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# THERMAL STABILITY OF 4-CHLORO-3-NITRO- AND 5-CHLORO-2-NITROBENZOATES OF RARE EARTH ELEMENTS

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## Abstract

The physico-chemical properties and thermal stabilities in air of rare earth element 4-chloro-3-nitrobenzoates and 5-chloro-2-nitrobenzoates were compared and the influence of the positions of the Cl and $NO_2$ substituents on their thermal stabilities was investigated. The complexes of both series are crystalline, hydrated or anhydrous salts with colours typical of $Ln^{3+}$. The carboxylate group in these complexes is a bidentate, chelating ligand. The $NO_2$ group in the chloronitro complexes does not undergo isomerization. The thermal stabilities of the 4-chloro-3-nitrobenzoates of Y and the lanthanides were studied in the temperature range 273–1173 K, but those of the 5-chloro-2-nitrobenzoates of these elements were studied only at 273–523 K, because they decompose explosively above 523 K. The positions of the Cl and $NO_2$ 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 $NO_2$ substituents on the electron density in the benzene ring.

**Keywords:** chloro-nitrobenzoates of rare earth elements, lanthanides, rare earth elements, thermal stability of complexes

## Introduction

4-Chloro-3-nitrobenzoic and 5-chloro-2-nitrobenzoic acids are white, crystalline solids, sparingly soluble in cold water [1, 2]. The salts of 4-chloro-3-nitrobenzoic acid with $Na^+$, $Ag^+$ $Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$ have been obtained in the solid state [1]. The salts of 5-chloro-2-nitrobenzoic acid with $K^+$, $Pb^{2+}$, $Ca^{2+}$ and $Ba^{2+}$ have been obtained as solids [2].

The literature contains no information on the salts of these acids with Y and lanthanide elements. We therefore decided to obtain these as solids and to examine some of their physico-chemical properties with special regard to their thermal stability in air. In previous papers, we presented experimental data on these complexes [3, 4]. Taking into account the various positions of the Cl and $NO_2$

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groups on the benzene ring, we decided to compare the thermal properties of the 4-chloro-3-nitrobenzoates and the 5-chloro-2-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-3-nitrobenzoates and 5-chloro-2-nitrobenzoates of Y and lanthanides were prepared by adding equivalent quantities of 0.1 M ammonium 4-chloro-3-nitrobenzoate or ammonium 5-chloro-2-nitrobenzoate (pH~5) to a hot solution containing the rare earth element nitrate (in the case of 4-chloro-3-nitrobenzoates) or chloride (in the case of 5-chloro-2-nitrobenzoates) 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 constant mass. The contents of carbon, hydrogen and nitrogen were determined by elemental analysis with $V_2O_5$ as oxidizing agent, and the contents of chlorine by the Schöniger method. The contents of rare earth elements were established by the oxalic acid method. The IR spectra of the prepared complexes, 4-chloro-3-nitrobenzoic acid, 5-chloro-2-nitrobenzoic acid, 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 DRON-2 diffractometer, using Ni-filtered $CuK_\alpha$ radiation. The measurements were made within the range $2\Theta=4-80^\circ$ by means of the Debye-Scherrer-Hull method in order to investigate their external crystalline form. The thermal stabilities of the 5-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of the rare earth elements were determined in air by the use of TG, DTG and DTA techniques. The measurements of the thermal stabilities of the 4-chloro-3-nitrobenzoates of Y and the lanthanides 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 273–1173 K at the following sensitivities: TG – 100 mg, DTA – 1/10, DTG – 1/5. The measurements on the 5-chloro-2-nitrobenzoates of the rare earth elements were made with a Q-1500D Derivatograph (MOM, Budapest, Hungary) at a heating rate of 2.5 K $min^{-1}$. The samples were heated only, in the temperature range 273–523 K at the sensitivities TG – 50 mg, DTG – 200, DTA – 200 (the results were recorded via use of the countershaft of an A/C converter manufactured by Medson). From the preliminary investigations relating to the conditions of the thermal decompositions of these complexes, it appears that, irrespective of changes in the experimental parameters, the 5-chloro-2-nitrobenzoates of the rare earth elements are stable up to 523 K, after which they decompose explosively, whereas the 4-chloro-3-nitrobenzoates do not behave similarly.

The results obtained are presented in Tables 2 and 3 in Figs 1 and 2.

**Table 1** Frequencies of maxima of absorption bands of $COO^-$ group vibrations for 5-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of Y and rare earth elements and sodium ($cm^{-1}$)

| Complex $L$=$C_7H_3NO_4Cl$ | 5-Chloro-2-nitrobenzoates | | | Complex $L$=$C_7H_3NO_4Cl$ | 4-Chloro-3-nitrobenzoates | | |
|---|---|---|---|---|---|---|---|
| | $\nu_{asCOO^-}$ | $\nu_{sCOO^-}$ | $\Delta\nu_{COO^-}$ | | $\nu_{asCOO^-}$ | $\nu_{sCOO^-}$ | $\Delta\nu_{COO^-}$ |
| $YL_3 \cdot H_2O$ | 1580 | 1390 | 190 | $YL_3 \cdot 2H_2O$ | 1600 | 1435 | 165 |
| $LaL_3$ | 1550 | 1380 | 170 | $LaL_3 \cdot 2H_2O$ | 1590 | 1425 | 165 |
| $CeL_3$ | 1555 | 1380 | 175 | $CeL_3 \cdot 2H_2O$ | 1590 | 1425 | 165 |
| $PrL_3$ | 1550 | 1380 | 170 | $PrL_3 \cdot 2H_2O$ | 1590 | 1420 | 170 |
| $NdL_3$ | 1550 | 1365 | 185 | $NdL_3 \cdot 2H_2O$ | 1590 | 1425 | 165 |
| $SmL_3 \cdot H_2O$ | 1565 | 1375 | 190 | $SmL_3 \cdot 2H_2O$ | 1590 | 1430 | 160 |
| $EuL_3 \cdot H_2O$ | 1550 | 1385 | 165 | $EuL_3 \cdot 2H_2O$ | 1590 | 1425 | 165 |
| $GdL_3 \cdot H_2O$ | 1555 | 1380 | 175 | $GdL_3 \cdot 2H_2O$ | 1600 | 1435 | 165 |
| $TbL_3 \cdot 2H_2O$ | 1575 | 1380 | 195 | $TbL_3 \cdot 2H_2O$ | 1590 | 1430 | 160 |
| $DyL_3 \cdot 2H_2O$ | 1575 | 1380 | 195 | $DyL_3 \cdot 2H_2O$ | 1600 | 1440 | 160 |
| $HoL_3 \cdot 2H_2O$ | 1580 | 1385 | 195 | $HoL_3 \cdot 2H_2O$ | 1600 | 1430 | 170 |
| $ErL_3 \cdot 2H_2O$ | 1575 | 1385 | 190 | $ErL_3 \cdot 2H_2O$ | 1600 | 1440 | 160 |
| $TmL_3 \cdot H_2O$ | 1580 | 1395 | 185 | $TmL_3 \cdot 2H_2O$ | 1600 | 1440 | 160 |
| $YbL_3 \cdot H_2O$ | 1580 | 1395 | 185 | $YbL_3 \cdot 2H_2O$ | 1600 | 1435 | 165 |
| $LuL_3 \cdot H_2O$ | 1580 | 1400 | 180 | $LuL_3 \cdot 2H_2O$ | 1600 | 1435 | 165 |
| NaL | 1600 | 1360 | 240 | NaL | 1610 | 1415 | 195 |

**Table 2** Temperature range of dehydration of 5-chloro-2-nitrobenzoates of Y and lanthanides in air atmosphere

| Complex | $\Delta T_1$/K | Mass loss/% | | $n$ | $T_{max}$/K | $T_b$/K |
|---|---|---|---|---|---|---|
| | | calcd. | found | | | |
| $YL_3 \cdot H_2O$ | 463–473 | 2.88 | 3.0 | 1 | 463.0 | 478 |
| $LaL_3$ | – | – | – | – | – | – |
| $CeL_3$ | – | – | – | – | – | – |
| $PrL_3$ | – | – | – | – | – | – |
| $NdL_3$ | – | – | – | – | – | – |
| $SmL_3 \cdot H_2O$ | 501–520 | 2.47 | 2.2 | 1 | 518.0 | 523 |
| $EuL_3 \cdot H_2O$ | 496–519 | 2.46 | 2.8 | 1 | 514.0 | 518 |
| $GdL_3 \cdot H_2O$ | 478–515 | 2.44 | 2.6 | 1 | 504.0 | 513 |
| $TbL_3 \cdot 2H_2O$ | 472–507 | 4.77 | 4.6 | 2 | 496.3 | 513 |
| $DyL_3 \cdot 2H_2O$ | 458–494 | 4.74 | 4.6 | 2 | 478.0 | 498 |
| $HoL_3 \cdot 2H_2O$ | 443–482 | 4.73 | 4.6 | 2 | 448.0 | 493 |
| $ErL_3 \cdot 2H_2O$ | 434–470 | 4.71 | 4.5 | 2 | 458.0 | 473 |
| $TmL_3 \cdot H_2O$ | 419–461 | 2.41 | 2.5 | 1 | 449.6 | 468 |
| $YbL_3 \cdot H_2O$ | 411–453 | 2.39 | 2.1 | 1 | 443.0 | 463 |
| $LuL_3 \cdot H_2O$ | 419–455 | 2.39 | 2.4 | 1 | 444.0 | 465 |

$L$=$C_7H_3NO_4Cl$; $\Delta T_1$=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

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

| Complex | $\Delta T_1$/K/ | Mass loss/% |  | $n$ | $\Delta T_2$/K | Mass loss/% |  | $T_k$/K |
|---|---|---|---|---|---|---|---|---|
|  |  | calcd. | found |  |  | calcd. | found |  |
| $YL_3 \cdot 2H_2O$ | 383–433 | 4.95 | 5.0 | 2 | 668– 973 | 84.46 | 84.84 | 1073 |
| $LaL_3 \cdot 2H_2O$ | 383–518 | 4.64 | 4.9 | 2 | 633–1053 | 79.00 | 78.78 | 1053 |
| $CeL_3 \cdot 2H_2O$ | 383–573 | 4.66 | 5.0 | 2 | 613– 893 | 77.73 | 78.02 | 1013 |
| $PrL_3 \cdot 2H_2O$ | 383–533 | 4.62 | 4.9 | 2 | 613– 983 | 78.14 | 78.74 | 983 |
| $NdL_3 \cdot 2H_2O$ | 378–468 | 4.60 | 4.8 | 2 | 618– 913 | 78.48 | 78.78 | 973 |
| $SmL_3 \cdot 2H_2O$ | 378–528 | 4.56 | 4.5 | 2 | 638– 928 | 77.88 | 77.50 | 928 |
| $EuL_3 \cdot 2H_2O$ | 378–533 | 4.56 | 4.5 | 2 | 638– 958 | 77.72 | 77.01 | 1123 |
| $GdL_3 \cdot 2H_2O$ | 388–438 | 4.52 | 4.5 | 2 | 763–1128 | 77.20 | 77.30 | 1093 |
| $TbL_3 \cdot 2H_2O$ | 383–423 | 4.52 | 5.0 | 2 | 653–1068 | 76.53 | 76.48 | 1253 |
| $DyL_3 \cdot 2H_2O$ | 383–423 | 4.50 | 4.3 | 2 | 648–1063 | 76.69 | 75.75 | 1248 |
| $HoL_3 \cdot 2H_2O$ | 373–423 | 4.48 | 4.2 | 2 | 653–1093 | 76.46 | 77.00 | 1183 |
| $ErL_3 \cdot 2H_2O$ | 373–423 | 4.47 | 4.5 | 2 | 663–1053 | 76.24 | 76.76 | 1223 |
| $TmL_3 \cdot 2H_2O$ | 373–413 | 4.46 | 4.2 | 2 | 663–1003 | 76.08 | 76.76 | 1103 |
| $YbL_3 \cdot 2H_2O$ | 373–413 | 4.44 | 4.2 | 2 | 663–1123 | 75.70 | 75.79 | 1123 |
| $LuL_3 \cdot 2H_2O$ | 363–403 | 4.44 | 4.2 | 2 | 663–1103 | 75.52 | 75.24 | 1103 |

$L=C_7H_3NO_4Cl$; $\Delta T_1$ - temperature range of dehydration

$n$=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

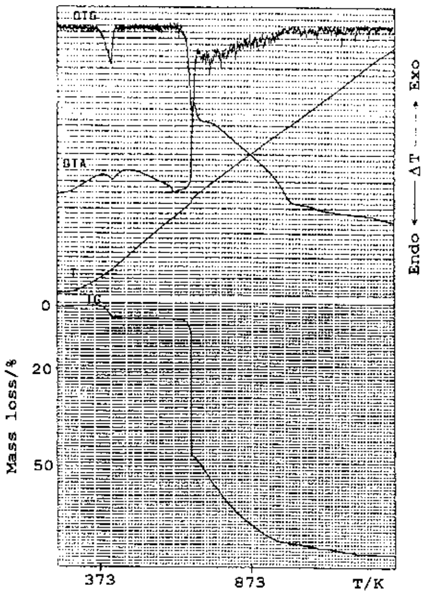

**Fig. 1** TG, DTG and DTA curves of 4-chloro-3-nitrobenzoates of Ho

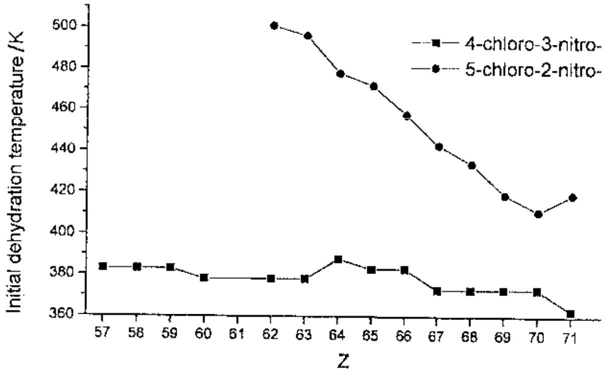

**Fig. 2** Variation in initial dehydration temperatures of 4-chloro-3-nitrobenzoates and 5-chloro-2-nitrobenzoates of rare earth elements and Y

## Results and discussion

The 4-chloro-3-nitrobenzoates and 5-chloro-2-nitrobenzoates of the rare earth elements are crystalline compounds with a metal to ligand ratio of 1:3. The 4-chloro-3-nitrobenzoates form dihydrates of general formula $Ln(C_7H_3NO_4Cl)_3 \cdot 2H_2O$ [3], whereas the 5-chloro-2-nitrobenzoates of these elements are anhydrous salts (La–Nd) or form monohydrates (Y, Sm–Gd, Tm–Lu) or dihydrates (Tb–Er) [4]. The colours of the 4-chloro-3-nitrobenzoates and 5-chloro-2-nitrobenzoates of the rare earth elements are typical of $Ln^{3+}$. The compositions of the complexes were established on the basis of elemental analyses and IR spectral data [3, 4]. They were found to be crystalline compounds characterized by low symmetry, a large unit cell and different structures, but their structures were not determined since no single-crystals of these complexes were obtained. In the series of light lanthanide 4-chloro-3-nitrobenzoates, the complexes of Sm, Eu and Gd seem to be isostructural [3, 4].

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 [3–6]. The $\nu_{asCOO^-}$ bands are shifted to lower frequencies, whereas the $\nu_{sCOO^-}$ bands are shifted to higher frequencies as compared to those of the sodium salts (Table 1). The IR spectral analysis indicates that the positions of the $\nu_{asCOO^-}$ and $\nu_{sCOO^-}$ bands change, depending on the positions of the Cl and $NO_2$ groups on the benzene ring and their different inductive and mesomeric effects on the electron density in the aromatic system. The IR spectral analysis of the complexes and sodium nitrite reveals that the $NO_2$ 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, 7–9]. A survey of the literature demonstrates that, under the influence of sunlight or on increase of the temperature, the transformation of nitro complexes to nitrito complexes may proceed [7, 8]. It has been found that isomerization of that nitro group may accompany the process of complex dehydration or be connected with the transformation in its inner sphere [9]. 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 $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ from the free ion values of ~1328 and ~1260 $cm^{-1}$ [9]. The results obtained show that the solid 5-chloro-2-nitrobenzoates and 4-chloro-3-nitrobenzoates of the rare earth elements form nitro complexes; in the IR spectra of the complexes, the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ absorption bands at 1540–1530 and 1360–1350 $cm^{-1}$, respectively, are displaced to higher frequencies relative to those for the free $NO_2$ 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, 7–9].

The thermal stabilities of the 4-chloro-3-nitrobenzoates of Y and the lanthanides were studied in the temperature range 273–1173 K, whereas the 5-chloro-2-nitrobenzoates of these elements were studied only in the interval 273–523 K: above 523 K, similarly to the 2-nitrobenzoates and 3-nitrobenzoates of these elements, they decompose explosively [10, 11]. In contrast, the 3-chlorobenzoates of the rare earth elements do not display such properties [12].

The 4-chloro-3-nitrobenzoates of Y and the lanthanides do not decompose explosively. Therefore, it is possible to conclude that the positions of the substituents on the benzene ring determine the thermal stabilities of the complexes; this 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 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 values of δ for the $NO_2$ and Cl groups are $\delta_m=+0.373$ and $\delta_p=+0.227$ for Cl, and $\delta_m=+0.712$ and $\delta_p=+0.778$ for $NO_2$ [13, 14].

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 5-chloro-2-nitrobenzoates of the rare earth elements, the presence of the $NO_2$ group in the ortho position does not stabilize the system because of the steric effect [13, 14] and the most important is the inductive effect caused by the Cl substituent.

All these complexes of Y and the lanthanides are stable in air at room temperature and do not undergo mass change during storage. The thermal analysis results reveal that the 5-chloro-2-nitrobenzoates of La–Nd are anhydrous complexes, those of Y, Sm–Gd and Tm–Lu are monohydrates, and those of Dy–Er are dihydrates (Table 2). The hydrated 5-chloro-2-nitrobenzoates of the rare earth elements lose the crystallization water molecules in one step in the temperature range 411–520 K. The monohydrates of the 5-chloro-2-nitrobenzoates of Y, Sm–Gd and Tm–Lu lose one water molecule in the range 411–520 K; the dihydrates of Tb, Dy and Ho lose two water molecules in the range 434–507 K. The dihydrated 4-chloro-3-nitrobenzoates of Y and the lanthanides also lose the crystallization water in one step in the temperature range 363–573 K and form anhydrous complexes, which in the range 613–1128 K decompose to $Ln_2O_3$ through the intermediate formation of LnOCl (Table 3, Fig. 1). The loss of crystallization water molecules in both series of the complexes is connected with the endothermic effects in the DTA curves [15–17]. The temperatures of initial dehydration of the 4-chloro-3-nitrobenzoates of the rare earth elements (363–388 K) are lower than those of the 5-chloro-2-nitrobenzoates (411–501 K) (Fig. 2). The higher thermal stabilities of the 5-chloro-2-nitrobenzoates result mainly from the presence of the Cl substituent in the meta position on the benzene ring. The hydrated rare earth element 5-chloro-2-nitrobenzoates have various stabilities (Table 2), which change regularly from Sm to Yb with decreasing ionic radius. The temperature of initial dehydration is lowest for the Yb complex (411 K) and highest for the Sm complex (501 K). In the case of the 5-chloro-2-nitrobenzoates the water molecule is the most weakly bound, while the most strongly bound is that in the Sm salt. For the 4-chloro-3-nitrobenzoates of Y and the lanthanides, the temperature of initial dehydration is lowest for the Lu complex (363 K) and highest for the Gd complex (388 K). In the temperature range 403–763 K, the TG curves attain a constant level, which is indicative of anhydrous complex formation. The anhydrous complexes decompose in the range 613–1128 K. The TG curves again attain a constant level at 928–1253 K. This corresponds to the formation of lanthanide oxide, the ultimate 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, which is probably connected with the lanthanide contraction. The thermal decompositions of the rare earth element 4-chloro-3-nitrobenzoates may be presented as follows:

$$LnL_3{\cdot}2H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3 \quad (\text{for } Ln\text{=La, Nd–Gd, Dy–Lu, Y})$$

or

$$\rightarrow Tb_4O_7, Pr_6O_{11}, CeO_2 \quad (\text{for Tb, Pr, Ce}),$$

where $L$=$C_7H_3NO_4Cl$

The comparison of thermal stability data obtained under different experimental conditions for the two series of rare earth element chloronitrobenzoates indicates that the various positions of the Cl and $NO_2$ 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 the benzene ring lead to the 5-chloro-2-nitrobenzoates being stable only up to 523 K, after which they decompose explosively, whereas the 4-chloro-3-nitrobenzoates do not exhibit such properties.

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