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Spectral and Thermal Studies of Light Lanthanide Complexes with 4-Methoxy-3-nitrobenzoic Acid

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4-Methoxy-3-nitrobenzoates of light lanthanides with a metal to ligand ratio of 1:3 have been obtained as hydrated salts. They have colours typical of Ln^{3+} ions (Pr-green, Nd-pink, Sm-cream, and La, Ce, Eu and Gd-white). The carboxylate group appears to be a bidentate chelating ligand. 4-Methoxy-3-nitrobenzoates of light lanthanides are crystalline compounds. During heating in air, they decompose explosively. Therefore, their thermal stability was studied in the temperature range 273–523 K. The complexes dehydrate in one or three steps. The solubilities of complexes were measured in water at 293 K. They are in the order of 10^{-4} mol dm^{-3}.

Key words: light lanthanides, 4-methoxy-3-nitrobenzoates, rare earth complexes, spectra, synthesis, thermal studies

INTRODUCTION

4-Methoxy-3-nitrobenzoic acid, $C_8H_7O_5N$, is a cream-yellow, crystalline solid, sparingly soluble in water and readily soluble in hot alcohol and ether.[1] Being crystallized from water, it forms needles. Its melting point is equal to 186–189 °C. The compounds of 4-methoxy–3-nitrobenzoic acid are not well-known. It is known from literature that its complexes have been obtained only with the following cations:[1] Na^+, K^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+}. 4-Methoxy-3-nitrobenzoates of Na and K are monohydrates, those of Ca and Sr are tetrahydrates while those of Ag, Ba and Pb are anhydrous salts. There is no information in the literature about the complexes of 4-methoxy-3-nitrobenzoic acid with light lanthanide elements. Therefore, we decided to obtain them as solids and to examine some of their physicochemical properties, including their thermal characterization during heating in air to 523 K and also their solubility in water at 293 K. The properties of 4-methoxy-3-nitrobenzoates of light lanthanides were compared with those of 3-nitro- and 4-methoxybenzoates of lanthanide elements.[2–4] The comparison allows us to estimate the influence of the position of substituents in aromatic ring on the properties of the complexes. Thermal stability investigations enable to evaluate the assumed position of water molecules in the outer or inner spheres of coordination, to know the mechanism of complex decomposition and to determine the *endo-* or *exo-* effects. Determination of the solubility is valuable because it gives information about the practical use of the acids for the separation of rare earth elements by extraction or ion-exchange chromnatography methods.

EXPERIMENTAL

4-Methoxy-3-nitrobenzoates of light lanthanides were prepared by adding equivalent quantities of 0.1 M ammonium 4-methoxy-3-nitrobenzoate (pH ~ 5) to a hot solution containing light lanthanide chlorides. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant weight. The carbon, hydrogen and nitrogen contents were determined by elemental analysis using a Perkin Elmer CHN 2400 analyzer. The contents of light lanthanides were analyzed by oxalic acid method (Table I).

In order to confirm the chemical composition of the salts, the IR spectra of the hydrated and dehydrated complexes, the spectra of 4-methoxy-3-nitrobenzoic acid, its sodium salt and sodium nitrite were run in the range 4000–400 cm^{-1} using a SPECORD M–80 spectrophotometer. Samples were prepared as KBr discs Table II.

TABLE I

Elemental analysis of 4-methoxy-3-nitrobenzoates of light lanthanides

Complex	% H		% C		% N		% Ln	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$LaL_3 \cdot 6H_2O$	3.62	3.48	34.50	34.03	5.03	5.04	16.64	16.15
$CeL_3 \cdot 0.5H_2O$	2.59	2.52	39.08	38.94	5.69	5.60	18.99	18.74
$PrL_3 \cdot H_2O$	2.69	2.54	38.57	38.54	5.62	5.50	18.85	18.51
$NdL_3 \cdot H_2O$	2.68	2.53	38.40	38.40	5.59	5.54	19.21	19.06
$SmL_3 \cdot 2H_2O$	2.86	2.58	37.20	37.20	5.42	5.42	19.41	19.36
$EuL_3 \cdot H_2O$	2.66	2.52	38.01	38.08	5.54	5.48	20.04	19.63
$GdL_3 \cdot 4H_2O$	3.19	3.02	35.12	35.39	5.12	5.54	19.23	19.16

L = $C_8H_6O_5N$

TABLE II

Frequencies of the absorption bands of COO^- and NO_2 group vibrations for 4-methoxy-3-nitrobenzoates of light lanthanides and sodium, and of CO and NO_2 for 4-methoxy-3-nitrobenzoic acid (ν / cm^{-1})

Complex	ν(C=O)	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$(OCO)	ν_{as}(NO_2)	ν_s(NO_2)	$\Delta\nu$(NO_2)	ν(M–O)
$LaL_3 \cdot 6H_2O$	–	1595	1415	180	1545	1365	180	525
$CeL_3 \cdot 0.5H_2O$	–	1590	1410	180	1540	1365	175	535
$PrL_3 \cdot H_2O$	–	1590	1410	180	1540	1370	170	540
$NdL_3 \cdot H_2O$	–	1590	1410	180	1540	1365	175	540
$SmL_3 \cdot 2H_2O$	–	1600	1420	180	1540	1365	175	545
$EuL_3 \cdot H_2O$	–	1595	1415	180	1540	1370	170	545
$GdL_3 \cdot 4H_2O$	–	1595	1420	175	1545	1365	180	550
NaL	–	1610	1425	185	1545	1365	180	520
HL	1700	–	–	–	1540	1360	180	–

L = $C_8H_6O_5N$

X-ray diffraction patterns of the complexes were measured on a DRON-2 diffractometer using CuK_α radiation. The measurements were performed within the range 2Θ = 5–80° according to the Deby-Scherrer-Hull method.

TABLE III

Temperature range of the dehydration process of 4-methoxy–3-nitrobenzoates of light lanthanides in air atmosphere and their solubilities in water at 293 K

Complex	ΔT / K	Loss of mass / %		n	Dehydration product	Ea	Solubility
		Calcd.	Found			kJ mol^{-1}	mol dm^{-3}
$LaL_3 \cdot 6H_2O$	320–405	12.94	12.71	6	LaL_3	40.0	2.710^{-4}
$CeL_3 \cdot 0,5H_2O$	410–450	1.22	1.35	0.5	CeL_3	83.6	3.110^{-4}
$PrL_3 \cdot H_2O$	420–450	2.41	2.25	1	PrL_3	71.5	3.510^{-4}
$NdL_3 \cdot H_2O$	420–458	2.40	2.10	1	NdL_3	98.4	4.210^{-4}
$SmL_3 \cdot 2H_2O$ (I stage)	348–383	1.66	1.20	0.5	$SmL_3 \cdot 1.5H_2O$	37.5	4.810^{-4}
$SmL_3 \cdot 1.5H_2O$ (II stage)	410–450	3.48	3.33	1.0	$SmL_3 \cdot 0.5H_2O$	88.9	
$SmL_3 \cdot 0.5H_2O$ (III stage)	454–510	4.65	4.53	0.5	SmL_3	63.4	
$EuL_3 \cdot H_2O$	410–448	2.37	2.52	1	EuL_3	89.8	5.210^{-4}
$GdL_3 \cdot 4H_2O$	355–425	8.78	9.04	4	GdL_3	54.4	5.510^{-4}

L = $C_8H_6O_5N$

ΔT = temperature range of dehydration process,

n = number of crystallization water molecules being lost in one or three endothermic steps,

Ea = energy activation of dehydration reaction

The thermal decomposition of the complexes in air in the range 273–523 K was determined with the Paulik-Paulik-Erday Q-1500D derivatograph with Derill convertor of the MOM Budapest Firm, recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1}. The 100 mg samples were heated in platinum crucibles in static air to 523 K with a sensitivity TG = 50 mg. DTG and DTA sensitivities were regulated by the computer Derill programme worked out by MOM the Budapest Firm (Table III, Figure 1). The products of dehydration were calculated from TG curves and verified by the diffraction pattern registration and IR spectra.

The solubilities of complexes in water at 293 K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic acid method (Table III).

RESULTS AND DISCUSSION

4-Methoxy-3-nitrobenzoates of light lanthanides were obtained as crystalline products of the general formula: $Ln(C_8H_6O_5N)_3 \cdot nH_2O$ (where n = 0.5; 1; 2; 4 and 6) (Table I). 4-Methoxy-3-nitrobenzoates of Pr, Nd and Eu are monohydrates, those of Sm, Gd and La are dihydrate, tetrahydrate and hexahydrate, respectively. Only the complex of cerium 4-methoxy-3-nitrobenzoate forms hemihydrate.

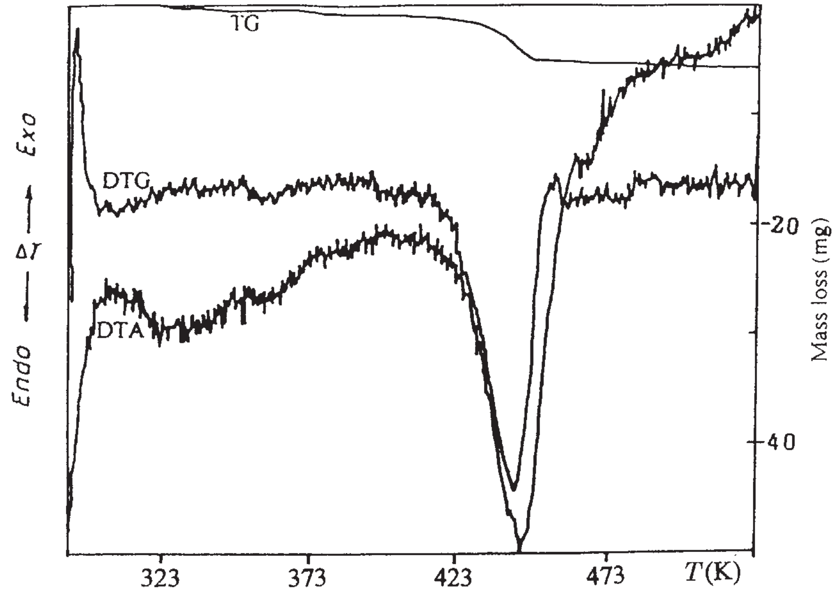

Figure 1. TG, DTG and DTA curves of praseodymium 4-methoxy–3-nitrobenzoate.

3-Nitrobenzoates of Y, Pr-Gd contain two water molecules while those of La and Ce two and a half.[2] The 4-methoxybenzoates of light lanthanides form hydrates (La, Ce) or anhydrous salts (Pr-Gd).[3,4]

The colours of 4-methoxy-, 3-nitro- and 4-methoxy-3-nitrobenzoates of light lanthanides are typical of Ln^{3+} ions[2–4] (it means: Pr-green, Nd-pink, Sm-cream and La, Ce, Eu and Gd-white), which is connected with the similar electron density in the complexes. Probably, in these molecules, the f→f electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave-lengths, depending on the nature, of the metal ion.[5–11] 4-Methoxy-3-nitrobenzoates of light lanthanides show similar IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salts. Table II presents the frequencies of typical absorption bands arising from asymmetric and symmetric vibrations of COO^- and groups and metal-oxygen bond for 4-methoxy-3-nitrobenzoates of light lanthanides and sodium, and of CO group for 4-methoxy-3-nitrobenzoic acid.[12–17] In the IR spectra of light lanthanide 4-methoxy-3-nitrobenzoates, the band at 1700 cm^{-1} completely disappears, which confirms that no COOH group is present in the complexes. In these spectra, the intense broad absorption bands at 3580–3110 cm^{-1} and strong bands at 1630–1620 cm^{-1} confirm the presence of crystallization water. The bands resulting from asymmetric and symmetric vibrations of $–O–CH_3$ group occur at 2960–2955 cm^{-1} and 2870–2860 cm^{-1}, respectively.[12–17] The bands due to asymmetric and symmetric NO_2 group vibrations are not significantly shifted with respect to those of the parent acid, thus one may conclude that the group does not coordinate with metal ions, similarly as in the case of 3-nitrobenzoates of light lanthanide elements.[2] In 4-methoxy-3-nitrobenzoates, the bands confirming M-O vibrations are being shifted to higher frequencies with increased atomic number of the element. It may suggest that 4-methoxy-3-nitrobenzoic acid forms with light lanthanides complexes of increasingly greater stability. For 3-nitrobenzoates of rare earth elements, the bands of M-O appear in the range 425–410 cm^{-1}.[2] The frequencies are lower compared to those of 4-methoxy-3-nitrobenzoates of rare earth elements (Table II). This difference is connected with the presence of $–O–CH_3$ group in *para* position and with the stronger influence of inductive and mesomeric effects of nitro group on electron density in 4-methoxy-3-nitrobenzoate molecules than in 3-nitrobenzoates. In 4-methoxy-3-nitrobenzoates of light lanthanides, the M-O bands are stronger than in the case of 3-nitrobenzoates. The bands of skeleton and of $–O–CH_3$ group vibrations in the IR spectra of light lanthanide 4-methoxy-3-nitrobenzoates are shifted to lower frequencies compared to those in the parent acid. The changes in their position are probably caused by the interaction between aromatic ring vibrations and $–O–CH_3$ group with groups of atoms or ions.

In the IR spectra of 4-methoxy-3-nitrobenzoates, two bands due to asymmetric, ν_{as}, and symmetric, ν_{s}, vibrations of COO^- group are shifted to lower frequencies than those for sodium salt. Accordingly, it is possible to assume that the carboxylate ion is a bidentate, chelating ligand.[12–14, 18] In 3-nitro- and 4-methoxybenzoates of rare earth elements, the carboxylate ion is also a bidentate, chelating ligand.[2–4] The magnitude of separation, $\Delta\nu_{\mathrm{OCO}^-}$, between the frequencies due to ν_{asOCO^-} and ν_{sOCO^-} in the light lanthanide 4-methoxy-3-nitrobenzoates indicates a lower degree of ionic bond in these complexes compared to the sodium salt.

In order to verify whether the obtained light lanthanide 4-methoxy-3-nitrobenzoates convert to the nitrito isomers (during precipitation or on heating) the IR spectra for hydrates of 4-methoxy-3-nitrobenzoates of light lanthanides, of dehydrated complexes and of sodium nitrite were recorded. A survey of the literature shows that, under influence of sunlight or, with an increase of temperature, the transformation process of nitro complexes to nitrito ones may occur.[19,20] It was found that isomerization of nitro group may accompany the dehydration process of the complex or it may be connected with the transformation process in its inner sphere.[20] As a monodentate the nitrite ion may bond either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrito one. The general effect of coordination via nitrogen is to rise the frequencies of both $\nu_{\mathrm{as(NO_2)}}$ and $\nu_{\mathrm{s(NO_2)}}$ from the free ion values ~ 1328 cm^{-1} and 1260 cm^{-1} to higher values.[21] The IR spectra of 4-methoxy-3-nitrobenzoates of light lanthanides isolated as solids show these frequencies at 1545–1540 cm^{-1} and 1370–1365 cm^{-1}, respectively (Table II).

The IR spectra recorded also for 3-nitrobenzoates of rare earth elements show that no transformation process of nitro group to nitrito takes place with rising temperature.[2,20,21]

From the X-ray powder diffraction of 4-methoxy-3-nitrobenzoates of light lanthanides it follows that the complexes are polycrystalline compounds. However, their structures have not been determined since their single crystals have not been obtained.

On heating in air, 4-methoxy-3-nitro- and 3-nitrobenzoates of light lanthanides decompose explosively above 523 K.[2] Their instability is caused by the presence of the group in benzene ring.[2,9] Contrary to them, 4-methoxybenzoates of rare earth elements are not decomposed in this way.[3,4] The thermal stability of 4-methoxy–3-nitrobenzoates of light lanthanides was studied in the range 273–523 K. The results obtained from their thermal decomposition reveal them to be hydrates containing various molecules of crystallization water, as it was established on the basis of elemental analysis (Tables I, III). All complexes are stable in air at room temperature and do not change their mass after storage. When heated at 273–523 K, they dehydrate in various ways. 4-Methoxy-3-nitrobenzoates of La-Nd, Eu and Gd lose crystallization water molecules in one step (320–458 K) and form anhydrous complexes. The dehydration process is connected with an endothermic effect shown in DTA curves.[22,23] The values change according to the appropriate amounts of water molecules in these complexes. The complex of samarium is decomposed in three steps. At first, it loses only half a molecule of water and then gradually one and finally a half to form the anhydrous complex. In the case of the decomposition of praseodymium 4-methoxy-3-nitrobenzoate (Figure 1), the weight loss starting at 420 K corresponds to the beginning of the dehydration process that takes place in the range 420–450 K. The strong DTG peak connected with weight loss is observed and endothermic effect also appears in the DTA curve. Next, above 450 K, the TG curve gains a constant level, which is indicative of the anhydrous complex formation. Considering the temperatures at which the dehydration process takes place and the way in which it proceeds, it is possible to assume that the molecules of crystallization water are of the outer-sphere water. According to Nikolaev *et al.*[24] and Singh *et al.*[25], water eliminated below 423 K can be considered as crystallization water whereas the water eliminated above 423 K may be that coordinated to the central ion. In our investigations, water is assumed to be crystallization water (with the exception of hemihydrate of samarium complex). This was also confirmed by IR studies.

From TG and DTA curves, the activation energies of dehydration reactions were calculated by the Fatieev and Pletniev method[26] using equation:

$$Ea = \frac{RT_{\max}^{2}}{m_0} \cdot \frac{\Delta m}{\Delta T}$$

where: R – gas constant; $T_{\max}$ – temperature of maximum weight loss; m_0 – weight loss at $T_{\max}$; m – weight loss at T, T – given temperature, $\Delta m = m_0 - m$, $\Delta T = T_{\max} - T$,.

The different values of activation energy may suggest that molecules of outer-sphere water are coordinated by different forces, depending on their position. The smallest value for samarium 4-methoxy–3-nitrobenzoate indicates that the water molecules are the most weakly coordinated whereas the highest value for neodymium complex shows that the water molecule is presumably the most strongly bound in complex coordination. From preliminary investigations on thermal properties of the complexes during their heating to 1173 K, it appears that they are ultimately decomposed to the oxides of respective metals. Oxides of lanthanides were identified by X-ray powder diffraction[27,28] and the measurements revealed them to be for La, Nd-Gd and CeO_2 and Pr_6O_{11}. In the case of 3-nitrobenzoates of rare earth elements, the initial dehydration temperature values are lower than those for 4-methoxy-3-nitrobenzaotes.[2] Hydrates of 4-methoxy-3-nitrobenzaotes are more stable than those of 3-nitrobenzoates, which is connected with the presence of methoxy- group in 3-nitrobenzoate ring that causes a decrease of electron density in aromatic ring.

The solubilities of 4-methoxy-3-nitrobenzoates of light lanthanides in water at 293 K were measured (Table III) and they are in the order of 10^{-4} mol dm^{-3}. The values of solubility increase with increasing atomic number of elements. The solubility order of light lanthanide 4-methoxy-3-nitrobenzoates is less than that determined for 4-methoxy- and 3-nitrobenzoates of those elements (10^{-3} mol dm^{-3}). The difference in the solubility values of the complexes is connected with the different electron densities established by the influence of the inductive and mesomeric effects in the molecules of the compounds, causing their different degrees of dissociation in water. The presence of $-O-CH_3$ group in 3-nitrobenzoate ring causes a decrease of solubility compared to 3-nitrobenzoates and also the presence of NO_2 group in 4-methoxybenzoate ring decreases the solubilities, compared to 4-methoxybenzoates. Taking into account the values of 4-methoxy-3-nitrobenzoate solubilities it is possible to state that 4-methoxy-3-nitrobenzoic acid cannot be used for the separation of rare earth elements by ion-exchange chromatography or extraction methods because it forms with rare earth elements complexes that are not easily soluble.

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SAŽETAK

Spektralna i termalna studija kompleksa lakih lantanoida s 4-metoksi-3-nitrobenzojevom kiselinom

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4-Metoksi-3-nitrobenzoati lakih lantanoida dobiveni su kao hidratne soli s omjerom metal : ligand = 1 : 3. Boje su im tipične za ione Ln^{3+} (Pr: zelen, Na: ružičast, Sm: žućkasto-bijel te La, Ce, Eu i Gd: bijeli). Karboksilna skupina javlja se kao bidentatan kelatni ligand. 4-Metoksi-3-nitrobenzoati lakih lantanoida kristalni su spojevi. Tijekom zagrijavanja na zraku, eksplozivno se raspadaju, pa je zato proučavana njihova toplinska stabilnost u rasponu od 273 K do 523 K. Kompleksi se dehidratiziraju u jednomu ili tri stupnja. Topljivosti kompleksa izmjerene u vodi pri 293 K, iznose oko 10^{-4} mol dm^{-3}.