

## **THERMAL STABILITY OF 4-CHLORO-2-NITRO- AND 4-CHLORO-3-NITROBENZOATES OF RARE EARTH ELEMENTS**

### **Influence of substituent positions**

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### **Abstract**

The physico-chemical properties and thermal stability in air of rare earth element 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoates of the general formulae  $\text{Ln}(\text{C}_7\text{H}_3\text{NO}_4\text{Cl})_3 \cdot 2\text{H}_2\text{O}$  were compared and the influence of the position of the Cl and  $\text{NO}_2$  substituents on their thermal stabilities was investigated. The complexes of both series are crystalline, hydrated salts with colours typical of  $\text{Ln}^{3+}$ . The carboxylate group in these complexes is a bidentate, chelating ligand. The  $\text{NO}_2$  group in the chloro-nitro complexes does not undergo isomerization. The thermal stabilities of the 4-chloro-3-nitrobenzoates of rare earth elements were studied in the temperature range 293–1173 K, but those of 4-chloro-2-nitrobenzoates of those elements were studied only at 293–523 K because they decompose explosively above 523 K. The positions of the Cl and  $\text{NO}_2$  substituents on the benzene ring influence the thermal properties of the complexes and their decomposition mechanisms. The different thermal stabilities of the complexes are connected with various inductive and mesomeric effects of the Cl and  $\text{NO}_2$  substituents on the electron density in benzene ring.

**Keywords:** chloronitrobenzoates of rare earth elements, rare earth elements, thermal stability of complexes

### **Introduction**

4-Chloro-2-nitro- and 4-chloro-3-nitrobenzoic acids are white, crystalline solids, sparingly soluble in cold water [1, 2]. Their salts with the following cations  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  have been obtained in the solid state [1, 2]. The literature contains no information on the salts of these acids with rare earth elements. Therefore, we decided to obtain them as solids and to examine some of their physico-chemical properties with special regard to their thermal stability in air during heating up to 1173 K. In our previous papers we presented experimental data on these complexes [3, 4]. Taking the various positions of the Cl and  $\text{NO}_2$  groups on the benzene ring into account, we decided to compare the thermal properties of the 4-chloro-

2-nitrobenzoates and the 4-chloro-3-nitrobenzoates of rare earth elements in order to investigate the influence of the positions of these substituents on the physico-chemical properties of the complexes.

## Experimental

4-Chloro-2-nitro- and 4-chloro-3-nitrobenzoates of rare earth elements were prepared by adding equivalent quantities of 0.1 M ammonium 4-chloro-2-nitro- or ammonium 4-chloro-3-nitrobenzoate (pH~5) to a hot solution containing the rare earth elements nitrates and crystallizing at 293 K. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass. The contents of carbon, hydrogen and nitrogen were determined by elemental analysis with  $V_2O_5$  as oxidizing agent, and the content of chlorine by the Schöniger method. The contents of rare earth elements were determined by measuring the concentration of  $Ln^{3+}$  ions in a saturated solution by a spectrophotometrical method using the spectrophotometer Specord M-40. The absorbance of the complexes was measured using the Arsenazo III in the formic buffer (pH=3.5) and the wavelength  $\lambda=650$  nm, and with the use of the blank as reference. The IR spectra of the prepared complexes, 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoic acids, the sodium salts of these acids and sodium nitrite were recorded in KBr discs on an M-80 spectrophotometer (Carl-Zeiss, Jena) in the range 4000–400  $cm^{-1}$  (Table 1). The X-ray diffraction patterns were taken on a HZG-4 (Carl-Zeiss, Jena) diffractometer using Ni filtered  $CuK_{\alpha}$  radiation. The measurements were made within the  $2\theta$  range 4–80° by means of the Debye–Scherrer–Hull method. The thermal stability and decomposition of the 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoates were determined using a Paulik–Paulik–Erdey Q-1500D derivatograph with a Derill converter recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K  $min^{-1}$  with a full scale. The 100 mg samples were heated in platinum crucibles in static air to 523 K (in the case of 4-chloro-2-nitrobenzoates) and to 1173 K (in the case of 4-chloro-3-nitrobenzoates) with a sensitivity of the TG, 100 mg (it means that the whole scale in the balance is equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm  $min^{-1}$ .  $Al_2O_3$  was used as the standard. The products of decomposition were calculated from the TG curves and verified by the registration of the diffraction pattern. From the preliminary investigations relating to the conditions of the thermal decompositions of these complexes, it appears that 4-chloro-2-nitrobenzoates are stable up to 523 K, after which they decompose explosively, whereas the 4-chloro-3-nitrobenzoates do not behave similarly. The measurements of the thermal stabilities of the 4-chloro-3-nitrobenzoates of rare earth elements were made on an OD-102 Derivatograph at a heating rate of 10 K  $min^{-1}$ . The samples were heated in air in the temperature range 293–1173 K at the following sensitivities: TG–100 mg, DTA–1/10, DTG–1/5. The results obtained are presented in Tables 2 and 3, and in Figs 1 and 2.

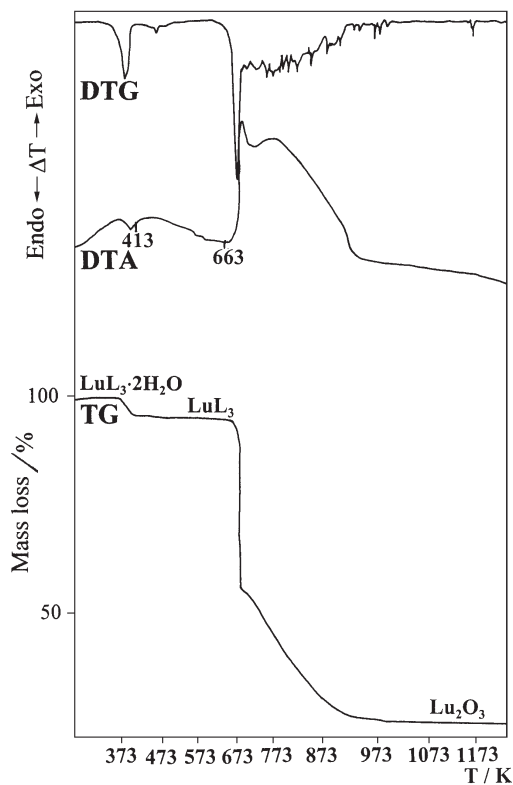


Fig. 1 TG, DTG and DTA curves of 4-chloro-3-nitrobenzoate of Lu

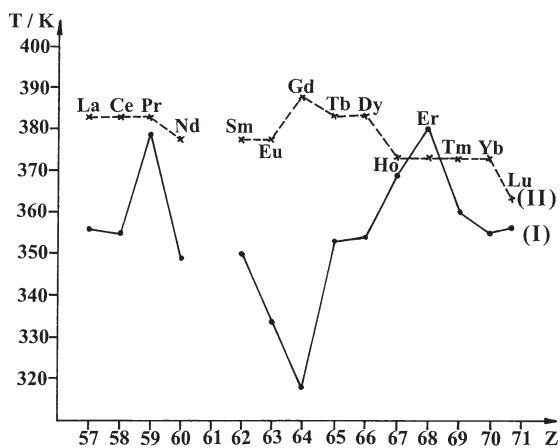


Fig. 2 Variation in initial dehydration temperatures of (I) 4-chloro-2-nitrobenzoates and (II) 4-chloro-3-nitrobenzoates of rare earth elements vs. atomic number of lanthanides

**Table 1** Frequencies of maxima of absorption bands of COO<sup>-</sup> group vibrations for 4-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of rare earth elements and sodium (cm<sup>-1</sup>)

Complex <i>L</i> =C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> Cl	4-chloro-2-nitrobenzoates			Complex <i>L</i> =C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> Cl	4-chloro-3-nitrobenzoates		
	$\nu_{\text{asCOO}^-}$	$\nu_{\text{sCOO}^-}$	$\Delta\nu_{\text{COO}^-}$		$\nu_{\text{asCOO}^-}$	$\nu_{\text{sCOO}^-}$	$\Delta\nu_{\text{COO}^-}$
YL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	YL <sub>3</sub> ·2H <sub>2</sub> O	1600	1435	165
LaL <sub>3</sub> ·2H <sub>2</sub> O	1550	1420	140	LaL <sub>3</sub> ·2H <sub>2</sub> O	1590	1425	165
CeL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	130	CeL <sub>3</sub> ·2H <sub>2</sub> O	1590	1425	165
PrL <sub>3</sub> ·2H <sub>2</sub> O	1540	1410	130	PrL <sub>3</sub> ·2H <sub>2</sub> O	1590	1420	170
NdL <sub>3</sub> ·2H <sub>2</sub> O	1540	1410	130	NdL <sub>3</sub> ·2H <sub>2</sub> O	1590	1425	165
SmL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	SmL <sub>3</sub> ·2H <sub>2</sub> O	1590	1430	160
EuL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	EuL <sub>3</sub> ·2H <sub>2</sub> O	1590	1425	165
GdL <sub>3</sub> ·2H <sub>2</sub> O	1550	1405	145	GdL <sub>3</sub> ·2H <sub>2</sub> O	1600	1435	165
TbL <sub>3</sub> ·2H <sub>2</sub> O	1550	1405	145	TbL <sub>3</sub> ·2H <sub>2</sub> O	1590	1430	160
DyL <sub>3</sub> ·2H <sub>2</sub> O	1550	1405	145	DyL <sub>3</sub> ·2H <sub>2</sub> O	1600	1440	160
HoL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	HoL <sub>3</sub> ·2H <sub>2</sub> O	1600	1430	170
ErL <sub>3</sub> ·2H <sub>2</sub> O	1552	1410	142	ErL <sub>3</sub> ·2H <sub>2</sub> O	1600	1440	160
TmL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	TmL <sub>3</sub> ·2H <sub>2</sub> O	1600	1440	160
YbL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	YbL <sub>3</sub> ·2H <sub>2</sub> O	1600	1435	165
LuL <sub>3</sub> ·2H <sub>2</sub> O	1550	1410	140	LuL <sub>3</sub> ·2H <sub>2</sub> O	1600	1435	165
NaL	1580	1400	180	NaL	1610	1415	195

## Results and discussion

The 4-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of rare earth elements are crystalline compounds with a metal to ligand ratio of 1:3. They form dihydrates of general formula Ln(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>Cl)<sub>3</sub>·2H<sub>2</sub>O [3, 4]. Their colours are typical of the particular Ln(III) ion, i.e. white for La, Ce, Eu, Gd, Tb, Dy, Tm, Yb, Lu and Y, cream for Sm, Ho, greenish for Pr, violet for Nd and pink for Er, having their origin in the lowest-energy f–f electronic transitions of the central ions.

The compositions of the complexes were established on the basis of elemental analysis and IR spectral data [3, 4]. They were found to be crystalline compounds of low symmetry, large unit cells and different structures. Their crystal structures have not been determined, as attempts to obtain single crystals failed.

On the basis of the displacements of the absorption bands of the carboxylate asymmetric and symmetric vibrations of the investigated complexes in comparison with those of the sodium salts of the corresponding acids, the carboxylate ion appears to behave as a bidentate chelating ligand [3–7]. The IR spectral analysis indicates that the positions of the  $\nu_{\text{asCOO}^-}$  and  $\nu_{\text{sCOO}^-}$  bands change, depending on the positions of the Cl and NO<sub>2</sub> groups on the benzene ring and their different inductive and mesomeric effects on the electron density in the aromatic system. Accordingly, their frequency

values are higher for 4-chloro-3-nitrobenzoates ( $\nu_{\text{asCOO}^-} = 1600\text{--}1590$ ,  $\nu_{\text{sCOO}^-} = 1440\text{--}1420$   $\text{cm}^{-1}$ ) compared to those for 4-chloro-2-nitrobenzoates ( $\nu_{\text{asCOO}^-} = 1552\text{--}1540$ ,  $\nu_{\text{sCOO}^-} = 1420\text{--}1405$   $\text{cm}^{-1}$ ).

The magnitudes of separation,  $\Delta\nu_{\text{COO}^-}$  ( $\Delta\nu_{\text{COO}^-} = \nu_{\text{asCOO}^-} - \nu_{\text{sCOO}^-}$ ) which characterize the metal–oxygen bond, change in the range from 170–160  $\text{cm}^{-1}$  for 4-chloro-3-nitrobenzoates to 145–140  $\text{cm}^{-1}$  for 4-chloro-2-nitrobenzoates. In these complexes being compared the participation of M–O ionic bond is presumably the largest in the case of 4-chloro-3-nitrobenzoates while the least one in the case of 4-chloro-2-nitrobenzoates. The bands of metal–oxygen group are being changed depending on the position of Cl and  $\text{NO}_2$  substituents in aromatic ring. The IR spectral analysis of the complexes and sodium nitrite reveals that the  $\text{NO}_2$  group does not undergo isomerization during the preparation of the complexes or under the influence of sunlight or on the increase of temperature during their dehydration [3, 4, 8–10]. It has been found that isomerization of nitro group may accompany the process of complex dehydration or be connected with the transformation in its inner sphere [10]. The nitrite ion may bond as a monodentate ligand either through a nitrogen atom, forming a nitro complex, or through one of the oxygen atoms, yielding a nitrito complex. The general effect of coordination via nitrogen is to raise the frequencies of both  $\nu_{\text{asNO}_2}$  and  $\nu_{\text{sNO}_2}$  from the free ion values of  $\sim 1328$  and  $\sim 1260$   $\text{cm}^{-1}$  [10]. The results obtained show that the solid 4-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of rare earth elements form nitro complexes. In the IR spectra of the complexes, the  $\nu_{\text{asNO}_2}$  and  $\nu_{\text{sNO}_2}$  absorption bands at 1540–1530 and 1360–1350  $\text{cm}^{-1}$ , respectively, are displaced to higher frequencies relative to those for the free  $\text{NO}_2^-$  ion. In the IR spectra of these complexes, no bands are observed that would confirm isomerization of the nitro group to result in bonding through the oxygen atom [3, 4, 8–10].

The thermal stabilities of the 4-chloro-2-nitrobenzoates of rare earth elements were studied in the temperature range 293–523 K, whereas the 4-chloro-3-nitrobenzoates of those elements in the range 293–1173 K. The 4-chloro-3-nitrobenzoates of rare earth elements do not decompose explosively. Accordingly, it is possible to conclude that the positions of the substituents on the benzene ring determine thermal stabilities of the complexes; it is strongly 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  $\delta$ , 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 values of  $\delta$  for the  $\text{NO}_2$  and Cl groups are  $\delta_{\text{m}} = +0.373$  and  $\delta_{\text{p}} = +0.227$  for Cl, and  $\delta_{\text{m}} = +0.712$  and  $\delta_{\text{p}} = +0.778$  for  $\text{NO}_2$  [11, 12].

In the 4-chloro-3-nitrobenzoates the presence of the Cl substituent in the para position stabilizes the aromatic ring since the inductive effect of the Cl substituent increases the electron density in the benzene ring. In the case of the 4-chloro-2-nitrobenzoates of rare earth elements, the presence of the  $\text{NO}_2$  group in the ortho-position does not stabilize the system because of the steric effect [11, 12] and the most important is the inductive effect caused by the Cl substituent.

**Table 2** Temperature range of dehydration process of lanthanide 4-chloro-2-nitrobenzoates in air atmosphere

Complex $L=C_7H_3NO_4Cl$	$\Delta T_1/K$	Mass loss/%		$n$	$T_{max}/K$	$T_b/K$
		calcd.	found			
LaL <sub>3</sub> ·2H <sub>2</sub> O	356–440	4.63	4.29	2	439	433
CeL <sub>3</sub> ·2H <sub>2</sub> O	355–435	4.62	4.29	2	434	438
PrL <sub>3</sub> ·2H <sub>2</sub> O	379–470	4.62	4.29	2	469	470
NdL <sub>3</sub> ·2H <sub>2</sub> O	349–460	4.60	4.29	2	459	465
SmL <sub>3</sub> ·2H <sub>2</sub> O	350–460	4.57	4.29	2	460	465
EuL <sub>3</sub> ·2H <sub>2</sub> O	334–432	4.56	4.55	2	431	435
GdL <sub>3</sub> ·2H <sub>2</sub> O	318–432	4.40	4.00	2	429	432
TbL <sub>3</sub> ·2H <sub>2</sub> O	353–420	4.50	4.00	2	418	431
DyL <sub>3</sub> ·2H <sub>2</sub> O	354–423	4.50	4.00	2	418	432
HoL <sub>3</sub> ·2H <sub>2</sub> O	369–413	4.40	4.00	2	412	415
ErL <sub>3</sub> ·2H <sub>2</sub> O	380–419	4.40	4.00	2	409	412
TmL <sub>3</sub> ·2H <sub>2</sub> O	360–419	4.50	4.40	2	400	405
YbL <sub>3</sub> ·2H <sub>2</sub> O	355–398	4.40	4.40	2	398	400
LuL <sub>3</sub> ·2H <sub>2</sub> O	351–395	4.40	4.40	2	390	394

$\Delta T_1$  – temperature range of dehydration process;

$n$  – number of crystallization water molecules lost in one endothermic step;

$T_{max}$  – temperature of maximum of endothermic effect in DTA curve

$T_b$  – temperature of anhydrous salt formation

The thermal analysis results reveal that the 4-chloro-2-nitrobenzoates are dihydrates (Table 2). They lose the crystallization water molecules in one step in the range 318–380 K. The dihydrated 4-chloro-3-nitrobenzoates of rare earth elements also lose the crystallization water in one step in the temperature range 353–573 K and anhydrous complexes are formed, which in the range 613–1128 K decompose to Ln<sub>2</sub>O<sub>3</sub> through the intermediate formation of LnOCl (Table 3, Figs 1, 2). The loss of crystallization water molecules in both series of the complexes is connected with the endothermic effects in the DTA curves [13–15]. The higher thermal stabilities of 4-chloro-3-nitrobenzoates results mainly from the presence of the NO<sub>2</sub> group in the meta-position on the benzene ring. The dihydrates of 4-chloro-2-nitrobenzoates of rare earth elements have various stabilities (Table 2), which do not change regularly. The temperature of dehydration is the lowest for the Gd complex (318 K) and the highest for the Er complex (380 K). In the case of the 4-chloro-3-nitrobenzoate of Lu the water molecule is the most weakly bound, while the most strongly bound is that in the gadolinium salt (388 K). In the temperature range 403–763 K, the TG curves attain a constant level, which is indicative of the anhydrous complex formation. The anhydrous complexes decompose in the range 613–1123 K. The TG curves again attain a constant level at 928–1253 K. This corresponds to the formation of lanthanide oxide, to be the final product of decomposition. The temperatures of oxide formation

do not vary regularly with increasing atomic number of the elements; they are higher for the heavy lanthanides than for the light ones.

The comparison of thermal stability data obtained under different experimental conditions for the two series of rare earth element chloronitrobenzoates indicates that various positions of the Cl and NO<sub>2</sub> substituents on the benzene ring may influence the thermal properties of complex decomposition. The various mesomeric and inductive effects of these substituents on the electron density in benzene ring cause that the 4-chloro-2-nitrobenzoates are being stable only up to 523 K, after which they decompose explosively, whereas the 4-chloro-3-nitrobenzoates do not exhibit such properties.

**Table 3** Temperature range of thermal stability of Y and lanthanide 4-chloro-3-nitrobenzoates and their decomposition in air atmosphere

Complex <i>L</i> =C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> Cl	$\Delta T_1$ /K	Mass loss/%		<i>n</i>	$\Delta T_2$ /K	Mass loss/%		$T_K$ /K
		calcd.	found			calcd.	found	
YL <sub>3</sub> ·2H <sub>2</sub> O	383–433	4.95	5.00	2	668–973	84.46	84.84	1073
LaL <sub>3</sub> ·2H <sub>2</sub> O	383–518	4.64	4.90	2	633–1053	79.00	78.78	1053
CeL <sub>3</sub> ·2H <sub>2</sub> O	383–573	4.66	5.00	2	613–893	77.73	78.02	1013
PrL <sub>3</sub> ·2H <sub>2</sub> O	383–533	4.62	4.90	2	613–983	78.14	78.74	983
NdL <sub>3</sub> ·2H <sub>2</sub> O	378–468	4.60	4.80	2	618–913	78.48	78.78	973
SmL <sub>3</sub> ·2H <sub>2</sub> O	378–528	4.56	4.50	2	638–928	77.88	77.50	928
EuL <sub>3</sub> ·2H <sub>2</sub> O	378–533	4.56	4.50	2	638–958	77.72	77.01	1123
GdL <sub>3</sub> ·2H <sub>2</sub> O	388–438	4.52	4.50	2	763–1128	77.20	77.30	1093
TbL <sub>3</sub> ·2H <sub>2</sub> O	383–423	4.52	5.00	2	653–1068	76.73	76.48	1253
DyL <sub>3</sub> ·2H <sub>2</sub> O	383–423	4.50	4.30	2	648–1063	76.69	75.75	1248
HoL <sub>3</sub> ·2H <sub>2</sub> O	373–423	4.48	4.20	2	653–1093	76.46	77.00	1183
ErL <sub>3</sub> ·2H <sub>2</sub> O	373–423	4.47	4.50	2	663–1053	76.24	76.76	1223
TmL <sub>3</sub> ·2H <sub>2</sub> O	373–413	4.46	4.20	2	663–1003	76.08	76.76	1103
YbL <sub>3</sub> ·2H <sub>2</sub> O	373–413	4.44	4.20	2	663–1123	75.70	75.79	1123
LuL <sub>3</sub> ·2H <sub>2</sub> O	353–413	4.44	4.20	2	663–1103	75.52	75.24	1103

$\Delta T_1$  – temperature range of dehydration process;

*n* – number of crystallization water molecules lost in one endothermic step;

$\Delta T_2$  – temperature range of anhydrous complex decomposition;

$T_K$  – temperature of oxide formation

The solubilities of 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoates of rare earth elements in water at 293 K were determined and they are in the order of 10<sup>-3</sup> mol dm<sup>-3</sup> [3, 4]. The same order of the solubilities results from the similar ability of these compounds to dissociate in water because of the same electron density in aromatic ring.

Concluding from the obtained results it appears that various positions of the Cl and NO<sub>2</sub> substituents on the benzene ring influence the values of the frequencies of the bands of M–O vibration and asymmetric and symmetric vibrations of COO<sup>-</sup>

group. They are higher for 4-chloro-3-nitrobenzoates of rare earth elements than for 4-chloro-2-nitrobenzoates. Depending on the Cl and NO<sub>2</sub> substituent positions on benzene ring the thermal stability of the complexes is also changed. 4-Chloro-3-nitrobenzoates of rare earth elements are not explosive compounds in the range 293–1173 K, while those of the 4-chloro-2-nitrobenzoates are stable only up to 523 K, which is connected with the orthoposition of NO<sub>2</sub> group.

The temperatures of the initial dehydration of the 4-chloro-3-nitrobenzoates of rare earth elements are higher compared to the 4-chloro-2-nitrobenzoates. It results from the various positions of the Cl and NO<sub>2</sub> substituents on the benzene ring and various mesomeric and inductive effects of these substituents on the electron density in benzene ring.

The obtained results also reveal that irrespective of the Cl and NO<sub>2</sub> substituent positions in benzene ring the ratio of metal:ligand in the complexes, their colours, the number of crystallization water molecules and the dentate of carboxylate group stay the same for both of two series of rare earth element chloronitrobenzoates.

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