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Complexes of Y, La, and Lanthanides with *m*-Aminobenzoic Acid

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Summary. *m*-Aminobenzoates of Y, La and lanthanides prepared in the reaction of the hydroxides of metal with *m*-aminobenzoic acid in solution have the general formula $Ln(m\text{-}C_6H_4NH_2COO)_3 \cdot nH_2O$ where $n = 4$ for Ho, Tm, $n = 5$ for Y, Sm, Dy, Er, Lu, and $n = 6$ for La-Nd, Eu, Gd, Tb, Yb. The water molecules in the hydrated compounds are in the outer coordination sphere. On heating in air at 350–410 K dehydration occurs and anhydrous *m*-aminobenzoates $Ln(m\text{-}C_6H_4NH_2COO)_3$ are formed. On the basis of the IR spectra it was found that the metal in hydrated *m*-aminobenzoate of lanthanides is simultaneously coordinated through amino- and carboxyl groups whereas in anhydrous *m*-aminobenzoates of lanthanides only trough the bidentate carboxyl group. From X-ray analysis it was stated that the hydrated *m*-aminobenzoates of lanthanides are isostructural in the whole range Y, La-Lu.

Keywords. Complexes; Lanthanides.

Komplexe von Y, La und Lanthaniden mit *m*-Aminobenzoesäure

Zusammenfassung. Zur Darstellung der Verbindungen des Typs $Ln(m\text{-}C_6H_4NH_2COO)_3 \cdot nH_2O$ (mit $n = 4$ für Ln = Ho, Tm, $n = 5$ für Ln = Y, Sm, Dy, Er, Lu und $n = 6$ für Ln = La-Nd, Eu, Gd, Tb, Yb) wurde die berechnete Menge von $Ln(OH)_3$ und $m\text{-}C_6H_4NH_2COOH$-Lösung bei 363 K gemischt und zur Kristallisation gebracht. Die Produkte wurden abfiltriert, mit Alkohol gewaschen und bis zur Gewichtskonstanz getrocknet. Die Verbindungen $Ln(m\text{-}C_6H_4NH_2COO)_3 \cdot nH_2O$ sind isostrukturell, mit geringer Löslichkeit in Wasser bei Raumtemperatur. Beim Erhitzen erfolgt zunächst Entwässerung bei 350–410 K, später bei 600–1 050 K unter Zersetzung zu CeO_2, Pr_6O_{11}, Tb_4O_7 und Ln_2O_3. Die Infrarotspektren der Verbindungen wurden registriert. Es wurde festgestellt, daß die Koordination der Seltenerdmetalle mit den Liganden sowohl durch Amino- als auch mit Carboxylgruppen erfolgt.

Introduction

In the previous papers the lanthanide complexes with *o*-aminobenzoic acid (anthranilic acid) have been investigated and it had been stated that the metal ions are coordinated through the nitrogen atom of the amino group and the oxygen atoms of the bidentate carboxyl group of the anthranilate ligands [1–4]. In this paper the rare earth element coordination compounds of *m*-aminobenzoic acid have been studied.

According to the latest research by Yoogd [19] the *m*-aminobenzoic acid molecules as in the case of *o*-aminobenzoic and *p*-aminobenzoic acid are of a nonzwitterionic form. However, in case of *m*-aminobenzoic acid the carboxyl group is somewhat disordered. The molecules are connected by hydrogen bonds between the carboxyl groups of the two different molecules in the asymmetric unit and are of the cyclic dimer type with O...O and N−H...O bonds.

According to the former data collected in the catalogue of Varsanyi [17], *m*-aminobenzoic acid as one of the three isomers has a dipolar form with COO^- and NH_3^+ groups. Because of this, the IR spectra of the acid have a quite different form than *ortho* and *para* isomers.

m-Aminobenzoic acid (which has two functional groups) forms a great number of complexes which have been investigated by many authors but the way of metal−ligand coordination is different with different authors.

Alyariya et al. [6] studied the infrared spectra of cadmium(II) compounds with *o*-, *m*- and *p*-aminobenzoic acid. They indicated that the metal ion was coordinated by nitrogen and oxygen atoms in the *o*-isomer but only by nitrogen in *m*- and *p*-isomers. The studies on Cr(III) complexes with *m*-aminobenzoic acid by Spitzyn [5] showed that metal was coordinated only through the bidentate carboxylate group. Aggarwal and Singh [7] prepared the tin(IV) coordination compounds of three isomers in many organic solvents and showed that coordination occured through nitrogen only. The compounds of *m*-aminobenzoic acid with thallium(I) were investigated by Lysiak [8] and Kharitonov [9], with platinum(IV) by Kukutshkin [10] with tetrahalides of germanium by Bielousova [11] and with lanthanum(III) acetates by Mangal [12]. Inomata and Makiwaki [13] obtained several divalent aminobenzoic acid coordination compounds and investigated their infrared spectra. They concluded that the metal compounds of *m*-aminobenzoic acid have a metal coordination both by nitrogen and oxygen atoms.

The aim of this paper is to obtain series of rare earth complexes with *m*-aminobenzoic acid, to determine some of their physico-chemical properties and to try to characterise the way of the metal-ligand coordination.

Experimental

m-Aminobenzoic acid coordination compounds were obtained by adding *m*-aminobenzoic acid solution at 363 K to newly precipitated coloidal hydroxides of Y, La and lanthanides with the molar ratio of the acid to Ln^{3+} 3 : 1. The precipitated compounds were filtered off, washed with alcohol and dried to constant weight under room conditions.

On the basis of elemental analysis the content of carbon, hydrogen and nitrogen was determined. The content of water was established by the derivatographic method from TG curves and from the weight loss while roasting the compounds to the oxides: Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 at 1 273 K. On the basis this results the formula of compound were stated (Table 1).

IR spectra of Na, Y, La and lanthanide compounds and aminobenzoic acid were recorded on a UR-20 spectrophotometer over the range 400–4 000 cm^{-1}. The samples were prepared as KBr discs. X-ray diffraction patterns were taken on a DRON-2 diffractometer using Ni filtered CuK_α radiation. The measurements were made by means of the powder Debye-Scherrer method within the range 2 Q = 5–60°.

Results and Discussion

On the basis of elemental analysis and the derivatograms recorded for *m*-aminobenzoates of lanthanides there was found the general formula: $Ln(m\text{-}C_6H_4NH_2COO)_3 \cdot nH_2O$ where $n = 4$ for Ln = Ho, Tm; $n = 5$ for Ln = Y, Sm, Er, Lu; $n = 6$ for Ln = La-Nd, Eu, Gd, Tb, Yb.

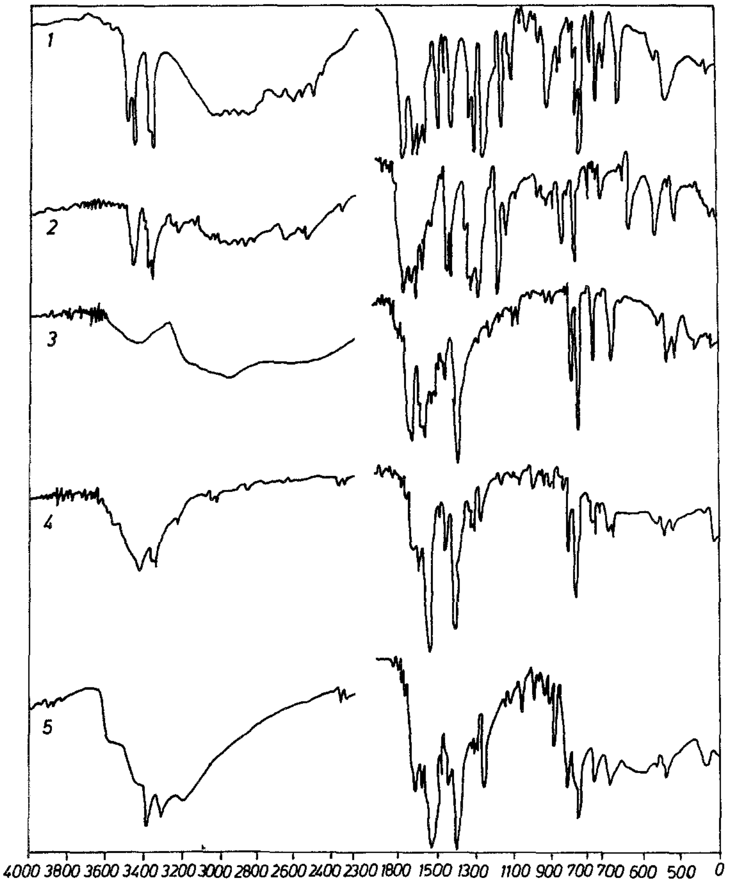

Fig. 1. The IR spectra of *1*: *ortho*; *2*: *para*; *3*: *meta*-aminobenzoic acid; *4*: sodium-*m*-aminobenzoate; *5*: neodymium *m*-aminobenzoate

The compounds were obtained in an elongated crystal form with a characteristic light violet colour. Their solubility is of the order of 0.4–1.0 g dm^{-3}. The compounds of La, Yb, Lu are better soluble in water than those of the remaining rare earth elements. In order to study the type of bonding between the ligand and metal ions and to elucidate the structure of compounds, the IR spectra were recorded. For interpretation of IR spectra the literature data on IR spectra of aminocarboxylic [6–13, 18] and carboxylic [14] acid compounds with various metals were used.

The aminobenzoic acids – *ortho, meta* and *para* can coordinate metal ions both by nitrogen of the NH_2 group and oxygen atoms of the carboxylate group. As a result the IR bands of carboxylate and amino groups of the complexes are shifted compared with IR bands of free acids [1, 3, 13, 16]. In IR spectra of *ortho* and *para* isomers in the range 3 300–3 500 cm^{-1}, sharp intensive symmetric and asymmetric valency bands of NH_2 group appear, but in case of *meta* isomer the spectrum in this range is quite different (Fig. 1), appearing as a broad band (ν_{OH+NH_3}), which may be due to an ionic form of the acid $^{-}O_2C-C_6H_4NH_3^+$ [17], resulting from shifting the proton from the carboxyl to the amino group. For this reason it is not possible to find out the existence of the N → *M* bond on the basis of the shifts of NH_2 bonds of the complexes in comparison with free acid bands as in the case of *ortho* isomers. However, the sodium salt spectrum of the *meta* isomer in which sharp absorption bands in the 3 345 and 3 430 cm^{-1} range belong to the vibrations of non-coordinated NH_2 group [18] should be used to detect NH_2 group bands shift. The form of IR spectra of lanthanide *m*-aminobenzoates are similar to each other and their absorption bands of $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ are displaced to lower frequencies in comparison to sodium salt. The values of the shifts equal about 30 cm^{-1} for symmetric and about 45–50 cm^{-1} for asymmetric vibrations, indicating the coordination of metal with the amino group in hydrated *m*-aminobenzoate of lanthanides. Values of shifts $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ for *m*-aminobenzoates of lanthanides are smaller than those obtained by Inomata and Makiwaki [13] for the complexes of d-electron metals, which are equal to about 170 cm^{-1}. This data may indicate the weaker $N \rightarrow M$ bond, which appears as a result of strong influence of the filled 5s 5p electron shells on 4f electrons of lanthanides. Similary the values of shift $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ of lanthanide anthranilates was 60–100 cm^{-1} [1], while for d-electron metal compounds it was about 150–180 cm^{-1} [19]. The low intensity of the absorption of the δ_{H_2O} band at 1 630 cm^{-1} and the low temperature of dehydration (350–410 K) show that water contained in lanthanide *m*-aminobenzoates is in the outer sphere of the complexes, as in the case of *o*-aminobenzoates [1, 3] and *p*-aminobenzoates of lanthanides [17]. After dehydration of lanthanide *m*-aminobenzoates the symmetric and asymmetric bands of NH_2 group have almost the same frequency as the sodium salt which indicates the lack of metal coordination through nitrogen in anhydrous complexes (Table 1).

The carboxyl group is another group taking part in bonding of *m*-aminobenzoic acid with lanthanides. Its characteristic bands in the IR spectra appear at 1 630 cm^{-1} for $\nu_s C{=}O$, 1 565 cm^{-1} for $\nu_{as}COO^-$ and 1 385 cm^{-1} $\nu_s COO^-$ (Table 1). The band at 1 630 cm^{-1} disappears in the IR spectra of the complexes, but the deformation vibration band of water molecules (δ_{H_2O}) appears in this range. As a result of metal coordination the bands $\nu_s COO^-$ at 1 565 cm^{-1} are displaced to higher and $\nu_{as}COO^-$ at 1 365 cm^{-1} to lower frequencies compared to those of the free acid in dipolar form [17].

The shift values are 25–35 cm^{-1}. The magnitude of separation $\Delta\nu$ between the frequencies due to $\nu_{as}OCO$ and $\nu_{as}OCO$ are about 130 cm^{-1} and are smaller than for the sodium salt (Table 1). This values and the direction of the shifts in IR frequences of ν_{as} OCO and $\nu_{as}OCO$ may be used [14] as a spectral criterion for the mode of carboxylate binding. The small value of $\Delta\nu$ may indicate the chelating or bridging bidentate type of bonding, but the direction of shifts: $\nu_{as}OCO$ to lower and $\nu_s OCO$ to higher frequencies indicate that the carboxyl group in *m*-aminobenzoate ligand exists as bidentate symmetric and chelating. On the basis of these results it can be said that the lanthanide ions coordinate the *m*-aminobenzoate

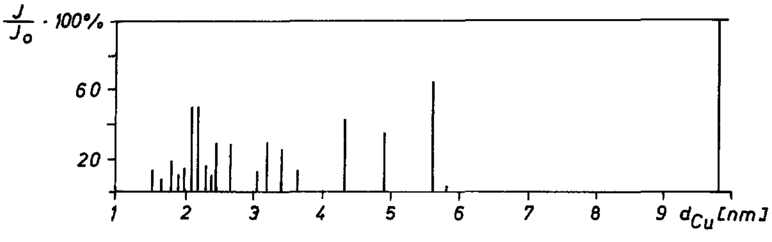

Fig. 2. Powder photograph of isostructural Y, La-Lu *m*-aminobenzoates

Table 1. Frequencies of absorption band of NH_2 and COO^- groups of *m*-aminobenzoic acid and its compounds

Compound	ν_s NH_2	$\Delta\nu$ NH_2[b]	ν_{as} NH_2	$\Delta\nu_{as}$ NH_2[b]	ν_s COO^-	$\Delta\nu_s$ COO^-[c]	ν_{as} COO^-	$\Delta\nu_{as}$ COO^-[c]	$\Delta\nu$ $\nu_{as}-\nu_s$
m-$C_6H_4NH_2COOH$	3 300 – 3 600				1 385	–	1 565	–	180
Na*L*[a]	3 345	–	3 430	–	1 405	+20	1 550	−15	145
Y$L_3 \cdot 6H_2O$	3 320	−25	3 383	−47	1 412	+27	1 540	−25	128
La$L_3 \cdot 6H_2O$	3 320	−25	3 385	−45	1 408	+23	1 530	−35	122
Ce$L_3 \cdot 6H_2O$	3 315	−30	3 385	−45	1 402	+17	1 530	−35	128
Pr$L_3 \cdot 6H_2O$	3 315	−30	3 385	−45	1 405	+20	1 530	−35	125
Nd$L_3 \cdot 6H_2O$	3 315	−30	3 380	−50	1 405	+20	1 530	−35	125
Sm$L_3 \cdot 5H_2O$	3 320	−25	3 385	−45	1 408	+23	1 535	−30	127
Eu$L_3 \cdot 6H_2O$	3 320	−25	3 385	−45	1 405	+20	1 535	−30	130
Gd$L_3 \cdot 6H_2O$	3 325	−20	3 385	−45	1 415	+30	1 540	−25	125
Tb$L_3 \cdot 6H_2O$	3 317	−28	3 380	−50	1 409	+24	1 533	−32	124
Dy$L_3 \cdot 5H_2O$	3 319	−26	3 385	−45	1 410	+25	1 540	−25	130
Ho$L_3 \cdot 4H_2O$	3 320	−25	3 383	−47	1 410	+25	1 540	−25	130
Er$L_3 \cdot 5H_2O$	3 315	−30	3 380	−50	1 410	+25	1 540	−25	130
Tm$L_3 \cdot 4H_2O$	3 315	−30	3 382	−48	1 412	+27	1 540	−25	128
Yb$L_3 \cdot 6H_2O$	3 315	−30	3 382	−48	1 410	+25	1 540	−25	130
Lu$L_3 \cdot 5H_2O$	3 315	−32	3 380	−50	1 410	+25	1 540	−25	130
LaL_3	3 350	+5	3 430	0	1 405	+20	1 530	−35	125
SmL_3	3 350	+3	3 430	0	1 400	+15	1 530	−35	130
GdL_3	3 350	+5	3 430	0	1 410	+25	1 540	−25	130
DyL_3	3 350	+3	3 430	0	1 405	+20	1 540	−25	135

[a] $L = C_6H_4NH_2COO^-$

[b] $\Delta\nu NH_2$ = shift of absorption band ν_{NH_2} compared with ν_{NH_2} of sodium *m*-aminobenzoate

[c] $\Delta\nu COO^-$ = shift absorption band ν_{COO^-} compared with ν_{COO^-} of free acid

ligands in hydrate complexes through the nitrogen atom of the NH_2 group and the oxygen atoms of the carboxylate group. Considering the chelating character bonding of metal through carboxyl group and the structure of the *m*-aminobenzoic ligand [19] it seems that each ligand has to coordinate two different lanthanide ions – one through the carboxyl, another through the amino group. In this situation each lanthanide ion (LK = 9) coordinates three ligands through the carboxylate group and three through the amino groups. This way of coordination is quite different than in the case of lanthanide anthranilates [1, 3].

In the anhydrous lanthanide *m*-aminobenzoates coordination of ligands by metal ion takes place only through the carboxylic group. The bonding seems to be also symmetric, bidentate and chelating. Coordination by NH_2 group is absent as in *ortho*- and *para*-aminobenzoates of lanthanides [1, 3, 16].

From the recordered diffractograms the *m*-aminobenzoates of lanthanides were found to be crystalline compounds with low symmetry and large sizes of the unit cells. The hydrated compounds are isostructural in the whole range Y, La-Lu (Fig. 2). The low temperature of dehydration of compounds shows that the water contained in them is in the outer sphere of the complexes.

The hydrated *m*-aminobenzoates of lanthanides are decomposed in two steps. At first in 350–410 K the dehydration process occurs and then the anhydrous compounds are decomposed, yielding oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 as a final products in the range of 600–1 050 K [20].

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