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SPECTROCHEMICAL AND THERMAL BEHAVIOUR OF THE 5-CHLORO-2-NITROBENZOATES OF RARE EARTH ELEMENTS

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Abstract

The conditions of the formation of yttrium and lanthanide 5-chloro-2-nitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K were determined. They are anhydrous or hydrated complexes and their solubilities are of the order of 10^{-3} mol dm^{-3}. The IR and X-ray spectra for the complexes were recorded. All complexes are crystalline compounds. Their thermal decomposition was studied. It was found that on heating above 523 K the complexes decompose explosively. Therefore their thermal decomposition was carried out in the temperature range 273–523 K. Hydrated complexes lose crystallization water molecules in one step. From the results it appeared that during dehydration process no transformation of nitro group to nitrito took place. Some of physico-chemical properties of rare earth element 5-chloro-2-nitrobenzoates were compared with 2-nitro- and 3-chlorobenzoates of those elements.

Keywords: 5-chloro-2-nitrobenzoates, complexes of rare earth elements, rare earth elements, spectrochemical investigations, thermal stability of complexes

Introduction

5-Chloro-2-nitrobenzoic acid is a crystalline solid, sparingly soluble in cold water but readily soluble in hot water and also in ethanol and benzene [1]. Its electrolytic dissociation constant is $1.52\cdot10^{-2}$ (25°C) and melting point 139°C. The compounds of 5-chloro-2-nitrobenzoic acid are very little known. A survey of the literature shows that it is possible to find papers on its salts with some cations and on the investigations of some of their chemical properties. The salts of 5-chloro-2-nitrobenzoic acid were obtained in the solid state only with the cations K^+, Pb^{2+}, Ca^{2+}, Ba^{2+} [1].

The 5-chloro-2-nitrobenzoates of Y and the lanthanide series have not been obtained so far. Therefore the aim of this work was therefore to obtain them as

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solids and to examine some of their physicochemical properties. Taking into account the presence of nitro- and chloro-groups in the benzene ring, the properties of the 5-chloro-2-nitrobenzoates of rare earth elements were compared with the corresponding 2-nitrobenzoates and 3-chlorobenzoates.

Experimental

The 5-chloro-2-nitrobenzoates of yttrium and the lanthanides were prepared by adding the equivalent quantities of 0.1 mol/l ammonium 5-chloro-2-nitrobenzoate (pH~5) to a hot solution containing the rare earth chlorides and crystallizing at 293 K. The solids formed were filtered off, washed with hot water and methanol 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. The content of chloride was determined by the Schöniger method. The contents of rare earth elements were established by the oxalic acid method. In order to confirm the chemical composition of the compounds, the IR spectra of the prepared complexes, of 5-chloro-2-nitrobenzoic acid, sodium 5-chloro-2-nitrobenzoate and of sodium nitrite were recorded as KBr discs on an M-80 spectrophotometer (Carl-Zeiss, Jena) in the range 4000–400 cm^{-1} (Table 2).

In order to estimate the external structure of 5-chloro-2-nitrobenzoates of rare earth elements the X-ray diffraction patterns were taken on a DRON-2 diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\Theta=4-80^\circ$ by means of the Debye-Scherrer-Hull method. The thermal stability of the complexes was studied by TG, DTG and DTA techniques. The measurements were made with a Q-1500D Derivatograph (MOM Budapest, Hungary) at a heating rate of 2.5°C min^{-1}. Test samples were heated at the following sensitivities: TG-50 mg, DTG-200, DTA-200 (the registration of the results cooperates with the countershaft of the A/C converter of the MEDSON Firm). In Table 3 the temperature range of the dehydration process for 5-chloro-2-nitrobenzoates of Y and the lanthanides are presented. The solubilities of 5-chloro-2-nitrobenzoates of Y, and the lanthanides in water at 298 K were determined by measuring the concentration of Ln^{3+} ions in saturated solution by means of the oxalic acid method. The solubility values are given in Table 3.

Results and discussion

The 5-chloro-2-nitrobenzoates of rare earth elements were obtained as crystalline products of the general formula: $Ln(C_7H_3NO_4Cl)_3$ or $Ln(C_7H_3NO_4Cl)_3\cdot nH_2O$ and a metal to ligand ratio of 1:3. The 5-chloro-2-nitrobenzoates of La–Nd were obtained as anhydrous salts, those of Y, Sm–Gd, Tm–Lu as monohydrates and those of Tb–Er as dihydrates (Table 1).

Table 1 Analytical data

Compound	H/%		C/%		N/%		Cl/%		*M*/%	
L=$C_7H_3NO_4Cl$	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$YL_3 \cdot H_2O$	1.55	1.62	35.64	35.67	5.94	5.89	15.06	14.95	12.57	12.60
LaL_3	1.21	1.25	34.10	34.02	5.68	5.72	14.41	14.39	18.79	18.72
CeL_3	1.21	1.30	34.04	34.14	5.67	5.72	14.38	14.44	18.93	18.53
PrL_3	1.21	1.33	34.01	34.20	5.66	5.78	14.37	14.35	19.01	18.93
NdL_3	1.20	1.28	33.86	33.92	5.64	5.74	14.30	14.28	19.39	19.33
$SmL_3 \cdot H_2O$	1.43	1.52	32.79	32.85	5.46	5.45	13.86	13.91	19.52	19.73
$EuL_3 \cdot H_2O$	1.42	1.55	32.72	32.70	5.45	5.50	13.83	13.99	19.73	19.75
$GdL_3 \cdot H_2O$	1.41	1.39	32.58	32.45	5.41	5.45	13.73	13.88	20.28	20.35
$TbL_3 \cdot 2H_2O$	1.63	1.61	31.70	31.65	5.28	5.32	13.39	13.52	19.99	20.16
$DyL_3 \cdot 2H_2O$	1.62	1.75	31.55	31.48	5.25	5.30	13.33	13.35	20.35	20.46
$HoL_3 \cdot 2H_2O$	1.62	1.62	31.50	31.62	5.25	5.22	13.31	13.53	20.61	20.63
$ErL_3 \cdot 2H_2O$	1.61	1.64	31.37	31.55	5.22	5.38	13.25	13.35	20.82	20.74
$TmL_3 \cdot H_2O$	1.39	1.45	32.00	31.92	5.33	5.42	13.52	13.58	21.50	21.39
$YbL_3 \cdot H_2O$	1.39	1.28	31.85	31.90	5.30	5.40	13.46	13.55	21.87	21.47
$LuL_3\,H_2O$	1.38	1.46	31.77	31.98	5.29	5.38	13.43	13.54	22.06	22.17

Similarly, the 2-nitrobenzoates of rare earth elements were obtained as mono- or dihydrates [2]. The number of waters of crystallization is not radically changed for both series of the above-mentioned complexes. In contrast, the 3-chlorobenzoates of rare earth elements form di-, tetra-, penta-, heptahydrates and some of them are anhydrous salts [3]. The colours of the 5-chloro-2-nitrobenzoates of lanthanides are typical of the Ln^{3+} ions while the colour of the 2-nitrobenzoates of those elements is yellow and is caused by the presence of NO_2 group in ortho position in the benzene ring. In these molecules the arrangement of the substituents is not coplanar with the benzene ring because of the steric effects caused by the NO_2 group in the ortho position [4]. The electrons of the NO_2 group are not conjugated with the ring Π electrons and thus they can be easily excited by visible light [4, 5]. In the molecules of the 5-chloro-2-nitrobenzoates of rare earth elements the f→f electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wavelength which depends on the nature of the metal ion. The colours of the complexes thus are typical of the corresponding trivalent ions. Similarly, the colour of the 3-chlorobenzoates of rare earth elements are typical of the Ln^{3+} ions [3].

The infrared spectrum of 5-chloro-2-nitrobenzoic acid shows the following absorption bands: a sharp band of the OH group at 3600 cm^{-1}, a strong band of COOH at 1716 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of the NO_2 group occurring at 1530 and 1350 cm^{-1}, respectively, the bands of ν(C–C) vibrations at 1608, 1572, 1416 and 1295 cm^{-1}, the bands of ν(C–H) vibrations at 3112, 1152, 980 cm^{-1} and the bands of ν(C–Cl) stretching vibrations at 760 and 725 cm^{-1}. The bands of skeleton vibrations appear at 695, 620, 560, 540 and 455 cm^{-1}. In the IR spectra of the 5-chloro-2-nitrobenzoates the band at 1716 cm^{-1} disappears, which confirms that no COOH group is present in the complexes. In these spectra (with the exception of those for La–Nd) the intense broad absorption bands at 3500–3100 cm^{-1} confirm the presence of water of crystallization. The bands arising from asymmetric and symmetric vibrations of the COO^- group occur at 1580–1550 cm^{-1} and 1400–1365 cm^{-1}, respectively. The bands at 1535–1530 cm^{-1} and 1355–1350 cm^{-1} are assigned to asymmetric and symmetric vibrations of the NO_2 group. They are not significantly shifted with respect to those of the parent acid and thus one must conclude that the NO_2 group is not coordinated to the metal ions, similarly as in the case of the 2-nitrobenzoates of rare earth elements [2, 6]. The ν(C–Cl) stretching vibration occurs at 780–675 cm^{-1} and the bands at 480–464 cm^{-1} are assigned to the metal-oxygen ionic bond. These bands are regularly shifted to higher frequencies in the series of lanthanide elements. It suggests that probably the degree of covalency of the M–O bond increases with increasing atomic number of the element. The smaller the ionic radius, the larger the ionic potential that may cause the ligand to form a stronger M–O bond which leads to a higher band frequency. The comparison of the M–O bond stabilities seems justified because the 5-chloro-2-ni-

Table 2 Freqencies of maxima of the absorption bands of COO^- group vibrations, ν_{C-Cl} and ν_{M-O} vibrations for 5-chloro-2-nitrobenzoates of rare earth elements and sodium (cm^{-1})

Complex $L=C_7H_3NO_4Cl$	ν_{asCOO^-}	ν_{sCOO^-}	$\Delta\nu$	ν_{C-Cl}	ν_{M-O}
$YL_3 \cdot H_2O$	1580	1390	190	700–675	480
LaL_3	1550	1380	170	770–745	464
CeL_3	1555	1380	175	765–745	466
PrL_3	1550	1380	170	765–745	468
NdL_3	1550	1365	185	775–750	469
$SmL_3 \cdot H_2O$	1565	1375	190	775–755	470
$EuL_3 \cdot H_2O$	1550	1385	165	760–745	472
$GdL_3 \cdot H_2O$	1555	1380	175	760–735	472
$TbL_3 \cdot 2H_2O$	1575	1380	195	760–695	474
$DyL_3 \cdot 2H_2O$	1575	1380	195	765–700	475
$HoL_3 \cdot 2H_2O$	1580	1385	195	780–700	476
$ErL_3 \cdot 2H_2O$	1575	1385	190	765–695	478
$TmL_3 \cdot H_2O$	1580	1395	185	765–695	478
$YbL_3 \cdot H_2O$	1580	1395	185	765–700	480
$LuL_3 \cdot H_2O$	1580	1400	180	775–700	480
NaL	1600	1360	240	770–705	480

trobenzoates of rare earth elements are compounds of the same type [2, 7]. The bands of skeleton vibrations are shifted to lower frequencies (680, 610, 550, 530, 440 cm^{-1}) compared to those in the acid. The changes in their positions are caused by the interaction between aromatic ring vibrations and the groups of atoms and ions. In the IR spectra of the complexes the bands of ν_{asCOO^-} are shifted to lower frequencies whereas the bands of ν_{sCOO^-} are shifted to higher frequencies compared to those of the sodium salt (Table 2).

Therefore it is possible to assume that the carboxylate ion is a bidentate chelating ligand [8, 9]. In the case of the 2-nitrobenzoates and 3 chlorobenzoates of Y and the lanthanides the carboxylate ion is also a bidentate, chelating ligand [2, 9, 10]. The magnitudes of separation, Δν, between the frequencies due to ν_{asCOO^-} and ν_{sCOO^-} in rare earth 5-chloro-2-nitrobenzoates indicate a lower degree of ionic bond in these complexes compared to the sodium salt. Having a greater ionic potential than a sodium ion, lanthanide ions have a stronger deforming effect on the ligand. In order to verify that the prepared rare earth 5-chloro-2-nitrobenzoates are not converted to the nitrito isomers (during precipitation or on heating to 573 K), the IR spectra of the hydrates of the 5-chloro-2-nitrobenzoates of Y and the rare earth elements and of the dehydrated complexes and also of sodium nitrite were recorded. A survey of the literature shows that under the influence of sunlight or with rising temperature the nitro complexes may be transformed to the nitrito analogues in an endothermic process [11]. It was found that the isomerization of the nitro group may accompany the dehydration process of the complex or be connected with the transformation process in its inner sphere [12]. As a monodentate ligand, nitrite ion may be bonded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrito complex. The general effect of coordination via nitrogen is a rise in the frequencies of both $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ compared to the values for the free ion, ~1328 cm^{-1} and ~1260 cm^{-1}, respectively [13]. The IR spectra recorded for all the hydrated and dehydrated 5-chloro-2-nitrobenzoates of rare earth elements show that the nitro group is not transformed to the nitrito group with rising temperature. No bands confirming the isomerization of the nitro group through the oxygen atom are observed [12, 13].

From the X-ray spectra recorded for the 5-chloro-2-nitrobenzoates of rare earth elements it appears that they are crystalline compounds characterized by low symmetry, large size of the unit cells and different structures. Similarly, the 2-nitro- and 3-chlorobenzoates of those elements have the same crystalline properties [2, 10].

It follows from earlier studies on the thermal stability of the 5-chloro-2-nitrobenzoates of rare earth elements that like the 2-nitrobenzoates of those elements on heating these complexes are explosively decomposed when heated above 573 K [2]. In contrast, the 3-chlorobenzoates of the rare earth elements do not have explosive properties and they decompose in various ways [3]. The great thermal instability of the 2-nitrobenzoates and 5-chloro-2-nitrobenzoates of Y and rare earth elements is caused by the presence of the NO_2 group in the benzene ring [2, 14, 15]. The thermal stability of the 5-chloro-2-nitrobenzoates of Y and lanthanides was studied in the temperature range 273–523 K. The results reveal that the complexes of La–Nd are anhydrous compounds, those of Y, Sm–Gd, Tm–Lu are monohydrates and those of Dy–Er are dihydrates (Figs 1, 2 and Table 3). The hydrated 5-chloro-2-nitrobenzoates of rare earth elements lose the water of crystallization in one step in the temperature range 411–520 K. The process is connected with an endothermic effect as shown by the DTA curves [16]. The anhydrous 5-chloro-2-nitrobenzoates are formed at 463–523 K. The loss in weight is about 3% in the case of monohydrates, and about 5% in the case of dihydrates of 5-chloro-2-nitrobenzoates.

As examples, the TG, DTG and DTA curves of the Y and Lu complexes are presented in Figs 1 and 2. Considering the temperatures at which the dehydration takes place and the way in which it proceeds it is possible to assume that the

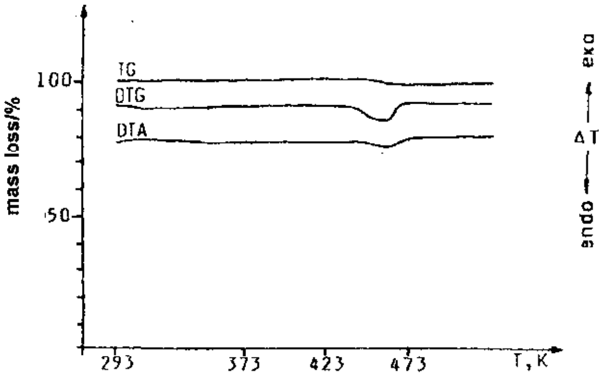

Fig. 1 TG, DTG and DTA curves of the 5-chloro-2-nitrobenzoate of Y

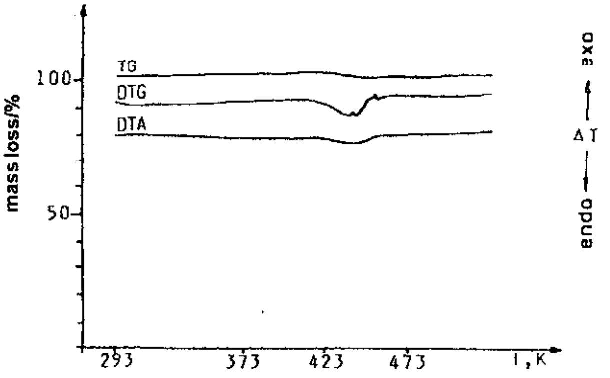

Fig. 2 TG, DTG and DTA curves of the 5-chloro-2-nitrobenzoate of Lu

water molecules form outer-sphere water. The hydrated complexes have various stabilities (Table 3, Fig. 3) changing regularly from Sm to Yb with decreasing ionic radii. It is the smallest for the ytterbium complex and the highest for the samarium one. The water molecule is the most weakly bound in the 5-chloro-2-nitrobenzoate of ytterbium and the most strongly in the complex of samarium. The temperatures of the endothermic peaks in the DTA curves decrease from Sm to *Ho with increasing atomic number of the elements (Fig. 3). The temperature of* formation of the anhydrous salt also decreases from Sm to Gd and Tb to Yb with decreasing ionic radii. The thermal stability of the 5-chloro-2-nitrobenzoates was compared with the 2-nitro- and 3-chlorobenzoates of those elements.

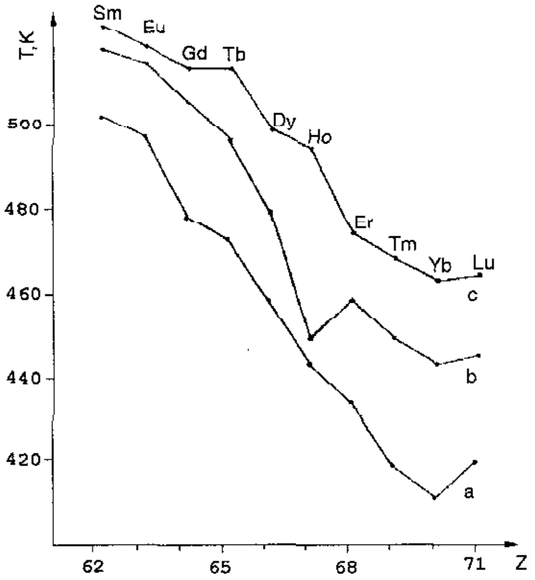

Fig. 3 Dependence of the: a) initial temperature of dehydration, b) T_{max} of the endothermic effects, c) temperature of formation of the anhydrous 5-chloro-2-nitrobenzoates of the lanthanides on the atomic number of the element, Z

2-Nitrobenzoates of rare earth elements are dehydrated in one or two steps [2]. Dihydrates of Y, La, Ce(III) and Pr(III) gradually lose water of crystallization in two steps, while the monohydrates of Nd, Sm, Eu(III) and Gd and the dihydrates of heavy lanthanides release water molecules of crystallization in one step. The thermally least stable complex is the hydrate of the ytterbium complex whereas the most stable is the 2-nitrobenzoate of Nd. In the temperature range from 435 K (for Yb) to 497 (for Dy) the anhydrous salts of rare earth elements are formed.

The 3-chlorobenzoates of rare earth elements decompose in two or three stages. The hydrates first lose some water molecules and then decompose to yield oxides through the intermediate LnOCl formation. Cerium(III) 3-chlo-

Table 3 Temperature range of the dehydration process of 5-chloro-2-nitrobenzoates of Y and lanthanides in air atmosphere with heating rate of 2.5°C min^{-1}

Complex L=$C_7H_3NO_4Cl$	ΔT / K	Mass loss/%		n*	T_{max}DTA/K	T_k/K	Solubility/ mol $dm^{-3}\cdot 10^{-3}$
		calcd.	found				
$YL_3 \cdot H_2O$	463–473	2.88	3.00	1	463.0	478	7.75
LaL_3	–	–	–	–	–	–	3.28
CeL_3	–	–	–	–	–	–	3.12
PrL_3	–	–	–	–	–	–	2.26
NdL_3	–	–	–	–	–	–	2.35
$SmL_3 \cdot H_2O$	501–520	2.47	2.27	1	518.0	523	2.49
$EuL_3 \cdot H_2O$	496–519	2.46	2.80	1	514.0	518	2.56
$GdL_3 \cdot H_2O$	478–515	2.44	2.60	1	504.0	513	2.83
$TbL_3 \cdot 2H_2O$	472–507	4.77	4.64	2	496.3	513	3.56
$DyL_3 \cdot 2H_2O$	458–494	4.74	4.60	2	478.0	498	4.36
$HoL_3 \cdot 2H_2O$	443–482	7.73	4.62	2	448.0	493	5.50
$ErL_3 \cdot 2H_2O$	434–470	4.71	4.50	2	458.0	473	7.08
$TmL_3 \cdot H_2O$	419–461	2.41	2.50	1	449.6	468	1.29
$YbL_3 \cdot H_2O$	411–453	2.39	2.19	1	443.0	463	1.30
$LuL_3 \cdot H_2O$	419–455	2.39	2.49	1	444.0	465	1.22

*n – loss of H_2O molecules
T_{max} DTA
T_k – Temperature of formation of anhydrous salt

robenzoate loses its water of crystallization in two stages and yields the anhydrous salt which is then decomposed directly to CeO_2. All these complexes melt before decomposition [3]. The solubilities of the 5-chloro-2-nitrobenzoates of Y and the rare earth elements in water at 293 K were measured and they are in the order of 10^{-3} mol dm^{-3}. The order of magnitude of the solubility for 5-chloro-2-nitrobenzoates is smaller than the value of the dissociation constant of 5-chloro-2-nitrobenzoic acid which is equal to $1.52\cdot 10^{-2}$. The 5-chloro-2-nitrobenzoate of yttrium is the most soluble salt while that of lutetium is the least soluble. The solubility decreases from Ce to Pr and next to Er increases and again decreases to Tm. From Tm to Yb the solubility increases and then decreases to Lu (Table 3). The solubilities of the 2-nitrobenzoates of Y and the rare earth elements are in the order of 10^{-2} mol dm^{-3} and those for the 3-chlorobenzoates in the order of 10^{-4} mol dm^{-3} [2, 10]. They increase in order:

3-chloro- < 5-chloro-2-nitro- < 2-nitro-

The order of magnitude of the solubility for 2-nitrobenzoates is higher than that of the dissociation constant of the parent acid ($6.2\cdot 10^{-3}$). In comparison with the 3-chlorobenzoates, the presence of NO_2 group in the benzene ring causes an increase in the solubilities, whereas the presence of Cl substituent in the benzene ring causes a decrease compared to 2-nitrobenzoates. The presented relationship of the solubility values of the complexes is connected with the different electron densities in the molecules of the compounds which cause their different degrees of dissociation in water.

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