes it appears that 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 $5s^2 5p^6$ octet. Therefore the metal ligand bonding in lanthanide complexes is mainly electrostatic in nature [64,65].

Conclusions

On the basis of the results obtained it appears that 4-chlorophenoxyacetates of Nd (III), Gd(III), and Ho(III) were synthesized as hydrated complexes. Their colours are typical for the particular Ln(III) ion, i.e. violet for Nd, white for Gd, and cream for Ho, 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 complexes are the same as those for the free lanthanide ions. The Ln-O band is mainly electrostatic in nature. The complexes are crystalline compounds that on heating in air to 1173K decompose in three steps. In the first step they dehydrate to form anhydrous complexes that next decompose to the oxides of appropriate metals with intermediate formation of LnOCl. The values of μ_{eff} calculated for the 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.

The solubilities of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates in water at 293K are of the order of $10^{-4} \text{mol} \cdot \text{dm}^{-3}$.

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