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Preparation and Study of Rare Earth 4-Aminosalicylates

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Summary. *p*-Aminosalicylates of Y, La and lanthanides prepared in the reaction of the ammonium *p*-aminosalicylate and lanthanide chlorides in solutions have the general formula $Ln(C_7H_6O_3N)_3 \cdot nH_2O$, where $n = 3$ for La, Ce; $n = 2$ for Pr, Nd, Sm, Eu; $n = 0$ for Y, Gd—Lu. Their solubilities in water are of the order of $10^{-3}\,\mathrm{mol\,dm^{-3}}$. Heating above 350–450 K leads to dehydration and decomposition at the same time. The IR and X-ray spectra for the obtained complexes were recorded. It was found that only complexes of La—Nd are crystalline compounds. The way of metal-ligand coordination is discussed.

Keywords. Lanthanides; Complexes; *p*-Aminosalicylates.

Darstellung und Charakterisierung der Komplexe von Seltenen Erdmetallen mit *p*-Aminosalicylsäure

Zusammenfassung. Zur Darstellung der Verbindungen des Typs $Ln(C_7H_6O_3N)_3 \cdot nH_2O$ (mit $n = 3$ für La, Ce; $n = 2$ für Pr, Nd, Sm, Eu; $n = 0$ für Y, Gd—Lu) wurde die berechnete Menge von Ammonium-*p*-aminosalicylat und $LnCl_3$-Lösungen bei *pH* 5.8 gemischt und zur Kristallisation gebracht. Ihre Wasserlöslichkeit bei 298 K ist in der Größenordnung $10^{-3}\,\mathrm{mol\,dm^{-3}}$. Beim Erhitzen erfolgt bei 350—450 K Entwässerung und Zersetzung zugleich. Die Infrarot- und Röntgenspektren der erhaltenen Komplexe wurden gemessen und dabei festgestellt, daß nur die La—Nd-Komplexe kristalline Verbindungen sind. Die Art der Koordination der Seltenerdmetalle mit den Liganden wird diskutiert.

Introduction

4-Aminosalicylic acid which has three functional groups forms a great number of complexes, but there is no uniform opinion concerning their structure in a solid state. Khudajerdiev [1] studied the IR spectra of iron *p*-aminosalicylate and indicated that the metal ion was coordinated through oxygen atoms of the carboxylic and probably through OH group.

Melnik [2] showed that in copper(II) 4-aminosalicylate coordination took place through the carboxylic as well as the amino group. Micera [3] also pointed out a large negative shift of the νNH_2 stretching frequencies showing that the amino group is involved in copper(II) coordination but Moore [4] on the basis of the NH_2 twisting frequency was of different opinion, namely that the amino groups were not involved in coordination of copper ions and that only the carboxylic group took part in the metal bonding. According to Azizov [5] in the *p*-aminosalicylate of manganese(II) the coordination occurs through the carbocylic group and the phenolic group does not take part in metal bonding, but it is not mentioned if the coordination through a nitrogen ion occurs. Investigating the complexes of some rare earth elements with different organic ligands Pirkes [6] gives the wavenumber of absorption bands of amino and carboxylic groups of neodymium *p*-aminosalicylate. On the basis of these data it can be said that coordination of neodymium occurs through the carboxylic and amino groups simultanously. Lapitskaya [7] reported about the La—Nd *p*-aminosalicylate complexes, determined their compositions and some properties. Moreover, no systematic studies of the lanthanide complexes with *p*-aminosalicylic acid have been reported.

The aim of this paper is to obtain experimental data concerning the structure of rare earth complexes with *p*-aminosalicylic acid, compare them with the previous results and attempt to solve the problem of metal-ligand coordination in these compounds on the basis of their IR spectra.

Experimental

The Y, La and lanthanide aminosalicylates were obtained by adding amonium aminosalicylate at *pH* 5.8 to lanthanide chlorides. The crystalline compounds were washed with water and dried at 303 K to constant weight.

The composition of the rare earth complexes was determined on the basis of elemental analysis of carbon, hydrogen and nitrogen, gravimetric analysis of metals by ignition of the complexes to the corresponding oxides and additionally by the derivatographic method from TG curves. It has been stated that the formulae of the compounds are: $Ln(C_7H_6O_3N)_3 \cdot nH_2O$, where $n = 3$ for La, Ce; $n = 2$ for Pr, Nd, Sm, Eu and $n = 0$ for Y, Gd—Lu.

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

Results and Discussion

4-Aminosalicylates of La, Ce, Pr, Nd are found to be crystalline compounds with low symmetry and are characterized by large sizes of the unit cells (Fig. 1). The remaining complexes from Sm to Lu and Y are non-crystalline. The contents of water in La—Nd complexes differs from that obtained by Lapitskaya [7]. The solubilities of compounds in water at 293 K are in the order of 10^{-3} mol dm^{-3} and change from $1.5 \cdot 10^{-3}$ to above $8 \cdot 10^{-3}$ mol dm^{-3} for light and are practically stable about $2 \cdot 10^{-3}$ mol dm^{-3} for heavy lanthanide complexes (Table 1). Hydrated compounds of La—Nd are stable until 418–443 K, Sm—Eu until 353 K, further heating leads to simultaneous dehydration and decomposition.

Anhydrous compounds of heavy lanthanides decompose in one step above 343 K forming the corresponding oxides [8]. In order to study the way of bonding between the ligand and lanthanide ion, the IR spectra of 4-aminosalicylic acid, sodium salt and lanthanide complexes of the acid were recordered. The IR spectral data for ligand, sodium and lanthanide compounds have been interpreted on the basis of the previously reported data concerning aminocarboxylic and carboxylic complexes. The assignements of main absorption bands in the IR spectra of acid, sodium salt and the obtained complexes are presented in Table 2.

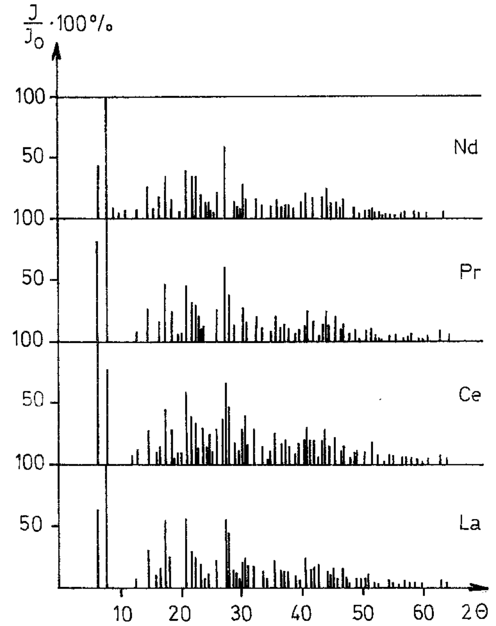

Fig. 1. Powder photograph of La(III), Ce(III), Pr(III), Nd(III) *p*-aminosalicylates

Table 1. Solubility of rare earth *p*-aminosalicylates in water at 293 K; $L = C_6H_3NH_2(OH)COO^-$

Complex	Solubility		Complex	Solubility	
	$g\,dm^{-3}$	$mol\,dm^{-3}\,10^{-3}$		$g\,dm^{-3}$	$mol\,dm^{-3}\,10^{-3}$
YL_3	0.88	1.61	TbL_3	0.14	0.23
$LaL_3 \cdot 3\,H_2O$	1.68	2.82	DyL_3	1.37	2.21
$CeL_3 \cdot 3\,H_2O$	1.37	2.29	HoL_3	0.87	1.40
$PrL_3 \cdot 2\,H_2O$	1.63	2.72	ErL_3	1.34	2.15
$NdL_3 \cdot 2\,H_2O$	2.12	3.52	TmL_3	1.49	2.38
$SmL_3 \cdot 2\,H_2O$	3.19	5.25	YbL_3	1.28	2.04
$EuL_3 \cdot 2\,H_2O$	4.37	7.19	LuL_3	1.24	1.96
GdL_3	5.28	8.61			

Comparison of the IR spectra of the ligand and 4-aminosalicylate of lanthanides shows that the broad band at 1 650–1 610 cm^{-1} due to $\nu_{C=O}$ and ν_{NH_2} vibrations becomes cleary less intensive and new bands due to complex formation appear at 1 590–1 560 cm^{-1} and 1 400–1 370 cm^{-1} which can be attributed to asymmetric and symmetric stretching vibrations of the COO^- ion, respectively. As a result of coordination of lanthanide ions, the bands $\nu_{as}COO^-$ are displaced to lower frequencies in comparison with sodium salt but the values of shifts are greater for light and smaller for heavy lanthanides (Table 2). The bands of symmetric vibrations $\nu_s COO^-$ are shifted to higher frequencies for La—Nd and to lower for Sm to Lu and Y complexes. The value of the energy differences of their vibration: $\nu_{as} - \nu_s$ is also about 170 cm^{-1} for La—Nd complexes and about 200 cm^{-1} for remaining complexes, which is the same as for the sodium salt. On the basis of these results one can expect another way of coordination in La—Nd complexes than in the remaining

Table 2. Frequencies of absorption band of COO^-, OH and NH_2 groups of *p*-aminosalicylic acid and its compounds

Compound	$\nu_s COO^-$	$\Delta \nu_s$[b]	$\nu_{as} COO^-$	$\Delta \nu_{as} COO^-$	$\nu_{as} - \nu_s$	δ_{OH}	$\Delta \delta_{OH}$[c]	ν_{COH}	$\Delta \nu_{COH}$[c]	δ_{OH}	$\Delta \delta_{OH}$[c]	$\delta_{tw.} NH_2$	$\nu_s NH_2$	$\nu_{as} NH_2$
H*L*[a]	—	—	—	—		885	—	1 290	—	1 445	—	1 170	3 385	3 490
Na*L*	1 365 1 390	—	1 570 1 595	—	205 205	887	+ 2	1 300	+ 10	1 453	+ 8	1 170	3 000	3 600
YL_3	1 380	− 10	1 550 1 580	− 20 − 15	200	850	− 35	1 300	+ 10	1 460	+ 15	1 168	3 380	3 400–3 490
La$L_3 \cdot 3H_2O$	1 375 1 400	+ 10 + 10	1 550 1 575	− 20 − 20	175 175	840	− 45	1 302	+ 12	1 452	+ 7	1 168	3 380	3 470
Ce$L_3 \cdot 3H_2O$	1 378 1 402	+ 12 + 12	1 570 1 578	− 20 − 18	172 176	840	− 45	1 305	+ 15	1 453	+ 8	1 168	3 380	3 470
Pr$L_3 \cdot 2H_2O$	1 378 1 400	+ 13 + 10	1 550 1 578	− 20 − 18	172 178	840	− 45	1 302	+ 12	1 452	+ 7	1 168	3 380	3 470
Nd$L_3 \cdot 2H_2O$	1 375 1 400	+ 10 + 10	1 550 1 575	− 20 − 20	175 175	850	− 35	1 305	+ 15	1 450	+ 5	1 163	3 380	3 400–3 490
Sm$L_3 \cdot 2H_2O$	1 380	− 10	1 550 1 580	− 20 − 15	200	850	− 35	1 300	+ 10	1 450	+ 5	1 165	3 380	3 400–3 490
Eu$L_3 \cdot 2H_2O$	1 380	− 10	1 550 1 580	− 20 − 15	200	845	− 40	1 305	+ 15	1 452	+ 7	1 165	3 385	3 400–3 490

Table 2 (continued)

Compound	$\nu_s COO^-$	$\Delta \nu_s$[b]	$\nu_{as} COO^-$	$\Delta \nu_{as} COO^-$	$\nu_{as} - \nu_s$	δ_{OH}	$\Delta \delta_{OH}$[c]	ν_{COH}	$\Delta \nu_{COH}$[c]	δ_{OH}	$\Delta \delta_{OH}$[c]	$\delta_{tw.} NH_2$	$\nu_s NH_2$	$\nu_{as} NH_2$
GdL_3	1 380	− 10	1 570 1 590	0 − 5	210	845	− 40	1 304	+ 14	1 455	+ 10	1 165	3 380	3 400–3 490
TbL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 302	+ 12	1 465	+ 20	1 170	3 385	3 400–3 490
DyL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 302	+ 12	1 465	+ 20	1 170	3 385	3 400–3 490
HoL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 300	+ 10	1 465	+ 20	1 170	3 380	3 400–3 490
ErL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 305	+ 15	1 465	+ 20	1 170	3 385	3 400–3 490
TmL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 302	+ 12	1 465	+ 20	1 170	3 385	3 400–3 490
YbL_3	1 385	− 5	1 560 1 590	− 10 − 5	205	850	− 35	1 302	+ 12	1 465	+ 20	1 170	3 390	3 400–3 490
LuL_3	1 387	− 3	1 560 1 590	− 10 − 5	203	850	− 35	1 305	+ 15	1 468	+ 22	1 170	3 385	3 400–3 490

[a] $L = C_6H_3NH_2(OH)COO^-$

[b] Shift of absorption bands ν_s and $\nu_{as} COO^-$ compared with bands of sodium *p*-aminosalicylate

[c] Shift of absorption bands of the OH group compared with the bands of the free acid

ones, which can also be confirmed by the fact that La—Nd complexes are crystalline whereas the others are not. Taking into consideration also the papers of Manhas [9] and Moore [4] it can be said that the carboxyl group appears more probably as bidentate in La—Nd complexes and is monodentate in Sm—Lu and Y complexes, but generally it is not possible to state the mode of lanthanide ion bonding through the carboxyl group on the basis of IR spectra. This is due to the fact that IR spectra of the complexes contain not only one band corresponding to both symmetric and asymmetric COO^- vibrations. There are two bands of ν_s COO^- in the case of La, Ce, Pr, Nd complexes and the $\nu_{as}COO^-$ band is splitted into two for all complexes (Table 2). Similarily in the case of lanthanide salicylates, Lewandowska [10] showed also a few bands of ν_s and ν_{as} carboxylic group vibrations and on the other hand Burns [1] determined the structure of La, Nd and Sm salicylates. It was shown that one salicylate ion is bidentate through its carboxyl group, another is bidentate through the combination of carboxylic and phenolic oxygens and four others are monodentate through the carboxylic oxygens. On the basis of this [10, 11] and our results it can be said that also non-equivalent bonds between lanthanides and carboxylic groups of the aminosalicylic ligand are formed.

In the IR spectra of free acid there are a few bands due to the phenolic groups (Fig. 2). The first of them is a broad band in the 3 200–2 400 cm^{-1} region which may be assigned to the intramolecular hydrogen bonding between the carboxylic and phenolic groups in the acid molecules [14]. This band disappears in the IR complex spectra indicating the rupture of the H-bonding in the lanthanide complexes. The deformation bands δ_{OH} at 885 cm^{-1} in the free acid and sodium salt are shifted about 40 cm^{-1} to the lower frequencies in the lanthanide complexes. Khudajerdiev stated that it might be a result of strong hydrogen bonding disappearance in the ligand molecule rather than participation of the phenolic group in metal coordination [1].

The strong and sharp valency vibration band of the OH group at 1 290 cm^{-1} in the free acid is slightly shifted 10–15 cm^{-1} to higher frequencies in the sodium salt as well as in lanthanide complexes, but shifts of deformation vibration δ_{OH} at 1 445 cm^{-1} are considerably greater for anhydrous Y, Gd—Lu than for the hydrated Nd—Eu complexes (Table 2). These low values of shifts might be neglected but

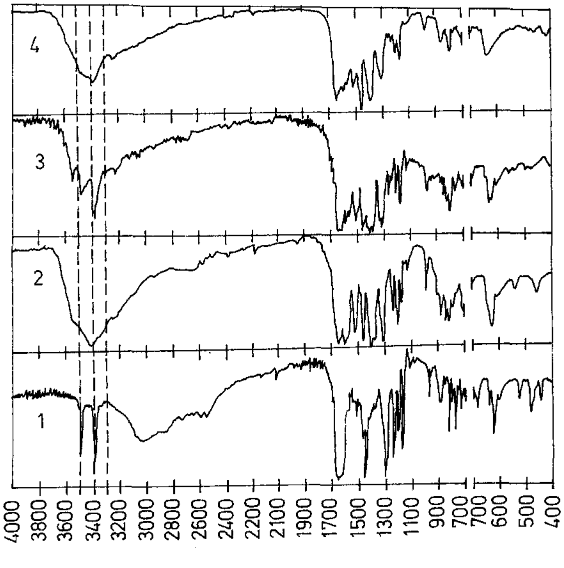

Fig. 2. The IR spectra of *1*: *p*-aminosalicylic acid; *2*: Na; *3*: Pr(III); *4*: Nd(III) *p*-aminosalicylates

taking into consideration the fact that in samarium salicylate [11] only one phenolic group out of the six coordinated ligands takes part in the bonding, we cannot definitely state on the basis of the IR spectra if any phenolic group is involved in the chelating of lanthanide in aminosalicylates. It is worth mentioning that one OH group which is chelated to the metal in samarium salicylate [11] is not ionized, the C—OH bond is of normal length and the angle is typical for a phenolic C—O—H angle.

If there is no loss of a proton by the phenolic group the peak at 1 300 cm^{-1} according to Khadikar remains in the same position for aminosalicylic acid and its complexes [12], but it is not sufficient evidence that coordination does not occur. The NH_2 group is the third one which may potentially coordinate the metal in aminosalicylates. In the spectrum of the free acid (Fig. 2) there are very sharp and intensive bands of ν_s and ν_{as} amino group. Upon the coordination of metal, these bands usually are shifted to lower frequencies as in aminobenzoates of lanthanides [15, 16] which is the evidence for metal-nitrogen coordination. In the case of lanthanide aminosalicylates in this region there are a few bands but negative shifts are not observed. It is clearly seen that the bands are splitted for light lanthanides and that the broad ones are typical for heavy lanthanide compounds; however, they occur in the same region as in the free acid and sodium salt spectra. Pirkes [6] reported for neodymium aminosalicylate the large negative shift of ν_s and ν_{as} bands but we cannot confirm it.

Moore [4] considered the 1 155 cm^{-1} band due to twisting vibration of NH_2 group responsible for the copper—nitrogen bonding. This band is known to be very sensitive to interaction with metal ions [17]. Similarity of its frequencies in the ligand and complexes studied by us indicate that the amine nitrogens are not involved in coordination of the lanthanide ions.

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