



J. Serb. Chem. Soc. 78 (9) 1335–1349 (2013)
JSCS–4501

Magnetic, thermal and spectroscopic properties of lanthanide(III) 2-(4-chlorophenoxy)acetates, $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot n\text{H}_2\text{O}$

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(Received 3 December 2012, revised 6 April 2013)

Abstract: 2-(4-Chlorophenoxy)acetates of lanthanides(III) were synthesized as polycrystalline hydrated solids with the general formulae: $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{La(III), Pr(III), Sm(III), Eu(III) or Tb(III)}$); $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Dy(III)}$) and $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot 3\text{H}_2\text{O}$ ($\text{Ln} = \text{Er(III), Tm(III), Yb(III) and Lu(III)}$). The complexes were characterized by elemental analysis, FTIR spectroscopy, magnetic and thermogravimetric studies and X-ray diffraction (XRD) analysis. The complexes have colours typical for the lanthanide(III) ions. The carboxylate groups bind as bidentate chelating agents. On heating to 1273 K in air, the complexes decompose in three steps. First they dehydrate in one stage to form anhydrous salts that then decompose to the oxides of the respective metals with the intermediate formation of their oxychlorides. The gaseous products of the thermal decomposition of the compounds under nitrogen were also determined. The magnetic susceptibilities of the complexes were measured over the ranges 76–303 K and 1.8–303 K, and their magnetic moments were calculated. The results showed that the 2-(4-chlorophenoxy)acetates of lanthanides(III) are high-spin complexes with weak ligand fields.

Keywords: 2-(4-chlorophenoxy)acetates; thermal stability; magnetic properties; lanthanides.

INTRODUCTION

Many metal carboxylates have been known from ancient times and since that moment the interest in their chemistry has been growing.¹ This type of compounds show the tendency to form various bondings in their molecules, hence they may be used in biotechnology, bioengineering and medicine.^{1–4} Depending on their magnetic properties, they are used in modern branches of techniques and technology as electric materials. Some are useful reagents for the synthesis of

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doi: 10.2298/JSC121203043F

organic compounds, being applied in metallation and oxymetallation reactions. Transition metal carboxylates are used as catalysts in many industrial processes and as selective oxidizing agents in organic chemistry. They also play an important role in inorganic and bioinorganic chemistry and in some areas of daily life.^{1,3,5} Many of them are components of several vitamins and drugs.¹ They serve for the production of biomedical materials and as the therapeutic agents being used in anti-cancer therapy. Carboxylic acids are applied for the absorption, preservation and separation of many gases. Having luminescence properties, their complexes with 4f electron elements find application in optical and electronic industries.^{1,6} They play significant roles in crystal engineering and serve for the production of paramagnetic organic materials.^{4,7-12} Their compounds form interesting group of single-molecule magnets (SMMs) that exhibit magnetization hysteresis at low temperatures, yielding special properties of macroscopic magnets.^{1,4,7-13}

2-(4-Chlorophenoxy)acetic acid is a white solid sparingly soluble in water. Its melting point temperature is 157 °C. It may be easily decomposed to CO, CO₂ and HCl. Therefore it has toxic properties. It belongs to the herbicide group of substances and may be used as a hormone for plant growth regulation.^{14,15}

In previous papers, studies of the 2-(4-chlorophenoxy)acetic acid anion with Mo, Li, Cu, Mn, Co, Ni, Nd, Gd and Ho were reported in which the complexes were characterized by elemental analysis, FTIR spectroscopy, thermogravimetric studies and X-ray diffraction measurements.^{14,15} In continuation of ongoing investigations on the carboxylates of transition metal ions, the synthesis of complexes of lanthanides(III) with the 2-(4-chlorophenoxy)acetic acid anion and an examination of some of their properties, such as thermal stability in air at 293–1273 K, magnetic properties in the range of 77–303 K and 1.8–300 K, and their FTIR spectra, are reported herein.

EXPERIMENTAL

Materials

All the chemicals and solvents used for the synthesis were commercially available and of reagent grade. They were used without further purification. A solution of the ammonium 2-(4-chlorophenoxy)acetate (0.1 mol L⁻¹, pH ~5) was prepared by the addition of an aqueous NH₃ solution (25 %, Polish Chemical Reagents, Gliwice, Poland) to an aqueous solution of 2-(4-chlorophenoxy)acetic acid (99 %, Aldrich). In order to obtain the chlorides of the rare earth element(III), 0.8 g of the oxides of lanthanides(III) (99.9 % pure, Aldrich) were digested in the equivalent amount of concentrated HCl (35–38 %, Polish Chemical Reagents, Gliwice, Poland). The solutions were constantly heated and evaporated to dryness. The residues of lanthanide(III) chlorides were dissolved in water, forming solutions of lanthanide(III) chlorides, the concentration of which was equal to 0.1 mol L⁻¹ and pH ~5.

Synthesis of the compounds

The 2-(4-chlorophenoxy)acetates of lanthanides(III) were prepared by adding equivalent quantities of 0.1 mol L⁻¹ ammonium 2-(4-chlorophenoxy)acetate (pH ~5) to hot solutions of

the lanthanide(III) chlorides. The solutions were heated for 1 h at 333–343 K under constant stirring to reach the equilibrium state. The solids were then filtered off, washed with hot water to remove ammonium ions, recrystallised and dried at 303 K to constant mass.

Sodium 2-(4-chlorophenoxy)acetate was prepared by the addition of an equivalent amount of a 0.1 mol L⁻¹ ammonium 2-(4-chlorophenoxy)acetate solution to a solution containing 0.1 g NaOH (analytically pure, Polish Chemical Reagents, Gliwice, Poland) and crystallizing.

Methods and apparatus applied

The contents of carbon and hydrogen in the complexes were determined by elemental analysis using a Perkin–Elmer CHN 2400 analyser. The content of chloride was determined by the Schöniger method.¹⁶ The amounts of M(III) metals were established by the X-ray fluorescence (XRF) method with energy dispersion using an ED XRF-1510 spectrophotometer (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 FIR spectra of complexes in Nujol mulls sandwiched between polyethylene plates were recorded over the range of 600–100 cm⁻¹ using the Perkin–Elmer 180 spectrometer.

The X-ray diffraction patterns of compounds 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 of 2θ 4–80° by means of the Bragg–Brentano method.¹⁷

The thermal stability and decomposition of the complexes were studied using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were performed under a under air, flow rate of 1 L h⁻¹, in the temperature range of 297–1273 K at a heating rate of 5 K min⁻¹. The initial mass of the samples of the lanthanides(III) 2-(4-chlorophenoxy)acetates used for the measurements ranged from 7.87 to 4.56 mg. The samples were heated in Al₂O₃ crucibles. The TG–FTIR measurements were also made under a nitrogen atmosphere in order to know the complex behaves under neutral, reduction atmosphere while in air under oxidation atmosphere, using a Q 5000 instrument (TA Instruments) with a Nicolet 6700 spectrophotometer. The experiments were performed in Pt crucibles under a nitrogen flow of 25 mL min⁻¹ at a heating rate of 20 K min⁻¹. The masses of the samples were in the range of 8.98–4.54 mg.

Magnetic susceptibilities of polycrystalline samples of the lanthanide(III) 2-(4-chlorophenoxy)acetates were investigated at 76–303 K and 1.8–303 K. The measurements were realised using the Gouy method on a Quantum Design SQUID-VSM magnetometer. The superconducting magnet is generally operated at a field strength ranging from 0 to 7 T. Measurement of the studied samples were made at a magnetic field 0.1 T. The SQUID magnetometer was calibrated with a palladium rod sample. In the case of the Gouy method, the mass changes were obtained using a Cahn RM-2 electrobalance. The employed calibrant was Hg[Co(SCN)₄], for which the magnetic susceptibility was assumed to be 1.644×10⁻⁵ cm³ g⁻¹. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal constants.^{4,18}

The effective magnetic moment values were calculated from the equation:

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

where μ_{eff} is the effective magnetic moment, χ_M is the magnetic susceptibility per molecule and T is the absolute temperature.

The solubility of 2-(4-chlorophenoxy)acetates of lanthanides(III) in water was determined at 298 K by the ASA method.¹⁹

RESULTS AND DISCUSSION

The lanthanides(III) 2-(4-chlorophenoxy)acetates were obtained as crystalline products of the general formula: $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot n\text{H}_2\text{O}$, where Ln = lanthanide, $n = 2$ for La(III), Pr(III), Sm(III), Eu(III) and Tb(III); $n = 1$ for Dy(III) and $n = 3$ for Er(III), Tm(III), Yb(III) and Lu(III).

Their colours are typical for Ln(III), which is connected with the similar electron density in the complexes. In their molecules, the f-f electronic transitions of the metal ions are those of the lowest energy and absorption occurs at relatively high wavelengths, the value depending on the nature of the metal ion.²⁰

The results of the elemental analyses are given in Table I.

TABLE I. Elemental analysis data (%) for the lanthanide(III) 2-(4-chlorophenoxy)acetates

Complex (L = $\text{C}_8\text{H}_6\text{ClO}_3$)	C		H		Cl		M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	39.40	39.20	3.00	2.95	14.60	14.50	19.00	18.90
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	39.29	39.07	3.02	2.78	14.50	14.30	19.20	19.12
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	38.79	38.85	2.98	2.76	14.31	14.20	20.23	20.60
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	38.68	38.50	2.96	2.81	14.30	14.25	20.42	20.30
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	38.35	38.27	2.93	2.79	14.15	14.53	21.14	22.00
$\text{DyL}_3 \cdot \text{H}_2\text{O}$	39.09	38.90	2.71	2.62	14.42	14.80	22.04	22.80
$\text{ErL}_3 \cdot 3\text{H}_2\text{O}$	37.05	36.99	3.11	2.98	13.67	13.70	21.49	21.60
$\text{TmL}_3 \cdot 3\text{H}_2\text{O}$	36.97	36.70	3.10	2.86	13.64	13.82	21.66	21.10
$\text{YbL}_3 \cdot 3\text{H}_2\text{O}$	36.75	35.90	3.06	3.00	13.59	13.40	22.08	22.00
$\text{LuL}_3 \cdot 3\text{H}_2\text{O}$	36.67	36.50	3.06	2.99	13.56	13.50	22.29	22.20

Infrared spectra

The Ln(III) 2-(4-chlorophenoxy)acetates exhibited similar solid state FTIR spectra (Table II). The band at 1708 cm^{-1} , originating from the RCOOH group, present in the spectrum of the acid is replaced in the spectra of complexes by two bands, one at $1608\text{--}1567 \text{ cm}^{-1}$ and the other $1340\text{--}1322 \text{ cm}^{-1}$, which are ascribed to the asymmetric and symmetric vibrations of the COO^- groups, respectively.^{5,21-33}

The bands with the maxima at $3429\text{--}3410 \text{ cm}^{-1}$, characteristic for $\nu(\text{OH})$ vibrations confirmed the presence of crystallization water molecules in the complexes. The bands of C-H were observed at $2929\text{--}2918 \text{ cm}^{-1}$ and those of the $\nu(\text{C}=\text{C})$ ring vibrations at $1624\text{--}1622$, 1496 , $1177\text{--}1174$, $1111\text{--}1104$ and $1068\text{--}1066 \text{ cm}^{-1}$. The $\nu(\text{C}-\text{Cl})$ vibration bands occurred at $736\text{--}704 \text{ cm}^{-1}$ while those of the asymmetric and symmetric $\nu(\text{C}-\text{O}-\text{C})$ vibrations are at $1082\text{--}1068 \text{ cm}^{-1}$

and 1060–1058 cm^{-1} , respectively. The bands at 508–449 cm^{-1} confirmed the ionic metal–oxygen bond vibrations.^{1,19} They change their positions in the FTIR spectra of complexes, which may suggest that the metal–ligand bonding have different stabilities. The O–H...O stretching vibrations bands⁵ were in the range 118–106 cm^{-1} . Their shapes changed according to the increase in the atomic number of elements and the degree of hydration in the 4-chlorophenoxyacetates. The bands at 138–122 cm^{-1} indicate internal C–C torsion vibrations and those at 283–267 cm^{-1} arise from vibrations of the aromatic ring. The values of the two band frequencies of the asymmetrical and symmetrical vibrations of the carboxylate groups of analysed complexes, and those of C–Cl and M–O stretching vibrations are presented in Table II.

TABLE II. Wavenumbers ($\tilde{\nu} / \text{cm}^{-1}$) of OCO⁻, C–Cl and M–O in the FTIR spectra of lanthanides(III) and Na 2-(4-chlorophenoxy)acetates and that of the COOH band in 2-(4-chlorophenoxy)acetic acid

Compound (L = C ₈ H ₆ ClO ₃)	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\Delta\nu(\text{OCO})$	$\nu(\text{C}-\text{Cl})$	$\nu(\text{M}-\text{O})$
LaL ₃ ·2H ₂ O	–	1596	1332	264	724	504
PrL ₃ ·2H ₂ O	–	1568	1322	246	720	508
SmL ₃ ·2H ₂ O	–	1572	1336	236	720	500
EuL ₃ ·2H ₂ O	–	1572	1336	236	716	504
TbL ₃ ·2H ₂ O	–	1608	1340	268	704	524
DyL ₃ ·H ₂ O	–	1580	1336	244	716	504
ErL ₃ ·3H ₂ O	–	1580	1328	252	736	504
TmL ₃ ·3H ₂ O	–	1580	1328	252	736	504
YbL ₃ ·3H ₂ O	–	1596	1336	260	724	508
LuL ₃ ·2H ₂ O	–	1596	1328	268	736	504
NaL	–	1620	1340	280	722	–
HL	1708	–	–	–	–	–

The separations of the $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ modes in the FTIR spectra of the complexes ($\Delta\nu(\text{OCO})$ from 268 to 236 cm^{-1}) are smaller than that of the sodium salt ($\Delta\nu(\text{OCO}) = 280 \text{ cm}^{-1}$), indicating that the degree of ionic nature of the M–O bond in the 2-(4-chlorophenoxy)acetates is smaller compared to that of the sodium salt. For the complexes, the shifts of the frequencies of bands $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ were lower and lower or the same, respectively, in comparison with those of the sodium salt. Accordingly, taking into account the spectroscopic criteria, especially the Nakamoto criterion,^{1,5,20,31,33,34} the carboxylate ions in the analysed complexes appear to be bidentate chelating groups. The structure of the carboxylate groups is bidentate chelating when the bands of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ in the FTIR spectrum of the analysed complex are shifted to lower and higher wavenumbers compared to those for the sodium salt; or the $\Delta\nu(\text{OCO})$ value of studied complex \ll than the $\Delta\nu(\text{OCO})$ value of the sodium salt.^{1,5,31} A bidentate bridging structure exists when the bands of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ in the FTIR spectrum of studied complex are shifted to higher wavenumbers, com-

pared to those for the sodium salt; or the $\Delta\nu(\text{OCO})$ value of the studied complex $\approx \Delta\nu(\text{OCO})$ value of the sodium salt.⁵ For monodentate geometry of carboxylate group, the bands of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ in the FTIR spectrum of the complex are shifted to higher and lower wavenumbers, respectively, in comparison with those for sodium salt; or the $\Delta\nu(\text{OCO})$ value of the studied complex is considerably larger than the $\Delta\nu(\text{OCO})$ of the sodium salt.

X-Ray powder diffraction

From the X-ray powder diffraction of 2-(4-chlorophenoxy)acetates of lanthanides(III), it follows that they are crystalline compounds (Fig. 1). The structures of 2-(4-chlorophenoxy)acetates were not determined since suitable single crystals were not obtained.

Thermal analysis

The thermal stability of the lanthanide(III) 2-(4-chlorophenoxy)acetates was studied in air in the temperature range of 293–1273 K (Fig. 2, Tables III and IV). The TG, DTG and DSC curves were recorded using the DSC/TG technique. When heated to 1273 K, the complexes decomposed in three steps. They were stable up to 312–365 K. Next, in the range of 312–433 K, all the studied 2-(4-chlorophenoxy)acetates dehydrated in one step, exhibiting endothermic peaks on the DSC curves, losing one, two or three molecules of water to form anhydrous compounds. The mass losses calculated from the TG curves, being equal to 2.27–6.93 %, correspond to the loss of 1, 2 or 3 molecules of water (theoretical values 2.44–6.95 %). From the temperature data, it follows that Pr(III) complex with the highest value of initial decomposition temperature is the most thermally stable compound, whereas the Tm(III) complex is the least stable one in the series of the analysed lanthanide(III) 2-(4-chlorophenoxy)acetates. The energetic effects accompanying the dehydration processes were also determined. The enthalpy values, ΔH , change from 60.20–21.43 kJ mol⁻¹ per one molecule of water. These values may indicate that the water molecules are coordinated to the central ions with different strengths depending on their various positions in the complex coordination spheres.²² The anhydrous lanthanide(III) complexes first form oxychlorides in the second step of their decomposition,^{1,35–37} as intermediate products formed by the gradual loss of the ligands (463–923 K). This process is accompanied by a strong exothermic effect on the DSC curves. The mass losses calculated from TG curves indicated oxychloride formation. In the third stage of decomposition, the intermediate LnOCl products decomposed to the oxides of appropriate metals: Ln₂O₃ (where Ln = La, Sm, Eu, Dy, Er, Tm, Yb or Lu) and Pr₆O₁₁ and Tb₄O₇, which were verified by comparing their FTIR spectra and powder diffractograms with those of the pure oxide. The final temperature values of their formation were in the range of 1073–1273 K. The masses of resi-

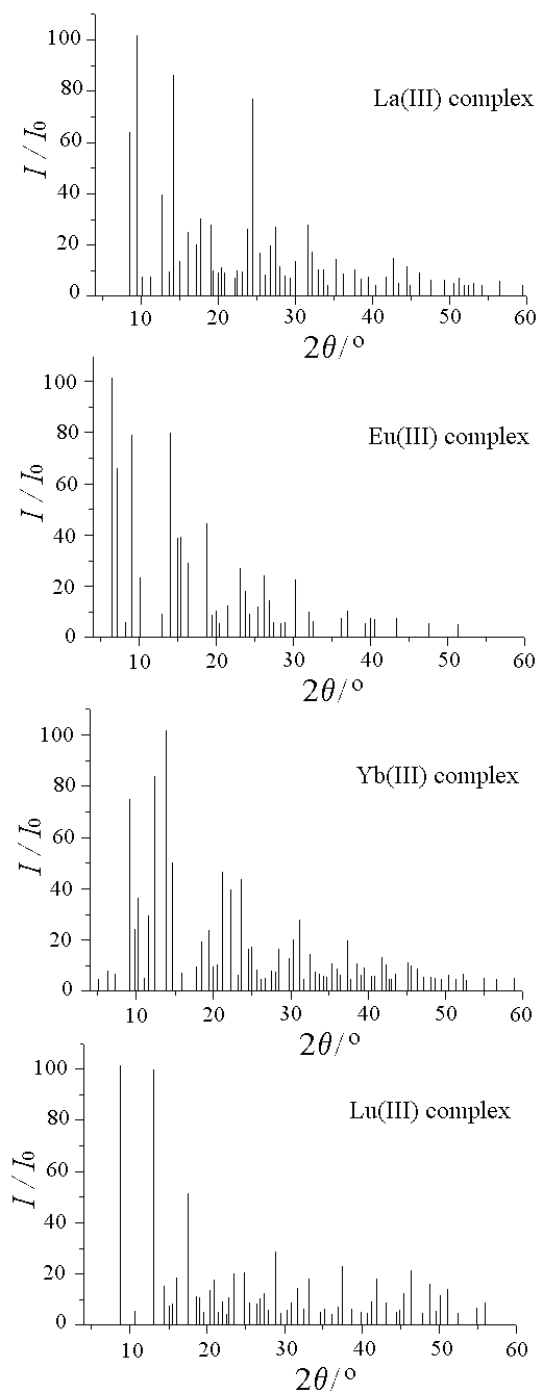


Fig. 1. Dependence of I/I_0 vs. 2θ for La(III), Eu(III), Yb(III) and Lu(III) 2-(4-chlorophenoxy)acetates.

dues determined from TG curve were 22.48–25.00 % (theoretical value 22.22–25.33 %). The results indicate that the thermal decomposition of lanthanide(III) 2-(4-chlorophenoxy)acetates in air proceeds in the following manner:

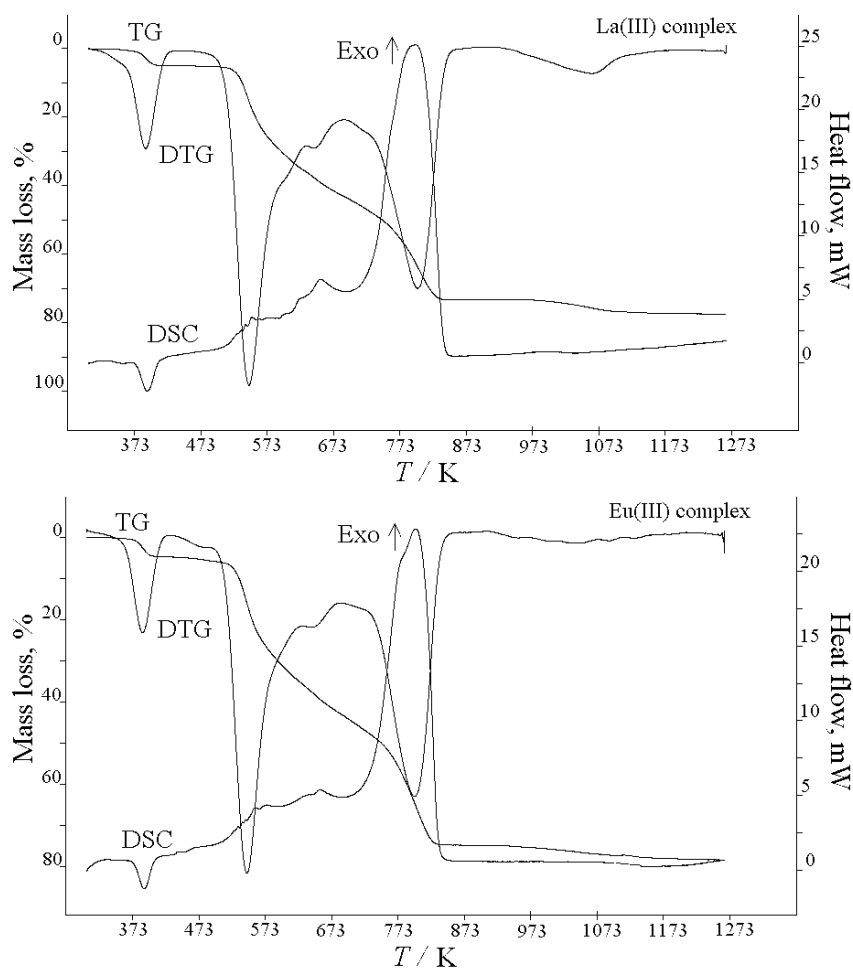
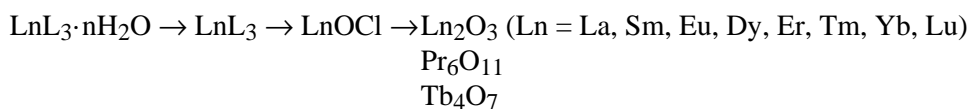


Fig. 2. TG, DTG and DSC curves for La(III) and Eu(III) complexes under an air atmosphere.

From the obtained data, it appears that the coordination number of the central ions is probably 7, 8 or 9. The molecules of water may be coordinated with the central ions despite their loss at a low temperature.^{38–41}

TABLE III. Temperature ranges of the thermal mass losses of lanthanide(III) 2-(4-chlorophenoxy)acetates in air at 293–1273 K

Complex (L = C ₈ H ₆ ClO ₃)	T ^a K	Mass loss, %		n ^b	T ^c K	Mass loss, %		T ^d K	Residue mass, %	
		Calcd.	Found			Calcd.	Found		Calcd.	Found
LaL ₃ ·2H ₂ O	353–413	4.92	4.92	2	523–858	73.96	73.12	1223	22.22	22.55
PrL ₃ ·2H ₂ O	365–390	4.91	4.85	2	580–898	73.90	74.86	1073	23.19	23.62
SmL ₃ ·2H ₂ O	339–389	4.85	4.78	2	563–877	72.84	73.29	1273	23.46	22.56
EuL ₃ ·2H ₂ O	358–423	4.83	4.68	2	463–853	72.68	74.77	1173	23.63	22.56
TbL ₃ ·2H ₂ O	328–393	4.79	4.52	2	503–923	72.00	71.83	1203	24.87	22.48
DyL ₃ ·H ₂ O	363–433	2.44	2.27	1	483–893	70.97	68.69	1188	25.30	24.06
ErL ₃ ·3H ₂ O	331–394	6.95	6.62	3	519–886	71.88	71.45	1273	24.59	25.00
TmL ₃ ·3H ₂ O	327–381	6.31	6.93	3	573–857	71.74	72.25	1273	24.58	23.76
YbL ₃ ·3H ₂ O	338–365	6.80	6.40	3	560–850	71.35	70.40	1250	25.14	24.90
LuL ₃ ·3H ₂ O	348–368	6.87	6.54	3	573–848	71.17	72.45	1123	25.33	24.80

^aTemperature range of dehydration process; ^bnumber of water molecules lost in the single step; ^ctemperature range of the decomposition of the anhydrous complex; ^dfinal temperature of decomposition process

TABLE IV. Enthalpy values of the dehydration process for the lanthanide(III) 2-(4-chlorophenoxy)acetates and their solubility in water at 293 K

Complex (L = C ₈ H ₆ ClO ₃)	ΔH^a / kJ·mol ⁻¹	ΔH_1^b / kJ·mol ⁻¹	Solubility, 10 ⁻⁴ mol·dm ⁻³
LaL ₃ ·2H ₂ O	48.20	24.10	4.70
PrL ₃ ·2H ₂ O	45.03	22.50	4.60
SmL ₃ ·2H ₂ O	42.87	21.43	5.30
EuL ₃ ·2H ₂ O	120.40	60.20	6.00
TbL ₃ ·2H ₂ O	78.48	39.24	7.60
DyL ₃ ·H ₂ O	59.99	59.99	3.80
ErL ₃ ·3H ₂ O	90.22	30.07	9.00
TmL ₃ ·3H ₂ O	80.54	26.84	9.50
YbL ₃ ·3H ₂ O	78.30	26.10	9.80
LuL ₃ ·2H ₂ O	83.30	27.76	9.90

^aEnthalpy value; ^benthalpy value for one molecule of water

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

The FTIR spectra recorded of the gaseous products released during complex decompositions revealed them to be molecules of H₂O, CO₂, CO, CH₄ 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 H₂O molecules in the products. At higher temperatures, the bands at 2250–2500 and 600–750 cm⁻¹ result from CO₂ vibrations, whereas the bands observed at 2000–2200 cm⁻¹ are characteristic for CO. The absorbance peak of methane (CH₄) appears around 3000 cm⁻¹ and HCl in the range of 3059–2650 cm⁻¹.^{41,42}

Solubility in water

The solubilities of lanthanide(III) 2-(4-chlorophenoxy)acetates in water (at 293 K) were also determined (Table IV). They were of the order of 1×10^{-4} mol dm^{-3} . Lu(III) 2-(4-chlorophenoxy)acetate was the most soluble salt, while the Dy(III) complex was the least soluble. Taking into account the values of the solubilities, it could be said that 2-(4-chlorophenoxy)acetic acid cannot be used for separation of lanthanide(III) ions by ion-exchange chromatography or by extraction methods because of their low solubility.

Magnetic properties

To estimate the nature of metal–ligand bonding in the analysed compounds and to try to find the reasons why their colours are typical for Ln(III) ions, the magnetic susceptibilities of the lanthanide(III) 2-(4-chlorophenoxy)acetates were determined over the range of 76–303 K. In order to determine whether the nature of atomic magnetic interactions changed at low temperatures, the magnetic susceptibilities of the complexes were investigated between 1.8 and 303 K.

The complexes obey the Curie–Weiss law.^{3,4} For all compounds, the values of the Weiss constant, Θ_m , had a negative sign, which may result from the anti-ferromagnetic spin or from a crystal field splitting of the paramagnetic spin state.^{3,4,43–46} The experimentally determined effective magnetic moment, μ_{eff} , values for the 2-(4-chlorophenoxy)acetates at 76 and 303 K are given in Table V.

TABLE V. The effective magnetic moment, μ_{eff} / μ_B , values for the Ln(III) 2-(4-chlorophenoxy)acetates at 76 and 303 K

Trivalent ion	$T = 76$ K	$T = 303$ K	Trivalent ion	$T = 76$ K	$T = 303$ K
Pr	2.75	3.26	Dy	10.45	10.69
Sm	1.09	1.56	Er	9.48	9.74
Eu	2.12	3.08	Tm	7.70	8.14
Tb	9.19	9.44	Yb	2.00	3.54

In the lanthanide(III) 2-(4-chlorophenoxy)acetates, the paramagnetic central ions remain practically unaffected by the diamagnetic ligands coordinated around them. The 4f orbitals, partly occupied by the magnetically active electrons, are very efficiently shielded by the fully occupied 5s and 5p orbitals. These 4f orbitals are almost uninvolved in the bonds between a rare earth(III) ion and its nearest neighbours. The lanthanide ion in a molecular compound behaves as free ion and its energy levels are the same as those in the free ion. The energy separation between the state of lowest energy and the first excited state varies from a few hundred to several thousands of wavenumbers. When this energy separation is small, the first excited state may be thermally populated, while only the ground state is thermally populated when the separation is large. The magnetic properties can be taken as those of the ground state alone and the lanthanide(III) ions in the

complexes act in the same manner as free ions. The values of μ_{eff} determined for all 2-(4-chlorophenoxy)acetates (except for europium) (Table V) were similar to those calculated for Ln(III) ions by Hund and Van Vleck (Table VI).⁴³ The values of magnetic moments determined for the complexes indicate that the energies of the 4f 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 element(III) ions remain the same as those in the free lanthanides. 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(III) ions are effectively shielded by the 5s²5p⁶ octet. Therefore the metal–ligand bonding in the analysed lanthanide(III) complexes is mainly electrostatic in nature.⁴⁶

TABLE VI. Magnetic moment values (μ_{eff}) of lanthanide(III) ions calculated by Hund and Van Vleck^{4,22,43,47} and those obtained experimentally for the Ln(III) 4-chlorophenoxyacetates of at room temperature

Trivalent ion	Configuration	$\mu_{\text{eff}}/\mu_{\text{B}}$		
		Calculated by Hund	Calculated by Van Vleck	Experimental
Pr	f ²	3.58	3.62	3.26
Sm	f ⁵	0.84	1.55–1.65	1.56
Eu	f ⁶	0.00	3.40–3.51	3.08
Tb	f ⁸	9.70	9.70	9.44
Dy	f ⁹	10.60	10.60	10.69
Er	f ¹¹	9.60	9.60	9.74
Tm	f ¹²	7.60	7.60	8.14
Yb	f ¹³	4.50	4.50	3.54

The magnetic properties of Er(III) were also studied over the temperature range of 1.8–300 K. Plots of magnetic susceptibility, χ_{m}^{-1} , and of the product $\chi_{\text{m}}T$ vs. T are shown in Fig. 3. 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 $\chi_{\text{m}}T$ vs. T curve, it follows that it decreases on cooling in the range 303–1.8 K. Between 303 and 48 K, the decrease is very slow showing the saturation paramagnetic state, while the decrease is drastic between 48 and 1.8 K.

The value of $\chi_{\text{m}}T$ for Er(III) 2-(4-chlorophenoxy)acetate at room temperature was 11.28 cm³ mol⁻¹ K, which is similar to that calculated theoretically for the free Er(III) ion, 11.48 cm³ mol⁻¹ K.^{4,47,48} At 1.8 K, the $\chi_{\text{m}}T$ value was 6.14 cm³ mol⁻¹ K. The decrease of the $\chi_{\text{m}}T$ vs. T curve in the range 48–1.8 K indicates a negative θ value, which may confirm antiferromagnetic intermolecular interactions. Therefore, the magnetic moment value of the Er(III) complex was equal to 7.01 (1.8 K) and 8.94 μ_{B} (48 K). Further, this value increases to 9.50 μ_{B} (303 K),

which is connected with the change in the unpaired electron order. This value is similar to that of the free Er(III) ion value ($9.59 \mu_B$).^{4,47}

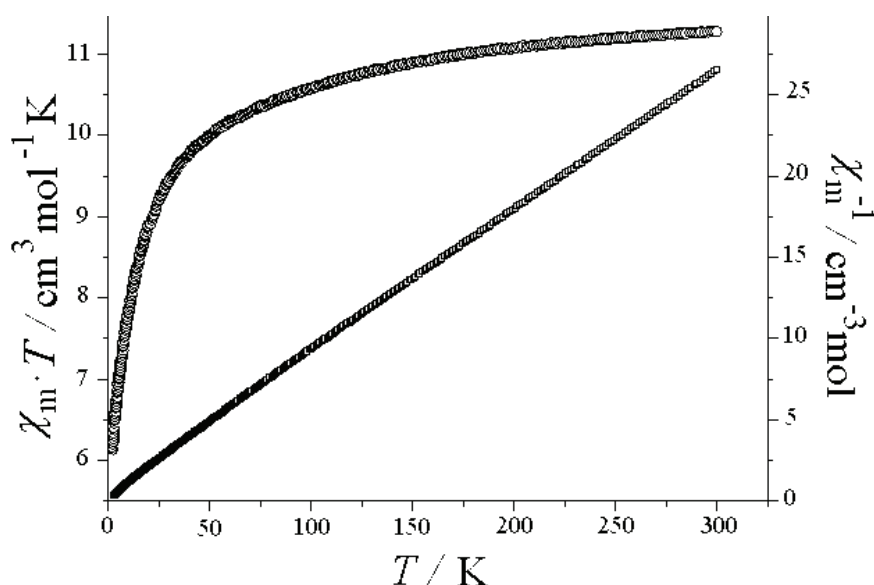


Fig. 3. Dependence of $\chi_m T$ (\circ) and χ_m^{-1} (\square) vs. T for 2-(4-chlorophenoxy)acetate of Er(III).

CONCLUSIONS

From the obtained results, it follows that the lanthanide(III) 2-(4-chlorophenoxy)acetates were prepared as mono-, di- or trihydrates with colours typical for the respective Ln(III) ions, having their origin in the lowest energy f-f electronic transitions of the central ions. The Ln-O bonds are electrostatic in nature. The compounds are crystalline complexes that on heating in air to 1273 K decompose in three steps. In the first step, all 2-(4-chlorophenoxy)acetates dehydrate to form anhydrous complexes, which further decomposed to the oxides of the corresponding metal(III), with the intermediate formation of LnOCl. The values of μ_{eff} calculated for all compounds were close theoretically calculated by Hund and Van Vleck for Ln(III) ions. There was no influence of the ligand field on the 4f electrons of the lanthanide(III) ions. The solubility of 2-(4-chlorophenoxy)acetates of lanthanides(III) in water was of the order of $10^{-4} \text{ mol dm}^{-3}$.

The complexes of Nd(III), Gd(III) and Ho(III) ions with the 2-(4-chlorophenoxy)acetic acid anion are di- and trihydrates^{14,15} and they exhibited properties similar to those of the complexes described in this paper. The Ln-O bonds were mainly electrostatic in nature. The complexes are crystalline compounds that on heating in air to 1173 K decompose in three steps. They dehydrate to form anhydrous complexes that further decompose to the oxides of the respective

metal, with the intermediate formation of LnOCl . The enthalpy values of dehydration processes were in the range 120.4–42.9 and 60.2–21.4 kJ mol^{-1} per one molecule of water. The values of μ_{eff} calculated for these compounds were similar to those calculated theoretically by Hund and Van Vleck for Ln(III) ions. Their solubilities in water at 293 K were of the order of $10^{-4} \text{ mol dm}^{-3}$.

ИЗВОД

МАГНЕТНА, ТЕРМАЛНА И СПЕКТРОСКОПСКА СВОЈСТВА КОМПЛЕКСА
ЛАНТАНИДА(III) СА 2-(4-ХЛОРОФЕНОКСИ)АЦЕТАТОМ, $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot n\text{H}_2\text{O}$

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Синтетисани су различити комплекси лантанида(III) са 2-(4-хлорофенокси)ацетатом као хидратисане поликристалне супстанце опште формуле: $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Sm(III)}, \text{Eu(III)}$ или Tb(III)), $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Dy(III)}$) и $\text{Ln}(\text{C}_8\text{H}_6\text{ClO}_3)_3 \cdot 3\text{H}_2\text{O}$ ($\text{Ln} = \text{Er(III)}, \text{Tm(III)}, \text{Yb(III)}$ или Lu(III)). За карактеризацију ових комплекса употребљени су елементална микроанализа, FTIR спектроскопија, магнетна и термогравиметријска мерења, као и метода дифракције рендгенских зрака (XRD). Боја комплекса је карактеристична за лантанид(III) јоне, а карбоксилатне групе у овим комплексима су бидентатно координоване. Загревањем на температури од 1273 K у атмосфери ваздуха комплекси се разграђују у три фазе. У првој фази комплекси губе кристалну воду, док се у следећој фази разлажу до оксида одговарајућих метала, чему претходи грађење одговарајућих оксихлорида као интермедијарних производа. Магнетна мерења су вршена у опсегу 76–303 K и 1,8–303 K и израчунате су вредности магнетних момената. Нађено је да 2-(4-хлорофенокси)ацетати са лантанидима граде високоспинске комплексе слабог лигандног поља.

(Примљено 3. децембра 2012, ревидирано 6. априла 2013)

REFERENCES

1. R. C. Mehrotra, R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983
2. R. L. Martin, in *New Pathways in Inorganic Chemistry*, E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe, Eds., Cambridge University Press, Cambridge, 1968, Ch. 9
3. Ch. J. O'Connor, *Progress in Inorganic Chemistry*, Wiley, New York, 1982
4. O. Kahn, *Molecular Magnetism*, VCH Publisher, New York, 1993
5. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, Toronto, 1997
6. G. Liu, X. Li, X. Ren, *J. Rare Earths* **29** (2011) 511
7. G. R. Desiraju, *Angew. Chem. Int. Ed.* **34** (1995) 2311
8. N. Ishikawa, M. Sugita, W. Wernsdorfer, *Angew. Chem. Int. Ed.* **44** (2005) 2931
9. N. Ishikawa, M. Sugita, N. Tanaka, T. Ishikawa, S. Koshihara, Y. Kaizu, *Inorg. Chem.* **43** (2004) 5498

10. N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Phys. Chem., B* **108** (2004) 11265
11. J. Q. Liu, Y. Y. Wang, L. F. Ma, W. H. Zhang, X. R. Zeng, F. Zang, Q. Z. Shi, S. M. Peng, *Inorg. Chim. Acta* **361** (2008) 173
12. N. Ishikawa, M. Sugita, T. Ishikawa, Y. Kaizu, *J. Am. Chem. Soc.* **125** (2003) 8694
13. R. Świsłocka, M. Kalinowska, W. Ferenc, J. Sarzyński, W. Lewandowski, *Cent. Eur. J. Chem.* **10** (2012) 1095
14. W. Ferenc, M. Bernat, J. Sarzyński, H. Głuchowska, *Ecl. Quim.* **33** (2010) 67
15. W. Ferenc, M. Bernat, J. Sarzyński, B. Paszkowska, *Ecl. Quim.* **33** (2008) 7
16. M. Franzini, L. Leoni, M. Saitta, *X-Ray Spectrom.* **1** (1972) 151
17. Z. Bojarski, *Krystalografia*, PWN, Warszawa, 2007
18. B. N. Figgis R. S. Nyholm, *J. Chem. Soc.* (1958) 4190
19. D. Glotzel, B. Segall, O.K. Anderson, *Solid State Commun.* **36** (1980) 403
20. W. Ferenc, B. Bocian, D. Mazur, *Croat. Chem. Acta* **72** (1999) 779
21. R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1991
22. K. Burger, *Coordination Chemistry: Experimental Methods*, Akadémiai Kiadó, Budapest, 1973
23. W. Lewandowski, H. Barańska, *Vibr. Spectr.* **2** (1991) 211
24. W. Lewandowski, *J. Mol. Struct.* **101** (1983) 79
25. E. Pretsch, T. Clerc, J. Seibl, W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer, Berlin, 1989
26. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman & Hall, London, 1975
27. G. Varsányi, *Assignments for Vibrational Spectra of 700 Benzene Derivatives*, Akadémiai Kiadó, Budapest, 1973
28. R. Łyszczek, *J. Therm. Anal. Calorim.* **108** (2012) 1101
29. A. K. Bridson, *Inorganic Spectroscopic Methods*, Oxford University Press, New York, 1998
30. A. Cross, A. R. Jones, *An Introduction to Practical Infrared Spectroscopy*, Butterworths, London, 1969
31. B. S. Manhas, A. K. Trikha, *J. Indian. Chem. Soc.* **59** (1982) 315
32. S. Xiao, J. Zang, X. Li, Q. Li, I. V. Ren, H. Li, *J. Rare Earths* **28** (2010) 12
33. Z. Lei, K. Zhao, Y. Gu, X. Li, *J. Rare Earths* **29** (2010) 303
34. G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **33** (1980) 227
35. W. Brzyska, *Lanthanides and Actinides*, Scientific – Technical Publishers, Warsaw, 1996
36. B. Czajka, B. Bocian, W. Ferenc, *J. Therm. Anal. Calorim.* **67** (2002) 631
37. W. Ferenc, A. Dziejulska-Kulaczkowska, J. Sarzyński, B. Paszkowska, *J. Therm. Anal. Calorim.* **91** (2008) 285
38. W. Ferenc, B. Cristóvão, J. Sarzyński, H. Głuchowska, *J. Rare Earths* **30** (2012) 257
39. A. V. Nikolaev, V. A. Logvinienko, L. I. Myachina, *Thermal Analysis*, Academic Press, New York, 1969
40. F. Paulik, *Special Trends in Thermal Analysis*, Wiley, Chichester, 1995
41. T. Xu, X. Huang, *Fuel* **89** (2010) 2185
42. L. Tao, G. B. Zhao, *J. Hazard. Mater.* **175** (2010) 754
43. J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932

44. S. F. A. Kettle, *Physical Inorganic Chemistry: A Coordination Chemistry Approach*, Oxford University Press, Oxford, 2000
45. A. Earnshaw, *Introduction to magnetochemistry*, Academic Press, New York, 1968
46. S. P. Sinha, *Systematic and Properties of the Lanthanides*, Reidel, Dordrecht, The Netherlands, 1983
47. C. Benelli, D. Gatteschi, *Chem. Rev.* **102** (2002) 2369
48. C. Meyer, B. J. Ruck, A. R. H. Preston, S. Granville, G. V. M. Williams, H. J. Trodahl, *J. Magn. Magn. Mater.* **322** (2010) 1973.